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THÈSE

**En vue de l'obtention du
DOCTORAT DE L'UNIVERSITÉ DE TOULOUSE
Délivré par l'Université Toulouse 3 - Paul Sabatier**

**Présentée et soutenue par
Yin ZHU**

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**Evaluation de la nanofiltration pour l'extraction d'acides gras
volatils produits par fermentation**

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**Evaluation of nanofiltration for the
extraction of Volatile Fatty Acids from
fermentation broth**

**Evaluation de la nanofiltration pour l'extraction
d'acides gras volatils produits par fermentation**

Abstract

Nanofiltration (NF) is a pressure-driven membrane process used for liquid-phase separation, which is promising for biomass separation and purification. In this work, two NF membranes (NF-45 and XLE) are used for the separation and valorization of volatile fatty acids (VFAs), one kind of useful chemical building blocks, from fermentation broth produced using municipal solid waste. The objective of this work is to investigate NF process for the separation and purification of VFAs from fermentation broth.

Experiments are carried out with synthetic solutions with increasing complexities, from single, binary and ternary solutions of VFAs, i.e., acetic (Ac), propionic (Pr), and butyric acid (Bu), to mixed solutions containing VFAs and inorganic salts at different compositions. The influence of ionic composition as well as of the solution pH on the transfer of the solutes are discussed. Then, a real fermentation broth containing three VFAs, inorganic ions and organic matters is also investigated.

For synthetic solutions containing dissociated VFAs (pH 8), it is observed that for a given VFAs proportion in the feed, regardless of the total concentration, the proportion of VFAs in the permeate remains constant when the filtration flux is higher than a specific value. From the perspective of mass transfer, this observation means that in a mixed solution, the individual charged solute transfer is controlled by the total amount of charge transferred through the membrane. Indeed, it is found that the individual VFA flux increases linearly with the total solute flux and does not depend on the total concentration but only on the VFAs proportions in the feed.

More complex solutions containing VFAs with the addition of three inorganic salts (Na_2SO_4 , NaCl , and CaCl_2) are further investigated. Again, constant permeate proportions for organic and inorganic solutes (anions as well as cations) are observed for a given feed proportion, when the filtration flux is higher than a certain value. Then, it is concluded that, for any couple of VFAs (Ac/Pr, Pr/Bu, or Ac/Bu), the plateau value of the relative proportion of the individual VFA in the

permeate is nearly fixed by its proportion in the feed, for all the conditions investigated. This conclusion can be extended to couples of VFAs/inorganic anions and couples of cations.

Solution pH significantly changes the retention of VFAs and the permeate proportion of VFAs. A model to describe the VFAs retention versus pH is presented. It is shown that the model can describe the retention of VFAs versus solution pH by considering an increase of the VFAs pKa values by about 1.2 units or a membrane effective pKa value of about 5.4 to 5.8.

Finally experiments are carried out with a real fermentation broth. It is observed that whatever charged or uncharged solutes, even for unknown organic matters in the real fermentation broth, a constant proportion in permeate is observed when the filtration flux is higher than a certain value. This observation indicate that the plateau value could be related to the nature of solutes and membranes, and this method could be used to compare the separation performances of different membranes.

Separation factor is used to characterize the separation performance of the two membranes on the real fermentation broth. The separation factors between VFAs in the real fermentation broth are higher than those obtained with synthetic solutions, indicate that there are additional parameters that could influence the separation performance of the nanofiltration process. The NF-45 membrane can more efficiently change the VFAs proportion in the permeate, Ac and Pr are greatly enriched in the permeate, while Bu is enriched in the retentate. The XLE membrane has a very high VFAs retention (>95%), it can change the proportion of VFAs and other organic matters (OM) in the permeate, and can be used to concentrate the VFAs fermentation broth and remove the hindering organics such as ethanol.

Keywords:

Nanofiltration, biomass valorisation, separation, organic acids

Nanofiltration, valorisation de la biomasse, separation, acides organiques

Table of Content

Abstract	1
Table of Content	3
Chapter I	7
Introduction	7
I.1 Properties, production, and applications of Volatile Fatty Acids	10
I.1.1 Properties and possible extraction of VFAs	10
I.1.2 Production of VFAs by fermentation	12
I.1.2.1 Microorganisms for VFAs fermentation.....	13
I.1.2.2 Biomass for fermentation produces VFAs.....	15
I.1.2.3 Fermentation process and the influence of fermentation conditions	16
I.1.3 Applications of VFAs	20
I.1.3.1 Biological nutrient removal	21
I.1.3.2 Bioenergy and biofuel.....	22
I.1.3.3 Biodegradable plastics (Polyhydroxyalkanoates).....	24
I.2 Nanofiltration process and its applications for VFAs valorization.....	25
I.2.1 Introduction of the nanofiltration process	26
I.2.2 Parameters to describe NF performance.....	28
I.2.2.1 Permeate flux	28
I.2.2.2 Retention.....	29
I.2.2.3 Separation factor	29
I.2.2.4 Yield and Purity	30
I.2.3 Retention mechanisms	31
I.2.3.1 Steric exclusion (size effect).....	31
I.2.3.2 Charge effect.....	32
I.2.3.3 Dielectric exclusion	34
I.2.3.4 Co-ions competition.....	35
I.2.4 Parameters influencing the nanofiltration performances.....	36
I.2.4.1 Feed composition.....	36
I.2.4.2 Solution pH	39

I.2.5	Recovery of VFAs using nanofiltration.....	41
I.3	Aims and outlines of the thesis	47
Chapter II.....	49	
Materials and methods.....	49	
II.1	Chemicals	52
II.2	Analytical methods.....	52
II.3	Membranes and nanofiltration (process) set-up	54
II.3.1	NF membranes.....	54
II.3.2	NF (process) set-up.....	57
II.4	Experimental procedures.....	58
II.4.1	Nanofiltration of synthetic solutions of VFAs	59
II.4.2	Nanofiltration of synthetic solutions of VFAs: influence of inorganic ions	60
II.4.3	Influence of the pH on the retention of VFAs	61
II.4.4	Nanofiltration of synthetic and real fermentation broths containing VFAs	62
II.5	Data treatment	65
Chapter III.....	67	
Nanofiltration of synthetic solutions of VFAs.....	67	
III.1	Retentions of VFAs in single and mixed solutions	70
III.1.1	Solutes retentions in single solutions.....	70
III.1.2	Individual solutes retentions in mixed solutions	72
III.2	Solute transfer in mixed solutions	86
III.2.1	Proportions of VFAs in the permeate	86
III.2.2	Solute transfer in mixed solutions	94
III.2.3	Solute transfer with XLE membrane	98
III.2.3.1	Individual solutes retentions in ternary solutions	98
III.2.3.2	Solutes transfer in ternary solutions.....	99
III.3	Conclusion.....	102
Chapter IV	105	
Nanofiltration of synthetic solutions of VFAs: influence of inorganic ions	105	
IV.1	Individual solutes retention in single solutions	108
IV.2	Individual solutes retention in mixed solutions.....	111
IV.2.1	Influence of VFAs co-ions (SO_4^{2-} and Cl^-) on individual solutes retentions....	111
IV.2.2	Influence of VFA counter-ions (Na^+ and Ca^{2+}) on individual solutes retentions...	116
IV.3	Solute transfer in mixed solutions.....	121
IV.3.1	Proportions of solutes in the permeate	121
IV.3.1.1	Proportions of anions in the permeate	121

IV.3.1.2	Proportions of cations in the permeate.....	127
IV.3.1.3	Relative proportions of VFAs in the permeate	131
IV.3.2	Solute transfer in mixed solutions	136
IV.3.2.1	Anions transfer.....	136
IV.3.2.1	Cations transfer	141
IV.3.3	Influence of the composition on the separation factors between VFAs	143
IV.4	Conclusions	148
Chapter V	151
Influence of the pH on the retention of VFAs.....	151
V.1	Solutes retentions in single and mixed solutions	154
V.1.1	VFAs retentions in single solutions.....	154
V.1.2	Individual VFAs retentions in mixed solutions	160
V.1.3	Global retentions in mixed solutions	171
V.1.4	Influence of concentration on the retentions of VFAs in single and mixed solutions	177
V.2	Description of the VFAs retention versus pH	179
V.3	Conclusion.....	192
Chapter VI	195
NF of VFAs fermentation broths	195
VI.1	Individual solutes retentions in synthetic and real fermentation broths.....	198
VI.1.1	Individual solutes retentions in synthetic broths	198
VI.1.1.1	Nanofiltration using XLE membrane.....	199
VI.1.1.2	Nanofiltration using NF-45 membrane	205
VI.1.2	Individual solutes retentions in the real fermentation broth	208
VI.1.2.1	Nanofiltration using XLE membrane.....	208
VI.1.2.2	Nanofiltration using NF-45 membrane	210
VI.1.3	Removal of organic impurities from the real fermentation broth.....	213
VI.2	Proportions of individual solutes in the permeate of synthetic and real fermentation broths	215
VI.2.1	Synthetic fermentation broths.....	215
VI.2.2	Real fermentation broth	219
VI.2.3	TOC proportions of VFAs and organic matters/impurities (OM) in the permeate of the real fermentation broth.....	228
VI.3	Performances of NF for the treatment of VFAs fermentation broth	229
VI.3.1	Case 1: Inorganic salts removal.....	229
VI.3.2	Case 2: VFAs composition modification.....	232

Table of Content

VI.3.3 Case 3: Organic matters removal.....	235
VI.4 Conclusions	236
General conclusions and perspectives	239
References	245
Nomenclature.....	260
Appendix: Chromatograms of VFAs.....	263

I.

Chapter I

Introduction

Global change leads to restrictions on carbon emissions, in order to develop a low-carbon economy, biomass resources are becoming a subject of increasing concern. On the other hand, with the increasing of the human population and the improvement of living standards, the per capita waste production is also growing rapidly, especially in developing countries. Convert waste into resources will constitute a virtuous circle, not only reducing carbon emissions but also produce valuable renewable resources at the same time, which will be a beneficial attempt.

Fermentation is a very economical process in transfer biomass into useful carbon resources. Fermentation has already been widely used in food processes, energy processes, and waste/wastewater treatment. With the help of fermentation, waste biomass can be transfer into useful chemical products. However, the produced streams contain not only the target solutes but also other impurities, a down-stream process for the further separation and valorization is thus required.

Membrane processes are low energy requirements, low cost, and high product yield separation processes, which are normally considered as environmentally friendly. As a still-developing technology, membrane processes have a bright future for the separation of molecules with different sizes and charges. Membrane process, especially nanofiltration (NF), has gained more and more attention in the field of biorefinery, and are highly recommended for the separation of renewable resources from fermentation broth.

The current project is aimed to produce Volatile fatty acids (VFAs), a promising chemical building blocks from municipal solid waste. This project will concern the production of VFAs-containing streams by anaerobic fermentation, and the possible recovery and separation of VFAs using nanofiltration.

The following sections will firstly introduce the production of VFAs via fermentation, the composition of the fermentation broth, and the operating conditions that influence the production. Then give an introduction to membrane processes, especially nanofiltration, and the previous results on VFAs valorization by nanofiltration process. The parameters influence nanofiltration performance, and nanofiltration on the application of VFAs is discussed.

I.1 Properties, production, and applications of Volatile Fatty Acids

Valorization of waste biomass into valuable chemicals is an interesting attempt; research in this area is accelerating [1]. As a group of organic carbon sources that could be produced from organic waste, VFAs are attracting more and more researchers' attention [2,3].

Volatile Fatty Acids (VFAs), also referred to as Short-Chain Fatty Acids (SCFAs), are fatty acids having up to six carbon atoms which can be volatilized at atmospheric pressure [4]. VFAs are a critical substrate for the production of biodegradable plastics and bioenergy, and have the potential to become chemical building blocks. As indicated in Table I-1, propionic acid is selected as one of the top 30 value-added chemicals from biomass by the U.S. Department of Energy [5].

Table I-1 List of top 30 potential building blocks, adapted from ref. [5]

Carbon number	Potential Top 30 candidates
1	Carbon monoxide & hydrogen (syngas)
2	None
3	Glycerol, 3-hydroxy propionic acid, lactic acid, malonic acid, propionic acid , serine, etc.
4	Acetoin, aspartic acid, fumaric acid, 3-hydroxy butyrolactone, malic acid, succinic acid, threonine
5	Arabinitol, furfural, glutamic acid, itaconic acid, levulinic acid, proline, xylitol, xylonic acid
6	Aconitic acid, citric acid, 2,5 furan dicarboxylic acid, glucaric acid, lysine, levoglucosan, sorbitol

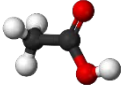
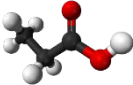
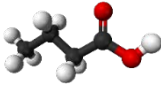
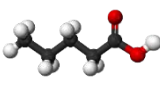
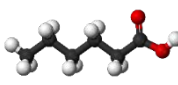
I.1.1 Properties and possible extraction of VFAs

As defined, VFAs are fatty acids with fewer than 6 carbon atoms, including acetic, propionic, butyric, valeric, caproic acids and their isomers. The main characteristics of the five types of VFAs are listed in Table I-2. The structures of VFAs are similar, from acetic to caproic acids, their molecular weights consecutively increase of $14 \text{ g}\cdot\text{mol}^{-1}$, which is an additional secondary carbon in the chain. Among those five types of VFAs, acetic, propionic, and butyric acids are the most commonly produced ones, the following discussions are mainly focused on these three VFAs.

Separation and extraction techniques rely on the difference between the physic-chemical properties of individual compounds. The properties of VFAs are introduced with possible treatments.

Acetic, propionic, and butyric acids have 2, 3, and 4 carbon atoms, respectively, and their size enlarged continuously. The increase of their size leads to the decreasing diffusion coefficient values, indicate that the sequence of diffusion coefficient of the three VFAs is acetic acid>propionic acid>butyric acid. Therefore, a separation process based on molecule size, e.g. nanofiltration at low pH, can retain more butyric acid than acetic and propionic acids [6].

Table I-2 Properties of VFAs

Name	Acetic acid	Propionic acid	Butyric acid	Valeric acid	Caproic acid
Structure					
Molecular weight (g.mol ⁻¹)	60.05	74.08	88.11	102.13	116.16
pKa (25°C)	4.76	4.88	4.82	4.84	4.88
Boiling point (°C)	117.9	141.15	163.75	185.8	205.8
Viscosity (mPa.s, 30 °C)	0.982[7]	0.962[7]	1.3852[7]		
Diffusion coefficient (D, ×10 ⁵ cm ² .s ⁻¹) (25 °C, 0.03~0.06 mol.L ⁻¹)	1.212[8]	1.057[8] 1.021[9]	0.946[8] 0.824[9]		

Furthermore, the boiling point values of VFAs also increase with their molecular weights, indicate that acetic acid is easier to be distilled from the mixture, shown that a traditional distillation process can separate the three VFAs [10,11].

VFAs have similar pK_a values. When deprotonated, the VFAs molecules are monovalent anions. Therefore, VFAs can be extracted from the fermentation broth by an electro-chemical driven process, e.g. electrodialysis [12].

In addition, due to the charge of VFAs, they can be absorbed and recovered from the broth using ion exchange resin; however, separation of individual VFA by adsorption was not achieved [11].

I.1.2 Production of VFAs by fermentation

VFAs production can be carried out via both synthetic methods from petrochemical derivatives, and biological methods such as fermentation. Nowadays, most (about 90%) of VFAs are produced through petro-based methods due to the lower cost. However, in the food and beverage industries, the VFAs used are required as natural produced, therefore bio-based VFAs must be used. The demands for bio-based VFAs are growing due to both increasing desire for natural products and increasing costs of crude oil [13]. Recently, the increasing demands for the valorization of biomass boost the demands of VFAs [2].

The bio-based VFAs production can be classified into two categories according to the purposes. The first category is to produce VFAs used for food or beverage industries, which requires high purity and high yield. Those VFAs are usually produced from sugar or grain using commercial bacteria. For instance, *Acetobacter*, *Gluconacetobacter*, and *Gluconobacter* are the most used bacteria families for acetic acid production [14]. The second category is to produce VFAs used for bio-based chemicals with the purpose to replace the petro-based chemicals and form cradle to cradle cycle. Nowadays, bio-based VFAs, especially waste-derived VFAs have been paid more and more attention [2].

In general, VFAs production from fermentation is an anaerobic process that includes hydrolysis and acidogenesis (which was also widely known as acidogenic fermentation [15] or dark fermentation [16]). This process is presented in Figure I-1. During the hydrolysis, complex organic polymers in waste are degraded and broken into smaller and simpler organic monomers by the enzymes produced by microorganisms. Then the organic monomers can be absorbed into the microorganism cell, at anaerobic condition, those monomers will transfer to organic acids such as acetic, propionic, and butyric acids, this step is so-called acidification.

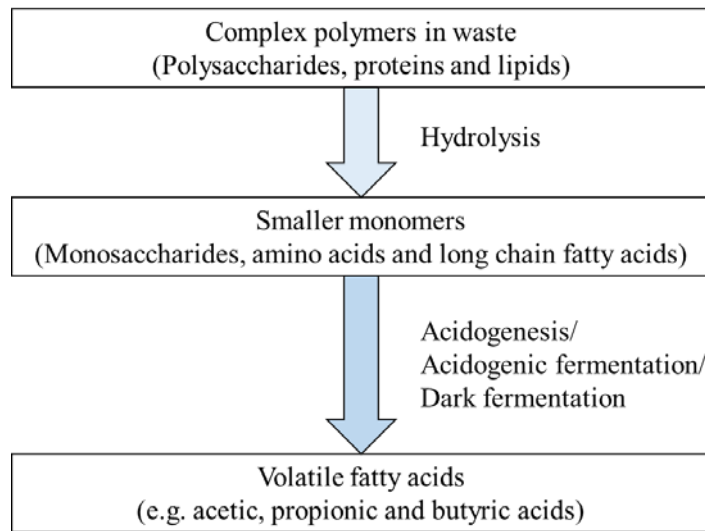


Figure I-1 Production of volatile fatty acids from waste, adapted from ref. [4].

I.1.2.1 Microorganisms for VFAs fermentation

The industrial acetic acid (vinegar) production is normally carried out using *Acetobacter*, *Gluconacetobacter*, and *Gluconobacter* strains [14,17]. *Acetobacter pasteurianus* is observed as the most common bacteria for vinegar production from rice [18], then, *Acetobacter aceti* and *Acetobacter xylinum* are used for higher fermentation temperature [19]. An overview of the different genera and species of acetic acid bacteria strains from 1898 to 2008 is given in ref. [20].

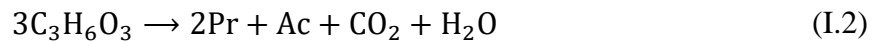
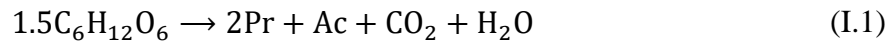
Propionic acid is produced using *Clostridium* (*Clostridium propionicum*) [21,22] and *Propionibacterium* (*Propionibacterium acidipropionici*) [23] strains. During the production of propionic acid using propionic bacteria, acetic acid is a common by-product. Modification of the operating conditions can increase the production of propionic acid. It is reported that decrease the fermentation pH from 7.0 to 6.0 increases the ratio of propionic: acetic from 0.45:1 to 1.8:1 [24].

Butyric acid can be produced using many strains such as *Clostridium*, *Butyrivibrio*, *Butyribacterium*, *Sarcina*, *Eubacterium*, *Fusobacterium*, and *Megasphaera* strains. Among those strains, *Clostridium* is the bacteria strain most used for butyric acid production [25]. During the production of butyric acid, acetic and propionic acid can be produced as by-products. The

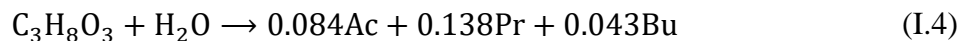
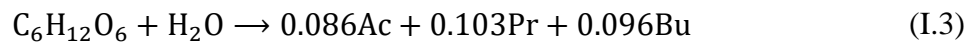
metabolic pathways for *Clostridium acetobutylicum* to produce acetic and butyric acid from glucose are known [26].

The above mentioned VFAs production bacteria strains can efficiently transfer specific carbon sources (e.g., glucose) into VFAs. However, during the production of waste-derived VFAs, the raw material often contains a variety of bacteria (e.g., food waste [27]), or even the raw material is bacteria cell itself (e.g., waste activated sludge [28]). Therefore, the competition between VFAs production bacteria and other bacteria reduces the productivity of VFAs and generates many by-products (i.e., methanol and ethanol [29,30]), which determined that the composition of the waste-derived fermentation broth are complex.

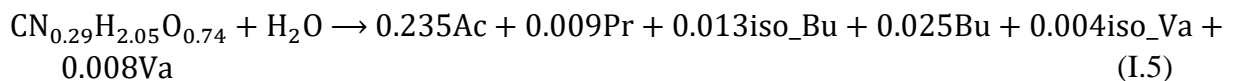
The fermentation broth contains not only acetic (Ac), propionic (Pr), butyric (Bu), valeric (Va) acids, but also remaining unfermented feed materials, for instance, glucose, peptone, glycerol, and inorganic salts such as NaCl, CaCl₂, NH₄Cl, etc. [31–34]. The pathways of production of VFAs have been given by some researchers. According to Fitz equation [35], the fermentation of propionate can be theoretically described as Eq. (I.1) (glucose as raw material) and Eq. (I.2) (lactic acid as raw material).



For glucose and glycerol as the raw materials, two experimental equations (Eq. (I.3), Eq. (I.4)) are provided by ref.[36].



However, the description of the production from complex raw materials such as waste activated sludge can be more difficult. Liu et al. [28] provided a theoretical equation (Eq. (I.5)) for acidogenic fermentation of proteinaceous sewage sludge by a stoichiometric coefficient method, showing that acetic acid is the main product of the fermentation of protein, which agrees with other results [37].



Control the fermentation condition such as adjust to an alkaline pH can change the bacteria genus level of distribution in the fermentation broth [38], but it is difficult to control the distribution of bacteria genus precisely. Due to the practical problems faced in waste-derived VFAs production, most publications use activated sludge as fermentation strain. Activated sludge usually contains a large genus of bacteria; meanwhile, waste activated sludge is also a good raw material for VFAs fermentation [33,39,40].

I.1.2.2 Biomass for fermentation produces VFAs

There is a great interest in producing VFAs by fermentation of various biomass like household solid waste [41] or waste streams such as wastewater [42] or waste activated sludge [43], with a double purpose of waste treatment and valorization. On the one hand, municipal solid waste (MSW) generated today is continuously increasing. The total urban waste generated each day almost doubled within 20 years [44], and an increasing trend can be expected up to 2050 [45]. Many biomass is produced while the utilization of them is few. Thus enormous cost has paid for the disposal of those solid wastes. On the other hand, unlike other biological processes, for the production of VFAs, fermentation process does not require the sterilization to cultivate a particular microorganism [3]. Therefore, VFAs fermentation is regarded as an energy-saving and economical process [3], and the organic-rich waste like MSW can be considered as the raw material.

The most commonly used wastes are excess sludge from wastewater treatment plants, food waste and organic fraction of municipal solid waste (OFMSW), wastewaters generated from agricultural, dairy, pulp and paper industries are used to produce VFAs too [4].

Primary sludge (PS, suspended solids and organics withhold or settled by the primary treatment processes like grilling or sedimentation) and waste activated sludge (WAS, the bacteria cells and adhesion suspended solids produced by aeration tank) are generated in 240 million wet tons in Europe, USA and China combined from municipal wastewater treatment plants [46]. Usually, one ton of dairy wastewater with chemical oxidation demand (COD) of 300 mg/L can produce 9 kilograms of excess sludge (contain 80% of water), and usually the cost to dispose or

reuse those sludge can contribute more than 50% of the total cost of the wastewater treatment [47]. On the other hand, both primary sludge and waste activated sludge are highly organic-rich. Primary sludge and waste activated sludge can have a total COD ranging from 14,800 mg/L to 23,000 mg/L [4], and usually have good carbon: nitrogen: phosphorus ratio, making them an appropriate source for VFAs production.

Food waste or kitchen waste is another organic-rich solid waste commonly used for VFAs production, mainly because it has a high total COD ranging from 91,900 to 166,180 mg/kg [4]. It is also the dominant component (22%-54%) in huge volumes of municipal solid waste (MSW). The challenge to utilize the food waste for VFAs production is to effectively separate it from MSW to avoid interference of other undesired components such as glass, plastics, aluminum cans, and ferrous metals [4]. Utilization of organic fraction of municipal solid waste (OFMSW) can face the same problem too, although it contains a total COD as high as 150,600 to 347,000 mg/kg [48].

High concentration organic wastewaters are commonly used for VFAs production. Food, agricultural, pulp, and paper industries wastewaters have a high concentration of COD. For instance, palm oil mill effluents, having a COD about 88,000mg/L, can be fermented into VFAs with a concentration as high as 15,300 mg/L [49]. The sugar industry also generates effluents with a total suspended solid of 5,000mg/L and soluble COD of 2,300-8,000mg/L, suitable for anaerobic digestion [50].

I.1.2.3 Fermentation process and the influence of fermentation conditions

As aforementioned, there are two steps (hydrolysis and acidogenesis) in the production of VFAs, hydrolysis is commonly considered as the rate-limiting step [51]. For instance, cell wall and extracellular polymeric substances (EPS) in excess activated sludge play as physical and chemical barriers protecting its intracellular from hydrolysis [52]. Moreover, the biodegradability of food waste, as well as OFMSW, can be lower if they contain a high percentage of lignocellulosic materials, fats or proteins.

Considering the hindrance of the cell wall, EPS, as well as macromolecules in the raw material for VFAs production, a physicochemical pre-treatment is usually applied before fermentation.

Chemical and physical pre-treatment using ozone [53], hydrogen peroxide [54], ultrasound [53], microwave [55] or thermal [51] can break the macromolecules into smaller ones and increase the soluble COD. In order to improve the yield and productivity, recently, hybrid pre-treatment such as ozone + ultrasound [56], hydrogen peroxide + microwave [54] and ultrasound + thermal [57] are also applied. The combined processes all involve the mechanism of accelerating the generation of OH• radicals, and then better oxidation performance is observed [54]. Single and combined pre-treatment can improve VFAs production. However, there is still a need for a comprehensive comparison of the techno-economic of those pre-treatments, a further improvement of cost-benefit improvement is required [4].

Besides the operating mode, the reactor can be classified into two types according to the existing forms of microorganism. For the first type of bioreactor, the microorganism is suspended in the reactor (such as a fluidized bed reactor and continuous stirred tank reactor). In the second type of reactor, with immobilized biomass, the microorganisms are attached to a packing material with a high specific surface (porous or not), which avoid the loss of microorganism.

Besides the composition of the raw material (feed composition), production of VFAs is also influenced by many parameters, such as solution pH, temperature, hydraulic retention time (HRT), solids/sludge retention time (SRT), organic loading rate (OLR), C/N/P rate, and microelements. Those factors affecting the fermentation process are shown in Figure I-2.

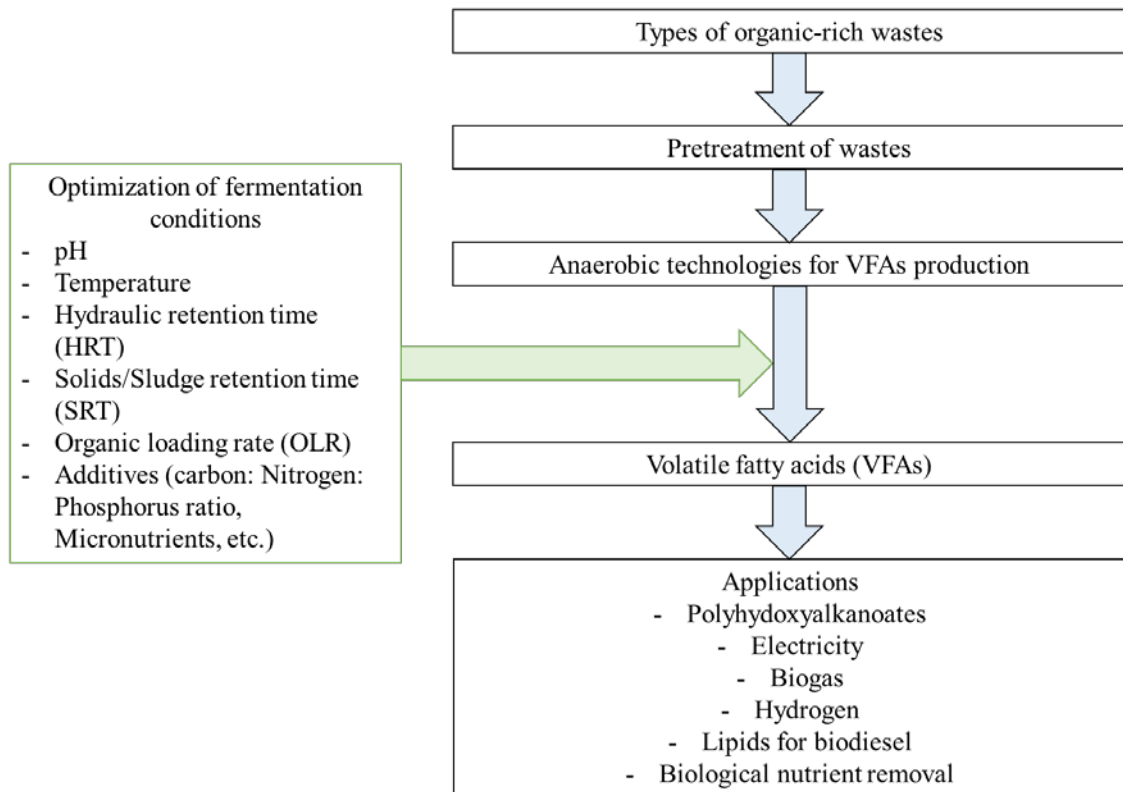


Figure I-2 Production of waste-derived volatile fatty acids and their applications, adapted from ref. [4]

Compositions of VFAs in fermentation broth from different raw materials and operating conditions are summarized in Table I-3.

Table I-3 Composition of VFAs in fermentation broths

Hydraulic retention time, HRT (h)	pH	Raw material	Acetic (mg/L)	Propionic (mg/L)	Butyric (mg/L)	Valeric (mg/L)	Caproic (mg/L)	Reference
-	-	Olive Mill Wastewater	6641	433	2252	495	922	[58]
36	5	Composite food waste	750	1373	1865	19		[27]
	6		1885	1000	1692	34		
	7		1481	1253	1365	29		
	8		2250	896	682	20		
	9		3154	1095	903	22		
	10		4192	1293	788	27		
245	11	Sludge	884	1468	1182	19		[28]
	3		806	1028				
	5		1838	988	1894	1180		
	7		4563	3594	4441	4764		
	9		8523	3819	3772	3912		
	11		8164	3412	3412	3585		
12	2184	1402	2428	994				
7.2-14.4	5	Sludge	666-980	20-100	2890-3036			[59]
3-12.5	6		713-1005	165-390	2597-3130			
3-9.1	7		1000-1259	40-145	2630-2900			
4-12.8	8		2480-2940	1420-1780	190-520			
14.2-15	5.2	Sugar beet	555-665	26-29	983-1664	5-6		[60]
	5.2	Sugar beet	519	5	1104	11		
	5.2	Sucrose	490-780		2350			
24-48	4.9-5.5	OFMSW	382-479	55-81	211-408			[61]
72-192	4.9-5.5		620-1080	193-611	2781-2744			
60	5.25-6.55	Sucrose	2708	1648	7172			[41]
54-95	5.5	Food waste	95-103	8-12	593-793			[62]
134	5.5		137	0	898			
40	4	Food waste	952	0	2181			[63]
12	5		1326	134	2151			
11	6		1529	142	1828			
18	7		1780	286	1555			
6	4	Glucose	5336	50	1810			[64]
	5		845	37	1730			
	6		1035	118	1423			
	7		1165	635	1333			
5.5	-	Municipal solid waste	2701	2277	3507			Real fermentation broth used in this work

pH is considered as the most important condition in VFAs fermentation. It can change the bacteria genus level of distribution in the fermentation broth, and low pH is beneficial for the acidification of soluble organic substrates [38]. The objective of VFAs production can be either focus on the total amount of VFAs produced from the substrate or higher yield of more favorable component, i.e., butyric acid. It is reported that alkaline pH is more suitable for acetic and propionic production, while acidic and neutral conditions can produce more butyric acid [59]. The pH value to obtain the maximum yield of VFAs is reported as pH 8 [59], pH 9 [65], pH 10 [27] and pH 11 [66]. Even though those reports have some difference in the optimum pH values, an alkaline pH, i.e., between 9 and 11 is more favorable for the production of VFAs from waste activated sludge [39,67,68]. However, if the production of butyric acid is the main propose, acidic pH can have better yield for butyric acid. It is shown that low pH values (4-6) are more favorable for butyric acid production [27,59,63,64]. Then, depends on the objectives, more total VFAs yield or more specific VFA production, the optimum fermentation pH can be alkaline or acidic.

Temperature is another important factor, depending on the microorganism used, the optimum temperature can be different. Hasan et al. investigated temperature range from 4 °C to 75°C, the yield of VFAs increase as temperature increased from 4 to 30°C and peaked at 30°C, then slightly decrease from 35°C to 75°C. They suggest the optimized temperature is 30°C [69]. Yang et al. use thermophilic micro-aerobic fermentation (temperature form 55 to 75°C) to produce VFAs from waste activated sludge, suggested that the optimized temperature is 60 °C, which has a yield of 2.9g COD/L [70].

The composition of VFAs in the real fermentation broth used in the current work are within the range of the previous results. To be better understand the influence of composition on separation performance, higher concentrations are used for the synthetic broths.

I.1.3 Applications of VFAs

The VFAs produced by acidogenic fermentation of waste can be used as variable renewable carbon resources such as produce biodegradable plastics, generate bioenergy and added to

wastewater treatment plant as carbon sources for nitrogen and phosphorus removal (shown in Figure I-2).

I.1.3.1 Biological nutrient removal

The accumulation of nitrogen (N) and phosphorus (P) in a water body can lead to severe environmental problems, such as eutrophication [71]. Therefore, strict wastewater emission standards on nitrogen and phosphorus were established by many countries [72]. It is generally recommended that the wastewater treated by conventional activated sludge wastewater treatment plant should have a nutrient composition of C:N:P=100:5:1 in order to have efficient nitrogen and phosphorus removal. However, the composition of N and P in wastewater usually exceeds the recommended ratio, and then additional carbon resources need to add to improve the nitrogen and phosphorus removal. VFAs can be used as an alternative to commercial carbon resources, e.g., methanol and glucose.

Many lab-scaled applications shown that waste-derived VFAs perform even better than the commercial carbon resources for the denitrification [73,74]. Then, it is further noticed that VFAs with shorter carbon chains ($C \leq 3$, formic, acetic, and propionic acid) are more efficient in transferring nitrate into nitrite than longer-chained VFAs [75].

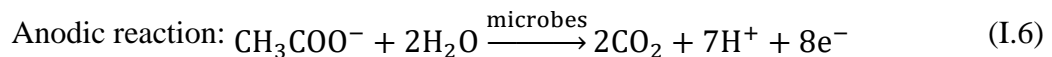
The use of VFAs for phosphorus removal is also investigated. The addition of VFAs can increase the uptake of phosphorus by activated sludge at the aerobic stage, and also increase the release of phosphorus at the anaerobic stage, then improved the phosphorus removal. Unlike the denitrification, it is shown that longer chained and branched VFAs (e.g., iso-butyric, iso-valeric acids) is more efficient for phosphorus removal [76]. In practice, during a long period of operation (5.5 years), it is shown that the addition of VFAs can optimize the enhanced biological phosphorus removal process [77].

Recently, a full-scale application of waste-derived VFAs used for nutrient removal in the domestic wastewater treatment plant is reported, the removal rates of nitrogen and phosphorus are 72.39% and 89.65% respectively, shown that it is technically and economically feasible to produce waste-derived VFAs for nutrient removal [43].

I.1.3.2 Bioenergy and biofuel

Traditional energies are facing a crisis; for instance, the limitation of carbon emission restrict the use of fossil fuel, nuclear power can be expensive and risk environmental pollution, hydro-energy may damage the ecosystem. Consequently, alternative energy should be given more attention. In the European Union, biomass can take more than half of the proportion amongst all the renewable resources [78]. Waste-derived VFAs were believed to be an inexpensive energy source that can generate different forms of energy. Direct generation of electricity can be achieved through microbial fuel cells, and valuable fuels can be produced by VFAs such as biodiesel, biogas or hydrogen.

Microbial fuel cell (MFC) is a bio-electrochemical system that is capable of converting chemical energy directly from organic substrates to electricity [79], regarded as a promising technology for wastewater treatment as well as energy recovery. Figure I-3 shows the construction of MFC. An MFC generally consists of an anaerobic chamber (anode) and an aerobic chamber (cathode), separate with a proton exchange membrane. Microbes in the anaerobic chamber oxidize substrates and generate protons, the protons transfer through the protons exchange membrane or a salt bridge and absorbed by the cathode at the aerobic chamber. Carbon dioxide was produced at the anaerobic chamber after the oxidation, and then protons combined with oxygen to form water. Electric current is generated by those reactions shown in Eqs. (I.6) and (I.7) (using acetate as an example substrate).



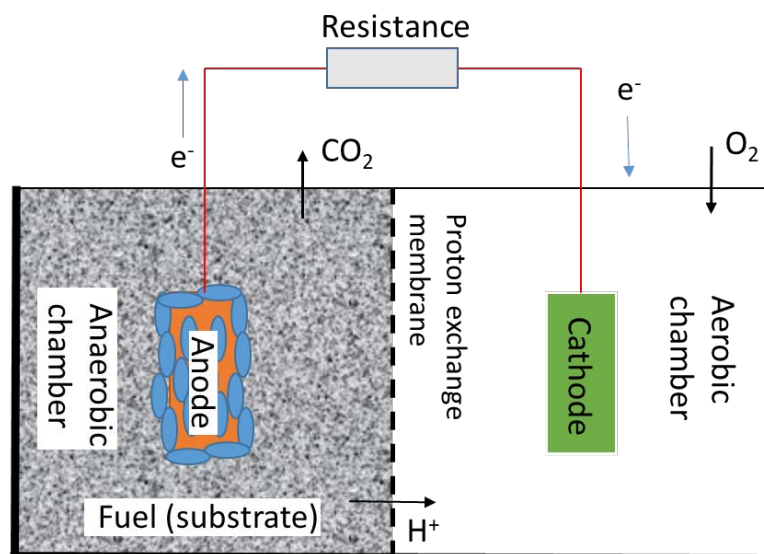


Figure I-3 Schematic diagram of a typical two-chamber microbial fuel cell, adapted from ref. [80]

In most MFC processes, fermentation broth contains rich VFAs can be directly used for electricity generation, make these processes economically attractive. Previous works indicated that energy recovery efficiency depends on the electron donors. For VFAs, acetic and propionic acids were considered preferred substrates in the operation of MFC, while longer chain fatty acids such as butyric and valeric acids will reduce the degradation rate [81].

Biodiesel is esters of fatty acids. Biodiesel is normally produced from vegetable oil, plant oil, or animal fat. Production of biodiesel from microbial lipids is considered as promising [82]. Due to shorter metabolic pathways and higher theoretical efficiency to convert VFAs into lipids than sugar-based carbon sources (e.g., glucose and glycerol). Waste-derived VFAs are suggested as better candidates for biodiesel production [83].

The production of microbial lipids is more favor shorter chain VFAs, i.e., acetic acid, due to that acetic acid is utilized prior to longer chained ones [84,85]. The use of mixed VFAs as the substrate with more acetic acid proportion (acetic: propionic: butyric = 6:2:1) is reported to have a high lipid yield [83].

Biogas is a valuable resource generated by anaerobic fermentation, and it is commonly used for heat and power generation as it contains 65-70% (v/v) of methane. Up-flow Anaerobic Sludge Blanket (UASB) is one of the most efficient biogas generators. Anaerobic digestion in a UASB

reactor involves a series of biochemical reactions, which can be classified into hydrolysis, acidogenesis, and methanogenesis. VFAs are the most important intermediate substrates during the three steps. According to Van Lier et al., 75% of methane production in UASB is derived from acetate [86]. Wong et al. use VFAs as the raw material, at the composition of acetate/propionate/butyrate at 6:3.7:4.4 g/L, organic loading rate (OLR) of 10.4g COD/L/day, the production of biogas can reach 322L/kg COD and the methane can hold 81% of the volume in biogas [87].

In general, one can observe that the applications of VFAs for energies and biofuel are more favor shorter chain VFAs than others.

I.1.3.3 Biodegradable plastics (Polyhydroxyalkanoates)

Among the potential utilization, the production of biodegradable plastics (i.e., polyhydroxyalkanoates) is one of the most promising applications of VFAs [88].

Polyhydroxyalkanoates (PHA) were recognized as a fully biodegradable and biocompatible polymer. Due to the similar characteristics, PHA is a promising alternative resource to petrochemical derivate plastic. Many publications on synthesizing of PHA from VFAs are reported previously, shown that VFAs are suitable for the production of PHA. The yield of PHA production from excess sludge fermented VFAs is reported to reach 56.5% of dry cell weight [37]. Another report showed a lower PHA yield (39%) from grass digested VFAs [89].

The production of PHA can be produced by mixed microorganisms, and the composition of PHA is more depends on the feed composition [90]. It is reported that a higher proportion of butyric acid is more favorable for the production of PHA [91]. For a common VFAs composition directly obtain from fermentation, the productivities are similar. PHA productivity is reported at 0.048 g.L⁻¹.h⁻¹ for VFAs obtained from palm oil mill effluent fermentation [92], similar productivity (0.06 g.L⁻¹.h⁻¹) is reported for VFAs generated from olive oil mill wastewater [93].

However, the co-existence of organic impurities, i.e., methanol and ethanol, in the fermentation broth hindered the productivity of PHA due to the increase of unfavorable population

of bacteria [29,30]. In addition, even though PHAs are promising alternative plastic for the future and can be produced from organic waste, the large scale utilization of PHA still facing a much higher cost (5-10 times than petroleum-based polymers) and the difficulty to extract [94].

Therefore, increase the proportion of the more favorable VFA, butyrate, remove the hindering organic impurities in the fermentation broth, can improve productivity. Besides, the extraction and processing of PHA still need more research [95].

I.2 Nanofiltration process and its applications for VFAs valorization

The bottleneck restricting the production of renewable resources from waste is the high recovery and separation costs. Many endeavors are made for the recovery of VFAs [58,96–98], and it is further pointed out that the separation of individual VFAs components can greatly revalue the waste-derived VFAs [2]. Therefore, Atasoy et al. suggest that any method attempts to separate VFAs is welcome [2].

A comparison of several traditional methods and membrane processes in the separation and recovery of VFAs from waste fermentation is given [99], showing that membrane processes have some advantages above traditional treatments (Table I-4).

Table I-4 Comparison of several processes in separation and purification of VFAs, adapted from ref. [99]

Methods	Advantages	Disadvantages
Precipitation	Well established Higher product yields Low capital costs Products of high purities	Generating solid wastes
Distillation	Well established Highly pure products Byproducts can be used as fertilizer	High energy High capital costs
Adsorption	Well established Easily operable	High resin costs High energy demand due to resin regeneration Separation is not highly selective

Solvent Extraction	Higher product yields Suitable for carboxylate salt production Lower costs	The feed needs to be acidified for efficient extraction Extractants needs to be regenerated by additional processes
Membrane Separation	Developing technology High product yields Suitable for a wide range of applications Low energy Economic Easy to scale up	Membrane fouling and clogging Largely untried in complex waste systems

Membrane processes include concentration-driven processes such as pervaporation (PV) and membrane extraction, pressure-driven processes, e.g., nanofiltration (NF), as well as electro-chemical driven membrane processes, for instance, electrodialysis (ED). Nanofiltration is recommended as one of the most promising membrane processes for VFAs separation [2]. The following sections are mainly focused on the nanofiltration process.

I.2.1 Introduction of the nanofiltration process

Nanofiltration (NF) is a pressure-driven membrane process used for liquid-phase separation. Pressure-driven membrane processes include Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse Osmosis (RO), which were classified by their pore size, charge and pressure (see Table I-5). Their structures are the same; at one side of the membrane, the pressure exerted on the solution as a driving force, the solution was separated as permeate and retentate. The pressure difference between the feed and permeate side (i.e., transmembrane pressure, TMP) can force the solvent to pass through while the particles and some dissolved components will be retained based on their properties such as size, shape, and charge.

MF has the largest pore (0.1 μ m to 10 μ m) and the highest permeability, a high flux can be observed at low pressure. MF generally to be used to separate suspended particles and microorganisms from the liquid. UF has smaller pores (2nm to 100nm), the permeability is much lower than MF, and higher operating pressure is required. UF can be used for the removal of suspended solids and high molecular weight solutes such as proteins. The pore size of NF is

smaller than UF, and the surface of the NF membrane is charged, which is usually used to remove multivalent ions and dissolved organic matters with a molecular weight above $150\text{g}\cdot\text{mol}^{-1}$. RO membrane is often considered as dense membrane without predefined pores, permeation of solutes are because of the solution-diffusion effect. RO is the most widely used process in seawater desalination, RO can also be used as a concentration step.

Table I-5 Overview of pressure-driven membrane processes and their characteristics, adapted from ref. [100]

	Microfiltration (MF)	Ultrafiltration (UF)	Nanofiltration (NF)	Reverse Osmosis (RO)
Permeability ($\text{L}/\text{h}\cdot\text{m}^2\cdot\text{bar}$)	>1000	10-1000	1.5-30	0.05-1.5
Pressure (bar)	0.1-2	0.1-5	3-20	5-120
Pore size (nm)	100-10000	2-100	0.5-2	<0.5
Rejection				
• monovalent ions	-	-	-	+
• multivalent ions	-	-/+	+	+
• small organic compounds	-	-	-/+	+
• macromolecules	-	+	+	+
• particles	+	+	+	+
Separation mechanism	Sieving Clarification, pretreatment, removal of bacteria	Sieving Removal of macromolecules, bacteria, viruses	Sieving/charge effects Removal of multivalent ions and relatively small organics	Solution - diffusion Ultrapure water, desalination
Applications				

Nanofiltration was first developed in the middle of the 1980s, due to the need for low energy consumption, low operation pressure, and high flux reverse osmosis (RO) membrane for water softening.

It was then realized that this kind of membrane has a special ability to separate low molecular weight organics such as glycine (with MW of 62) and glycerin (MW 92) from glucose (MW 180) and sucrose (MW 342) [101]. The retention mechanism in NF is a combination of different contributions, mainly due to the size (steric effect) and to the charge of the solutes and the membrane. NF is efficient for the recovery and selective removal of different kinds of products

from complex solutions. Then more and more researchers reported the potential of NF in the field of organic separation and purification [102–104].

After three decades of development and advance, nanofiltration becomes a mature process in many domains for instance water softening [105], brackish water desalination[106], wastewater treatment [107], whey demineralization [108,109], organic acid production[34] or drinking water production[110].

Recently, many new membranes were invented to improve the NF performances, such as surface modified membrane [111], nanoparticles enhanced membrane [112], 2D materials fabricated membrane [113,114]. Those newly emerged membranes could be promising to solve some remaining problems that slow down the application of NF in industries, such as fouling control and improving the separation between solutes [115]. Then, additional prospects are pointed out, for instance, the predictive modeling of NF processes for more complex solutions (i.e., with solutions have more than 2, 3, or 4 ions), and also new applications for a wider range of cases (e.g., renewable resources) [116].

I.2.2 Parameters to describe NF performance

It is essential to measure the performance of NF processes. A good way to compare the performances of different membranes is to compare their characteristic parameters. There are many parameters that can be used to measure the efficiency of NF processes, for instance, permeate flux, retention, separation factor, purity, and yield (product recovery) of a target product.

I.2.2.1 Permeate flux

The pressure is the driving force to push water and solutes toward the permeate side of the NF membrane. The pressure between the concentrate side and permeate side is called transmembrane pressure (TMP). The permeate flux can be defined as the volumetric flux rate of permeate per unit area of the membrane, usually denoted as J_v ,

$$J_V = \frac{1}{A} \cdot \frac{dV}{dt} \quad (\text{I.8})$$

V , total volume permeated through the membrane within time t ,

A , effective area of the membrane,

t , time of duration of filtration.

The unit of permeate flux is $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, permeate flux is calculated by measurement of the volume of permeate during a certain time, then divide the effective filtration area. Generally, permeate flux increases with the transmembrane pressure.

The flux obtained with pure water (J_w) varies linearly with the transmembrane pressure (ΔP). Then, the membrane permeability (L_{po}) can be determined using the following equation:

$$L_{po} = \frac{J_w}{\Delta P} \quad (\text{I.9})$$

The unit of pure water permeability is $\text{m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$.

I.2.2.2 Retention

Retention is also used to characterize the ability of the membrane to retain a given solute.

$$R(\%) = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \quad (\text{I.10})$$

C_f The concentration of the solute in the feed ($\text{mol} \cdot \text{L}^{-1}$),

C_p The concentration of the solute in the permeate. ($\text{mol} \cdot \text{L}^{-1}$).

I.2.2.3 Separation factor

Separation factor (S_f) can be used to define the separation efficiency considering the separation of two solutes, a and b. It is calculated according to the following relationship

$$SF = \frac{(C_a/C_b)_p}{(C_a/C_b)_f} = \frac{1-R_a}{1-R_b} \quad (\text{I.11})$$

Depends on the retention sequence of solutes a and b, the separation factor observed can be between 0 and 1 or from 1 to ∞ . SF values higher than 1, mean that the NF retentate is a solution enriched in solute b compared to the feed. The increase in value of the separation factor means better separation efficiency of the NF process on the two solutes.

I.2.2.4 Yield and Purity

Yield also can be used to characterize the separation performance of NF. If the purified fraction of the target solute is in the permeate, the yield is defined according to the following equation:

$$Yield(\%) = \left(\frac{V_p C_p}{V_f C_f} \right) \cdot 100 \quad (I.12)$$

Otherwise, if the purified fraction is the retentate, the yield is defined according to the following equation:

$$Yield(\%) = \left(\frac{V_r C_r}{V_f C_f} \right) \cdot 100 \quad (I.13)$$

V_p The solute volume of permeate,

V_r The solute volume of retentate,

V_f The solute volume of feed,

C_p Solute concentration of the permeate,

C_r Solute concentration of the retentate,

C_f Solute concentration of the feed,

Finally, the target solute purity can be defined as the concentration of solute over the total concentration (concentration of solute and impurities), in the enriched compartment.

$$Purity(\%) = \left(\frac{C_s}{C_s + C_i} \right) \cdot 100 \quad (I.14)$$

C_s Concentration of the target solute,

C_i Concentration of impurities in the solution.

I.2.3 Retention mechanisms

The retention of solutes is due to three mechanisms, so-called steric exclusion, Donnan exclusion, and Dielectric exclusion.

I.2.3.1 Steric exclusion (size effect)

For neutral and non-polarized solutes, which could be considered as spherical particles, the steric effect considers that the retention of a solute is fixed according to the ratio between its size and that of the membrane pores.

The resulting retention can be written as:

$$R = \left\{ 1 - \left[1 - \left(\frac{R_s}{R_p} \right)^2 \right] \right\}^2 \quad (\text{I.15})$$

R_s Radius of the solute;

R_p Radius of membrane pore.

The size effect has been widely reported [117–120].

However, it was also reported that the retention of a neutral solute does not depend only on its molecular weight, but that its shape can have an influence too. Laufenberg et al. found that branched isomers of propanol and butanol can have significantly higher retention than their straight-chain isomers, which means that the structure or the shape of a molecule can be an important factor during RO process as well as NF [121].

The water shell surrounding the solutes can also enlarge the solute size compared to Stokes radius and lead to an increase of the steric effect. Once the number of water molecules form the solute water shell is reduced (i.e., dehydration), the retention of solute decreases. It is reported that the retention of glucose is reduced in the presence of salt ions, especially of those show low

retention [122]. Further investigation showed that the decrease of saccharides retention can be due to the dehydration of saccharides in the presence of electrolytes [123,124].

I.2.3.2 Charge effect

When considering the transfer of charged solutes, for instance, acetate ion, propionate ion, sulfate ion, and chloride ion, etc., the charge effect (Donnan effect) should be taken into account.

Nanofiltration membranes are usually charged as a characteristic of the membrane material. The polymer membranes are commonly negatively charged while some ceramic nanofiltration membranes can be positively charged [125]. The exclusion mechanism is the fact that charged membrane materials will repulse co-ions and attract counter-ions. If we consider the nanofiltration membrane surface as a solid plane surface, the negative charge on the membrane surface and the counter-ion attracted to it will form an electrical double layer. The charge properties of NF membrane can be characterized by some methods like streaming potential and streaming current (to measure the membrane surface zeta potential), electro-osmosis (determine zeta potential through membrane pore, i.e., perpendicular to the membrane surface) or charged solute retention.

Donnan exclusion is severely affected by ionic strength and solution pH. As the concentration of charged solutes increases, the thickness of the slipping region boundary layer decreases, and the zeta potential decreases. The decrease of membrane charge due to increase in ionic strength makes the electrostatic repulsion weaker, and then lower ions retention at high concentration compared to that in low concentration is observed. This phenomenon is called “screening effect”.

For a negatively charged membrane, as the solution pH decreases, H^+ will combine to the weak acid group (generally carboxylic acid group). When the pH reaches a certain degree, the membrane charge will be totally neutralized. This pH value is called the isoelectric point (IEP) of the membrane. IEP is one of the characteristics of the membrane and mainly depends on the membrane material. Most polyamide membranes have an IEP between pH 3 to pH 5 [126]. pH affects the exclusion by decreasing the membrane charge, which also narrows the electrical double layer.

At neutral pH, when the concentration of solutes is low, and the solute size is significantly smaller than the membrane pore size, the charge effect is the primary mechanism in electrolytes retention. Schaep et al. used two negative charged NF membranes and one positively charged NF membrane, obtained the retentions of NaCl, MgCl₂, NaSO₄, MgSO₄ at different concentrations. It is suggested that, for loose membrane (NTR 7450), charge effect is the major exclusion mechanism. On the other hand, for the denser membrane, since the pore size is close to the radius of the solute, the steric effect can play a role in solutes retention [127]. The same phenomenon also exists in organic electrolytes. Khunnonkwao et al. reported that the retention of succinic acid by nanofiltration membrane (NF-45) at 0.1 mol.L⁻¹ at pH 7 is higher than 90%. When the concentration increases to 0.7 mol.L⁻¹, the retention dramatically decreases to less than 20% [128]. Bouchoux et al. also reported that when the concentration of sodium lactate increases from 0.1M to 1M, the retention of sodium lactate decreases from 80% to 25% [34].

For the retention of weak acids, dissociation needs to be taken into consideration. The percentage of the dissociated form of a weak acid is fixed according to its pK_a and pH of the solution. Dissociation of a weak acid *HA* is shown in Eq. (I.16)



The dissociation constant K_a is the equilibrium constant of dissociated and undissociated compound, given by Eq. (I.17), then, the pK_a of weak acid *HA* is defined in Eq. (I.18).

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad (\text{I.17})$$

$$pK_a = \log_{10}(K_a) = \log_{10} \frac{[H^+][A^-]}{[HA]} \quad (\text{I.18})$$

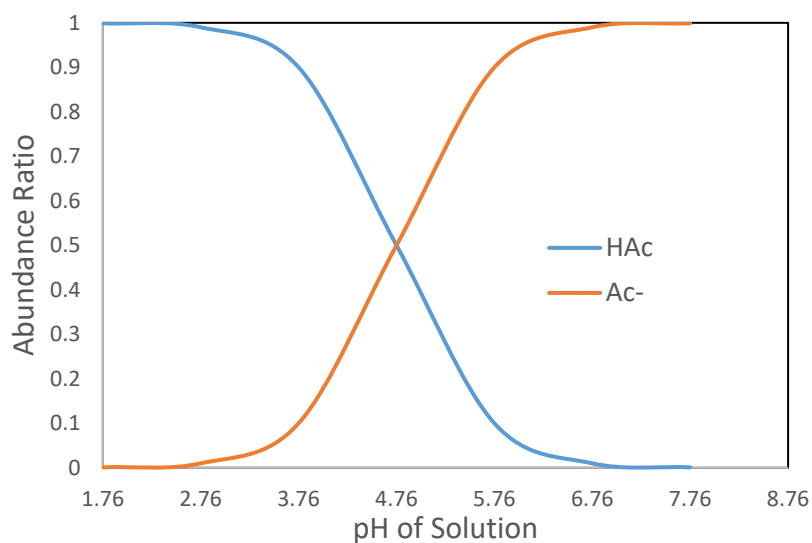


Figure I-4 Relationship between pH of solution and dissociation status of acetic acid

As the solution pH changes, the ratio of the dissociated and undissociated forms changes. As an example, acetic acid has a pK_a of 4.76, at pH 4.76, the concentration of HAc and Ac^- are equal (Figure I-4). If the pH of solution is lower than pH 4.76, more acetic acid should exist at a neutral/uncharged form; less charge effect should occur. However, if the pH higher than pH 4.76, there should be more acetate than acetic acid. At neutral pH (pH=7), more than 99% of acetic acid exists as Ac^- , the charge effect can significantly affect the retention of acetate in diluted solution.

For polyprotic acids, multiple pK_a values are observed, the composition of their aqueous solution in a certain pH can be more complicated.

pH can dramatically affect the retention of a weak acid in a dilute solution. In neutral form (at pH 2.2), retention of succinic acid is about 25%, while in the ionized form (pH 7.6), the retention can be close to 100% [129].

I.2.3.3 Dielectric exclusion

The dielectric effect was considered another charge effect since the beginning of the 21st century [130]. This is because a model only considering the steric effect and Donnan equilibrium cannot successfully predict the retention of divalent ions. For instance, the retention of $CaCl_2$, $MgCl_2$, and $MgSO_4$ predicted by the Donnan steric pore model (DSPM) is always lower than the

experimental value[131,132]. The mechanisms of dielectric exclusion still need investigation. Two kinds of mechanisms are proposed, that are image forces [133] and ion solvation[134].

Generally, it is believed that the dielectric constant values in the bulk solution and in the polymeric matrix are different. The dielectric constant of an aqueous solution is usually much higher than the value in the polymeric matrix. As an example, Sanjob et al. reported that the dielectric constant of water could be decreased as much as 50% in a nanocavity compared to the value in bulk water [135].

I.2.3.4 Co-ions competition

In a bulk solution, the total amount of anions and cations are equal and the solution maintain neutral, this condition is called electroneutrality.

As aforementioned, nanofiltration membrane has lower retention for monovalent anions, for instance, Cl^- and Ac^- , than divalent ones such as SO_4^{2-} and succinate because of the weaker charge effect as well as smaller size (possibly due to less hydration number). When a mixture of monovalent and divalent ions such as NaCl and Na_2SO_4 was filtrated by a nanofiltration membrane, negative retention of Cl^- sometimes appeared (Figure I-5). Indeed, divalent anion SO_4^{2-} has a bigger size as well as stronger electric repulsion, can be almost totally retained by the membrane, while monovalent cations Na^+ having a smaller size, can easily pass through it. Due to the electroneutrality across the membrane, the transfer of Na^+ has to be equilibrated by monovalent anions, Cl^- . Then, for some feed composition, the concentration of Cl^- in the permeate can be much higher than that in the feed, meaning a negative value of the Cl^- retention. For other permeating ions and non-permeate ions, this phenomenon also exists, i.e. Nielsen and Jonsson reported a lower than -200% retention of NaNO_3 in the mixture of $\text{NaNO}_3 : \text{Na}_2\text{SO}_4 = 1 : 10$ [136].

Negative retention is a particular case of co-ions competition. In general, during the filtration, once two or more than two co-ions exist in the solution, co-ions competition should occur.

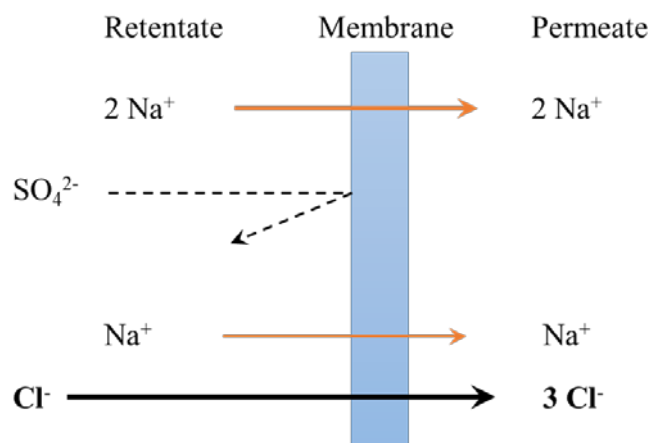


Figure I-5 Schematic diagram of negative retention of NaCl in a mixture of NaCl and Na₂SO₄, adapted from [137].

Negative retention due to co-ions competition was used to improve the selectivity of nanofiltration, to achieve negative retention of one solute, while maintaining positive retention as high as possible for the other. Polyelectrolytes were commonly used as an additive substance to improve the separation [138]. Divalent salts like Na₂SO₄ also were reported to be beneficial for the improvement of separation [139]. For instance, by adding 0.25 mole of Na₂SO₄ into the binary solution of glucose and lactate, the maximum separation factor between glucose and lactate increases from 1.1 to 1.9, meanwhile, the flux to obtain the highest separation factor increases from $0.05 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ to $0.2 \times 10^{-5} \text{ m}^3 \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ [34].

I.2.4 Parameters influencing the nanofiltration performances

I.2.4.1 Feed composition

Retention of ions contained in single electrolyte solutions was widely reported. The influence of ions size and charge was discussed [140], and a qualitative prediction of the retention sequence of ions with different valence and size was given [141]. It was observed that the retention of symmetric electrolytes (i.e. NaCl, KCl, and MgSO₄) in diluted solution is governed by the membrane co-ions due to electrostatic repulsion, and that the retention of asymmetric electrolytes (i.e., Na₂SO₄, CaCl₂, and MgCl₂) is dominated by the ions with the highest valence [142]. Many

models based on irreversible thermodynamics are built and can successfully describe the retention of single electrolyte solutions [125,132,143].

However, when more complex solutions are concerned, like multi-electrolytes systems, there are interactions between the different ions. Then, the retention of ions in mixed solutions cannot be predicted from the ones obtained with single solutions. An attempt to use an irreversible thermodynamic model to predict the individual ions retentions in a $\text{Cd}^{2+}/\text{Ni}^{2+}$ binary solution showed that the experimental retention of the less retained ion, Cd^{2+} , is 10% lower than that predicted by the model [144]. With binary systems containing two co-ions and only one counter-ion, it was reported that when one of the co-ions is totally retained by the membrane, the retention of the other decreases significantly. It was attributed to the co-ions competition. For instance, during NF of a mixture containing NaCl and an organic acid sodium salt, with a molecular weight (MW) of $700 \text{ g}\cdot\text{mol}^{-1}$ and retention higher than 99%, negative retention of Cl^- was observed [145]. The same results, i.e., negative retention of the less retained ion, were also reported with ions of smaller molecular weight (lesser than $200 \text{ g}\cdot\text{mol}^{-1}$), especially with solutions containing multivalent and monovalent ions. As an example, negative retention of Cl^- was observed in the presence of SO_4^{2-} [146], as well as for Na^+ in the presence of Ca^{2+} [147].

Such interactions of charged solutes in mixed solutions not only depend on operating conditions such as filtration flux but also on the feed composition, i.e., concentration and proportions of ions. It was reported that for a mixed solution containing NaCl and an organic acid sodium salt, the retention of Cl^- decreases to more negative values when the proportion of organic acid salt in the feed increases [14]. This was also observed with solutions containing Na_2SO_4 and NaNO_3 , for which negative values are obtained for the retention of NO_3^- when the concentration ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ in the feed increases from 1 to 5. Again, more negative values are observed for an increasing concentration ratio up to 10 [136]. Negative retentions of acetate were also reported during NF of a succinate/acetate binary solution for certain feed compositions, i.e., for a concentration about 0.7M and an acetate/succinate ratio of 6, while both acetate and succinate retentions are positive for lower concentrations or lower acetate/succinate ratio [128]. More complex mixtures containing formate, acetate, lactate, and succinate salts were investigated too. It was found that the retention of the less retained solutes, lactate, acetate, and formate, decreases

in the presence of a more retained solute, succinate, and that this decrease is more important for increasing proportion of succinate [148]. An overview of the negative retention phenomenon is provided, the possible mechanisms behind are discussed. The author concluded that current experimental results are not sufficient to predict the negative retention phenomenon, and further investigations are required [149].

Besides the ions, co-existing neutral and charged solutes could also influence the performance of nanofiltration

Many authors reported the decrease of uncharged solutes retentions in the presence of inorganic salts. For instance, the retention of glucose decreased in the presence of KCl [150] and NaCl[104]. On the other hand, the retentions of charged solutes also decrease in the presence of inorganic salts, like retention of sodium lactate in the presence of NaCl and Na₂SO₄ [139].

The mechanisms of the solutes retentions decrease in the presence of inorganic salts are not the same for neutral and charged solutes. The decrease of the retention of uncharged solutes in the presence of inorganic salts can be due to their dehydration, leading to a smaller hydration size [124,151]. Another possibility could be due to the swelling of the membrane due to the adsorption of salts [150]. On the other hand, the influence of inorganic salts on the retention of charged solutes could occur due to the screening effect and co-ions competition as previously mentioned. The addition of inorganic salts increases the ionic concentration of the solution, then the electrostatic interaction between membrane and charged solutes is weakened, and lower retention is observed [128]. In addition, the existence of more retained co-ions (i.e., SO₄²⁻), could compete with the less retained co-ions (i.e., lactic acid), which leads to a decrease in retention of less retained co-ions [139].

For organic impurities, the influence on the retention of organic acid is also reported. The influence of uncharged organic solute such as glucose is negligible on the retention of other solutes, both for the charged solute, i.e., NaCl [152], and uncharged solute, i.e., xylose [153]. The charged organic solutes act as the inorganic salts, which could influence solutes retentions by both increasing the ionic concentration [128], and compete with the less/more retained co-ions [148].

However, most of the results are obtained in synthetic solutions. For more complex solutions, especially with real fermentation broth, some unexpected results were reported. For instance, it is reported that the retention of butyric acid in a real digestion liquor maintained at nearly 100%, for all the conditions (pH and transmembrane pressure) investigated [6]. Meanwhile, the retentions of other VFAs (acetic and propionic acids) decrease when the solution pH decreases [6]. Another publication shows that the retention sequence of acetate and butyrate is Ac<Bu in synthetic solutions by DL membrane, changed to Bu<Ac when filtrate a real fermentation broth with the same type of membrane.

The aforementioned results indicate that there could be more complicated solutes interactions in the real fermentation broth than in synthetic solutions.

I.2.4.2 Solution pH

A thin-film composite membrane (TFCM), like NF-45 membrane, is composed of a thin nanoporous active layer made of polyamide, then supported by a macroporous layer made of polysulfone [154]. The membrane charge can come from the dissociation of functional groups, adsorption of ions from solution, and the adsorption of polyelectrolytes, ionic surfactants, and charged macromolecules [155]. Among those sources, dissociation of functional groups is commonly considered as the main contribution of the pH-dependent membrane charge [156,157]. For TFCMs, the solutes separation only involves the polyamide active layer, and the functional groups (carboxylic and amino groups) on the active layer determine the membrane surface charge [156,158]. It is commonly observed that when the solution pH is higher than the isoelectric point (IEP) of the membrane, the membrane surface charge increases with pH. This theory can be proved by the measurement of the zeta potential of the membrane [159,160]. However, the zeta potential measurement is solute-dependent and cannot provide a quantitative measurement of the membrane charge. Recently, heavy-ion probes were used as a new method to determine the membrane charge, and dissociation of carboxylic functional groups on the active layer is referred to as the primary source of membrane charge [156,157].

For the nanofiltration of strong electrolytes, the charge of solutes is nearly unchanged, the influence of solution pH on solutes retention can be attributed to the dissociation of membrane functional groups leading to the variation of the membrane surface charge. For small symmetric salts, i.e., NaCl and KCl, various reports have shown that when the solution pH becomes higher than the IEP of the membrane, the retentions of salts increase with pH due to the increase of membrane charge [150,159,161,162]. However, for weak electrolytes such as organic acids, the retention mechanism is more sophisticated, as both the charge of membrane and solutes vary with solution pH [142]. Besides, the size of organic acids can be much larger than the size of inorganic electrolytes. Thus, the molecular weight (MW) of organic acids needs to be first discussed. When the MW of an organic acid is higher than the molecular weight cut off (MWCO) of the membrane, regardless of the solute and membrane charge, high retention is observed. Therefore, the retentions of organic acids that have MW higher than MWCO of the membrane are independent of solution pH [163].

For the nanofiltration of small monovalent organic acids, i.e., acetic acid, low retention is expected for its neutral form, since its MW (60 g.mol^{-1}) is much lower than the MWCO of nanofiltration membranes ($200\text{-}500 \text{ g.mol}^{-1}$). When the solution pH increases, the proportion of dissociated acetic acid increases; meanwhile, the membrane surface charge also increases, then stronger electrostatic interactions between membrane and solutes are expected, and then higher retention in diluted solution should be observed. It is reported that the retention of acetic acid increased from nearly 0% at pH 2.9 to more than 90% when the solution pH increased to 9.1 at acetic acid concentration of 5g/L (about 83 mM) [164]. Similar results are reported by other authors [165,166]. Those observations suggested that in diluted solutions, the retention of small monovalent organic acids with MW lower than MWCO of the membrane is mainly fixed by charge effect.

Retention observed for a weak electrolyte solution can be considered as the combination of the retentions of undissociated and dissociated form, and the proportion of those two forms are determined by dissociation constant and solution pH. Then, if the retentions of those two forms as a function of solution pH are acquired individually, the retention of the solute can be estimated by their proportion at different solution pH according to the dissociation constant (K_a). It is

reported that the mass transfer parameter of undissociated lactic acid is independent of solution pH, while the mass transfer parameter of dissociated lactic acid linearly increases with pH. The retention of lactic acid at different pH can be simulated from those two parameters [143]. However, the authors only investigated a short range of pH values (2.88 to 4.93), and the influence of ionic concentration is not discussed.

Besides the weak electrolyte in the solution, the functional groups at the membrane surface can be dissociated when pH changes. It is suggested that an effective dissociation constant (K_{eff}) can be used to describe the dissociation of membrane functional groups [167]. The $\text{p}K_{\text{eff}}$ values for various polyamide films are reported as 5 to 9 [167]. Thereafter, the concentration of membrane functional groups at the membrane surface is reported to be determined by heavy ions probes, and the dissociation constant of membrane is simulated [156,157].

As previously introduced, the retention of small weak acids in dilute solution depends on the dissociation of solute as well as the dissociation of membrane. Thus, it is expected to observe an increase of the retentions of weak acids with solution pH following an S-shaped dissociation curve. This S-shaped retention curve was observed in the retention of sulfamethoxazole and ibuprofen by a loose NF membrane [168], as well as nanofiltration of succinic acid [128] and sulfuric acid [146,169,170].

The retentions of weak electrolytes in diluted solutions are strongly influenced by pH, and the variation of the retention versus pH could be linked to the dissociation constant of solute as well as the effective dissociation constant of membrane.

I.2.5 Recovery of VFAs using nanofiltration

Aliphatic acids, such as formic and acetic acids are considered as toxic components during many fermentation processes [171,172]. The attempt to use NF for the removal of acetic acid from fermentation broth is reported in an industrial scale application in 1996 [173]. High retention (99%) of glucose while low retention (60%) of acetic acid was achieved as 30 °C, pH 5.6 and acetate concentration of 20g/L [173]. Then many other reports also showed that NF can remove acetic

acid from fermentation broth and keep sugars in the retentate at the same time [171,172]. Based on the knowledge that VFAs can inhibit many fermentation processes, the continuous removal of VFAs from fermentation broth can be beneficial for the fermentation. An attempt is reported that the regular extraction of VFAs from the fermentation broth by NF can significantly decrease the total acid concentration in the fermentation broth, even though the improvement of VFAs yield is not significant from the control (without extraction) [6].

The demands for the separation between VFAs are raises since recently. Separation of volatile fatty acids is a difficult task for membrane processes since they have similar molecular weight, similar pKa, same structure, and same charge. So far, several articles were published recently using nanofiltration to separate acetic acid from propionic and butyric acids [6,98,165,174,175]. The main results are presented in Table I-6.

According to those publications, Different kinds of Nanofiltration membranes either self-made or commercial produced have been tested, synthetic solutions and real fermentation broth have been used, the concentration of single VFA differ from 1mM to 100mM, the mixture of VFAs have a wide ratio and contain several kinds of salts concentrated from 0 to 120mM. Broad operation conditions have also been applied, as pH from 3 to 11 and pressure form 1.3 to 24 bar.

From the results shown in Table I-6, it can be concluded that the retention of VFAs differs amongst different membranes. However, operating conditions can have a much more significant influence on the retention of VFAs than the influence of different NF membranes. As shown in the table, when pH and operating pressure change, the retention of VFAs can differ from close to 0% (at pH close to 3 and low pressure) to higher than 90% (at pH higher than 7 and high pressure). The composition and salts concentration can also have an influence on VFAs retention. However, based on the results reported, it is not possible to predict the NF performances on VFAs for different conditions. Therefore, further investigations are needed.

As previously mentioned, applications of VFAs can either require shorter chain VFAs (i.e., acetic acid) for nutrient removal, energy, and biofuel or need longer chain VFAs (i.e., butyric acid) for bio-plastics. Then, the separation of acetic and butyric acids can be beneficial for both applications. According to the retentions of acetic and butyric acids reported in mixed solutions,

the separation factor (as previously defined, $S_f = \frac{1-R_a}{1-R_b}$, $R_a < R_b$, the separation factor is always higher than one) calculated for different conditions are given in Table I-7. It is shown that except for ref. [6], the separation coefficient values between acetic acid and butyric acid are lower than 1.72. Therefore, the selectivity of NF for VFAs separation still needs to be improved.

Table I-6 Retention of VFAs by different NF membranes at various conditions

Membrane and producer	pH	Temperature (°C)	Pressure (bar)	Retention (%)			Flux ($10^{-3} \text{L}\cdot\text{m}^{-3}\cdot\text{m}^{-2}\cdot\text{h}$)	Resource	Impurity	Concentration (mM)	salt concentration (mM)	reference
				Acetic	Propionic	Butyric						
Desal-5 DK (GE)	-	25	-	38	-	-	-	fermentation broth	sugars alcohol long-chained acid	28.1	-	[176]
	-	25	-	-	-	31	-	fermentation broth	sugars alcohol long-chained acid	9.18	-	[176]
	2.9-9.1	-	4.9-24.5	0-94.2	-	-	-	mixed solution	xylose 50g/L	83.26	-	[177]
	3-7	25	8-24	0.08-59.6	22.3-52.5	100	-	digestion liquor	Hexanoic acid 25g/L, sugars 20mg/L	17.5	-	[6]
	3.14-10.72	-	15	19.9-87.5	-	31.14-79.95	2.09-28.8	mixed solution and sludge digestion liquor	about 2.5g/L other OM	50-100	50mM-100mM NaCl CaCl ₂ Na ₂ CO ₃ NaHCO ₃	[98,174]
Desal-5 DL (GE)	3-7	25	8-24	0-62.5	28.5-46.4	100	-	digestion liquor	Hexanoic acid 25g/L, sugars 20mg/L	17.5	-	[6]
	3.14-10.72	-	15	17.3-84.6	-	-14.86-83.73	5.06-39.6	mixed solution and sludge digestion liquor	about 2.5g/L other OM	50-100	50mM-100mM NaCl CaCl ₂ Na ₂ CO ₃ NaHCO ₃	[98,174]
ES10 (Nitto Denko)	3.3-8.4	25	1.3-2.8	14.1-99.6	-	-	-	single solution and binary solution		0.83-8.33	0-4mM NaCl and 2mM MgSO ₄	[165]
	3.62-8.52	25	1.3-2.8	-	26.6-97.9	-	-	single solution		0.67-6.75	0.4-4mM NaCl+2mM MgSO ₄	[165]
HL (GE)	3.14-10.72	-	15	1.1-74.5	-	-0.67-72.19	11.42-52.8	mixed solution and sludge digestion liquor	about 2.5g/L other OM	50-100	50mM-100mM NaCl CaCl ₂ Na ₂ CO ₃ NaHCO ₃	[98,174]
	3.45-8.39	25	1.3-2.8	-	3.4-84.9	-	-	single solution		0.67-6.75	0.4-4mM NaCl+2mM MgSO ₄	[165]
LF10 (Nitto Denko)	3.14-10.72	-	15	24.8-91.3	-	17.18-90.71	3.6-21.1	mixed solution and sludge digestion liquor	about 2.5g/L other OM	50-100	50mM-100mM NaCl CaCl ₂ Na ₂ CO ₃ NaHCO ₃	[98,174]
NF270 (Dow Filmtec)	3.33-8.25	25	1.3-2.8	2.9-84.1	-	-	-	single solution and binary solution			50-500mg/L-0-4mM NaCl and 2mM MgSO ₄	[165]
	8.25	-	15	-	-	69.74	15.4	sludge digestion liquor		15.81	about 2.5g/L other OM	[98,174]
NF200 (Dow Filmtec)	2.8-3.6	-	8-10	1.9-13.4	-	-	-	single solution and mixed solution	Organic acid 9.5g/L, ethanol 10%v/v	8.33-66.67	-	[178]
	3.14-10.72	-	15	32.1-86.1	-	21.87-83.16	3.04-37.5	mixed solution and sludge digestion liquor	about 2.5g/L other OM	50-100	50mM-100mM NaCl CaCl ₂ Na ₂ CO ₃ NaHCO ₃	[98,174]

Chapter I

CPA2-2540 (Hydranautics)	-	21-43	17.2	35.7-73.0	-	-	17.69-38.46	single solution		1.25-9.6	-	[175]
	-	21	17.2	-	65.1-80.1	-		single solution		1.38-8.06	-	[175]
NF-1 (PA) (self-made)	natural solution pH	-	-	89	-	-	-	single solution		-	-	[179]
NF-2 (PA) (self-made)	natural solution pH	-	-	10-99.5	-	-	-	single solution		-	-	[179]
NFX (self-made)	natural solution pH	-	8-10	-15.2	-	-	-	single solution		8.33-66.67	-	[178]
Sempas Membranechnik GmbH (Jäger Umwelt-Technik)	natural solution pH	-	-	46.9	-	-	-				-	
		-	-	-	65.7	-	-	single solution		10	-	[180]
		-	-	-	-	81.99	-				-	
PA 100 (self-made)	3-9	-	-	28.0-19.2	-	-	-	mixed solution	Sugars, furfural acids	25	-	[172]
PA150 (self-made)	3-9	-	-	3.06-28.9	-	-	-	mixed solution	Sugars, furfural acids	25	-	[172]
PA400 (self-made)	3-9	-	-	5.15-25.74	-	-	-	mixed solution	Sugars, furfural acids	25	-	[172]
PES 150 (self-made)	3-9	-	-	0.4-49.5	-	-	-	mixed solution	Sugars, furfural acids	25	-	[172]
MPF-34 (Koch Membrane Systems)	-	25	-	-	-	77	-	fermentation broth	Sugars, alcohol, long-chained acid	8.64	-	[176]

Table I-7 Separation of acetic and butyric acids by previous research

Membrane	pH	Pressure (bar)	Solution	Acetic retention	Butyric retention	Separation coefficient	Ref.
Desal-5 DL	3	8	acidogenic digestion liquor	0.01	1	∞	[6]
	5	8		0.24	1	∞	
	7	8		0.62	1	∞	
Desal-5 DK	3	8	liquor	0.00	1	∞	[6]
	5	8		0.11	1	∞	
	7	8		0.60	1	∞	
ES 10	7.3	2.8	Synthetic wastewater	0.95	0.97	1.72	[165]
NF270	7.3	2.8		0.75	0.81	1.31	
Desal-5 DK	8.25	15	liquor of digested	0.57	0.45	1.28	[98]
Desal-5 DL	8.25	15	agricultural sludge	0.46	0.34	1.22	
Desal-5 HL	8.25	15	(HAc, HPr	0.24	0.40	1.27	
NF270	8.25	15	concentration 21.10	0.53	0.70	1.57	
LF10	8.25	15	and 15.81mM)	0.72	0.62	1.36	
Desal-5 DK	-	15	mix solution of acetic and butyric acids (50mM)	0.29	0.37	1.13	
Desal-5 DL	-	15		0.17	0.29	1.17	
Desal-5 HL	-	15		0.27	0.30	1.04	
NF270	-	15		0.32	0.22	1.15	
LF10	-	15		0.29	0.30	1.01	

I.3 Aims and outlines of the thesis

The thesis project is part of the RECOWER project. The RECOWER project, which is the abbreviation of pRocEss COupling fermentation and separation for solid WastE valorization, is one of the five projects funded by 3BCAR Carnot Institute in 2017 with a duration of 36 months. It aims to couple fermentation and separation processes to valorize solid urban wastes for the production of platform molecules.

The schematic diagram of the RECOWER project is shown in Figure I-6. This project is cooperated between two research units, TBI and LGC. The fermentation broth contains VFAs generated from bio-waste using a leaching bed reactor (LBR) by TBI, then, the VFAs-rich fermentation broth is treated via membrane processes such as NF and ED by LGC. The aim of the current thesis project is to investigate the nanofiltration of VFAs-containing streams, explore the possibility of nanofiltration for the separation and purification of waste-derived VFAs.

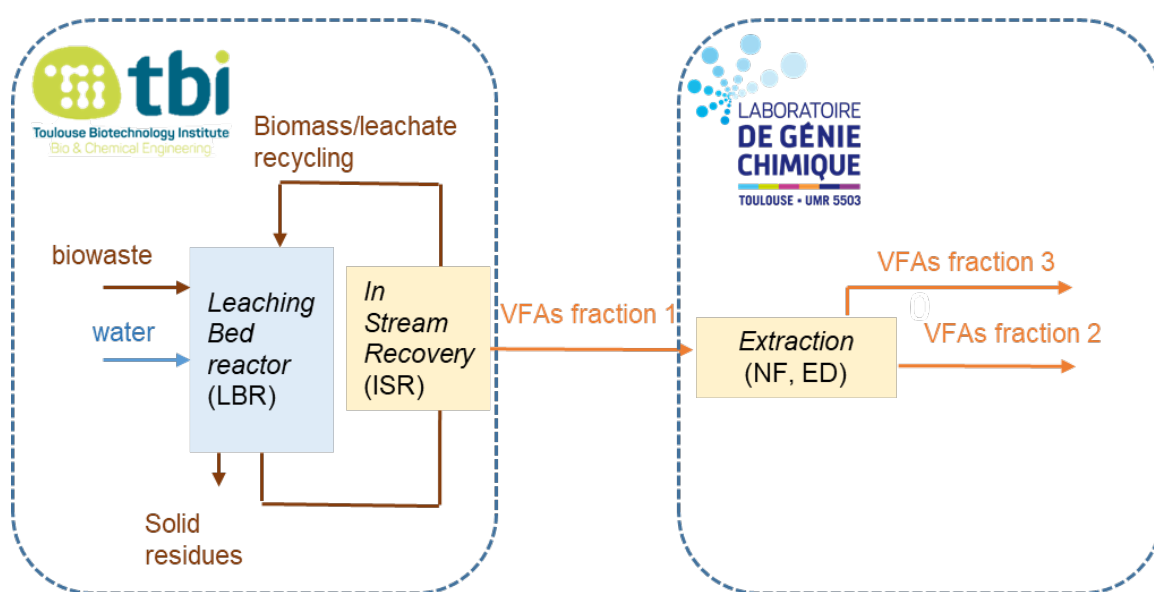


Figure I-6 Schematic diagram of the RECOWER project: production and valorization of VFAs from solid waste

As previously mentioned, the composition of the feed, solution pH, as well as the inorganic and organic impurities present in the broth are of great importance for the performance of nanofiltration. The subsequent investigation should consider those factors. The main objective of this thesis is to investigate the influence of those factors on the performance of nanofiltration

process, estimate the separation performance, and propose the possible applications of fermentation broth using nanofiltration. The following chapters will discuss the aforementioned factors separately, and then the real fermentation broth which could be influenced by all those factors will be addressed.

The material and methods used are presented in Chapter II.

In Chapter III, the experimental investigation is carried out use synthetic solutions of VFAs with different compositions at pH 8, to study the influence of feed compositions on the nanofiltration performance. Synthetic solutions of increasing complexity are investigated from single solutions (acetate, propionate, and butyrate) at different concentrations to binary and ternary mixtures of VFAs at different compositions. The retentions of individual VFAs, proportions of individual VFAs in the permeate as well as the individual solute flux and total solute flux are discussed, to reveal the mass transfer mechanism of VFAs in mixed solutions.

The influence of the co-existing inorganic anions and cations on the separation performance of NF on VFAs at pH 8 is discussed in Chapter IV. The co-ions competition between anions (VFAs⁻, Cl⁻, and SO₄²⁻) and between cations (Na⁺ and Ca²⁺) is carefully discussed at different compositions. Then, the influence of divalent cations on VFAs retention is also studied. This chapter extended the objectives in Chapter III to the more complex solutions, the influence of the feed composition on electrolytes retentions is deeply discussed.

Chapter V studies the impact of the pH on the retention of VFAs, both in single solutions and mixed solutions. Synthetic solutions at in single, binary, and ternary solutions with different concentrations at pH range from 3 to 8 are investigated, the dissociation of VFAs as well as membrane functional groups are discussed. Then a model is proposed to describe the retention of VFAs in synthetic solutions versus pH at different total concentrations.

The application of the nanofiltration process for the synthetic and real fermentation broths is reported in Chapter VI. Two NF membranes are used for the treatment of synthetic and real fermentation broths; the pH of the real fermentation both is adjusted in order to improve the selectivity of the NF process. This Chapter will discuss the possible influence of unknown organic impurities for the retention mechanism of VFAs, then can give experimental references for the feasibility of the NF process for the application of VFAs containing streams.

II.

Chapter II

Materials and methods

Chapter II

This chapter listed all the chemicals and instruments used in this project. The properties of the membranes used are also given. Then, the methods used to characterize the membrane properties and collect the experimental data are provided. The compositions of the solutions used for several investigations are listed separately. Finally, the treatment of those experimental data is also provided in detail.

II.1 Chemicals

The chemicals used for the experimental investigation including three VFAs (acetic, propionic, and butyric acids) and VFAs sodium salts (sodium acetate, sodium propionate, sodium butyrate), as well as three inorganic salts (Na_2SO_4 , NaCl , and CaCl_2). The VFAs and VFAs sodium salts were provided by Acros organics, with more than 99% of purity. The characteristics of the VFAs, VFAs sodium salts, and inorganic salts were listed in Table II-1, Table II-2, and Table II-3, respectively.

Table II-1 Characteristics of VFAs

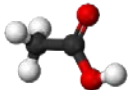
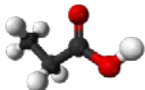
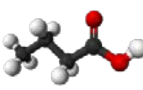
Name	Acetic acid	Propionic acid	Butyric acid
Structure			
Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)	60.05	74.08	88.11
pK_a (25°C)	4.76	4.88	4.82

Table II-2 Characteristics of VFAs sodium salts

VFAs sodium salts	Sodium acetate	Sodium propionate	Sodium butyrate
Chemical formula	CH_3COONa	$\text{C}_2\text{H}_5\text{COONa}$	$\text{C}_3\text{H}_7\text{COONa}$
Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)	82.03	96.07	110.88

Table II-3 Characteristics of the inorganic salts

Inorganic salts	Molecular weight ($\text{g}\cdot\text{mol}^{-1}$)
Na_2SO_4	142.04
NaCl	58.44
CaCl_2	110.98

II.2 Analytical methods

In the NF experiments, solution pH, and temperature in the feed, permeate, and retentate were measured before and after the filtration at once. Solutes (VFAs and inorganic salts, both anions and cations) concentrations in the feed, permeate, and retentate were taken samples and measured.

The concentrations of Ac, Pr, and Bu in single solutions were measured by a refractometer (ATAGO AX500, USA). VFAs concentrations in mixed solutions were obtained by High-Performance Liquid Chromatography (HPLC) (Jasco LC Net II / ADC, Japan) equipped with a Shodex SH1011 (Showa Denko, Japan) column and a UV detector (wavelength was set at 280nm). The details of the HPLC conditions are depicted in Table II-4. All the samples with high VFAs concentration were diluted to be in the concentration range from 5mM to 50mM.

Table II-4 Characteristics of the high-performance liquid chromatography analysis

HPLC Jasco	
Column	Shodex SH1011 (Showa Denko, Japan)
Temperature	50°C
Mobile phase	H ₂ SO ₄ 10mM
Flow rate	1 mL.min ⁻¹
Pump	PU2089plus
Auto sampler	AS2055plus
Injection volume	10µL
Detector	UV (280 nm)

The concentrations of salts were measured by ion chromatography (IEC, Dionex, France). The characteristics of the ion chromatography system are listed in Table II-5. Samples were diluted to a maximum of 1000 folds by ultra-pure water before analysis (all samples with high concentrations were diluted to the concentration range from 0.5 mM to 5 mM).

Table II-5 Characteristics of the ion chromatography analysis

Dionex ICS 3000	
Ion type	Anion, cation
Column	IonPac™ AS11, IonPac™ CS12
Temperature	30°C
Mobile phase	NaOH: 5 mM (95%)+100mM (5%); MSA (Methanesulfonic acid): 20mM (100%)
Flow rate	1 mL.min ⁻¹
Pump	GP40
Auto sampler	AS50
Injection volume	25µL
Suppresser	ASRS_4mm (137mA) CSRS_4mm (59mA)
Conductivity detector	CD20

For the real fermentation broth, the concentration of total organic carbon (TOC) was measured by TOC Shimadzu 5050A. The details of the TOC analyzer were listed in Table II-6. (TC: Total carbon; IC: inorganic carbon; TOC: the difference of TC and IC.) The samples were diluted to a maximum of 25 folds before analysis (all samples with a high concentration of TOC were diluted to the concentration range from 50 mg.L⁻¹ to 200mg.L⁻¹).

Table II-6 Characteristics of the total organic carbon (TOC) analysis

TOC Shimadzu 5050A	
Analyte	TC, IC, TOC (TC-IC)
TC method	Catalytically aided combustion oxidation
IC method	Pre-acidification
Acidification	H ₃ PO ₄ (25% v/v)
Flow rate	150 mL.min ⁻¹ (carrier gas)
Detection range	50 ppb – 4000 ppm

II.3 Membranes and nanofiltration (process) set-up

II.3.1 NF membranes

Two types of flat sheet composite membranes, NF 45 and XLE (Filmtec, Dow), were used in this thesis project, the main characteristics of which are provided in Table II-7.

Table II-7 Characteristics of NF-45 and XLE, Dow Filmtec membranes

	MWCO (g.mol ⁻¹)	Material of active layer	Maximum Temperature (°C)	Max. pressure (bar)	pH range	Membrane isoelectric point	Pure water permeability (m.s ⁻¹ .bar ⁻¹ , 25°C)
NF-45	150-300	Polyamide	45°C	41[181]	2-12 (recommended 3-10)	4.0[182]	1.57×10 ⁻⁶ [183]
XLE	100	Polyamide	45°C	41	2-11	4 [184]	2.16×10 ⁻⁶ [185]

The pure water permeability and the retention of 100mM of glucose solution of NF-45 and XLE membranes are given in Figure II-1. The experimental points were fitted using a model proposed by Timmer et al. [143] as follows.

$$R_i = \frac{R_{si} \times J}{J + B_{si}} \quad (\text{II.1})$$

In this equation, B_{si} is the mass transfer parameter of solute i and R_{si} is the rejection parameter of solute i . J is the filtration flux. B_{si} and R_{si} were experimentally obtained by fitting.

In the following chapters, individual solute retention and global retention are also fitted using the same model.

Besides, Eq. (II.1) also gives the variation of solute retention versus filtration flux. Then, the retention of solute at a specific filtration flux can be calculated from the fitted function.

It is shown that the pure water permeability of XLE membrane ($1.5 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$) is lower than NF-45 membrane ($2.0 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$). Then the glucose retention of XLE membrane is nearly 99.9% at high filtration flux, much higher than that of NF-45 (92%). This observation indicates that XLE membrane is much tight than NF-45 membrane, and a much higher VFAs retention is expected.

The current project was aimed to reveal the solutes transfer mechanism, larger retention variation is beneficial for the comparison of different operating conditions. Therefore, most of the experiments were done by NF-45 membrane, while XLE membrane was used for verification and comparison between two types of membranes.

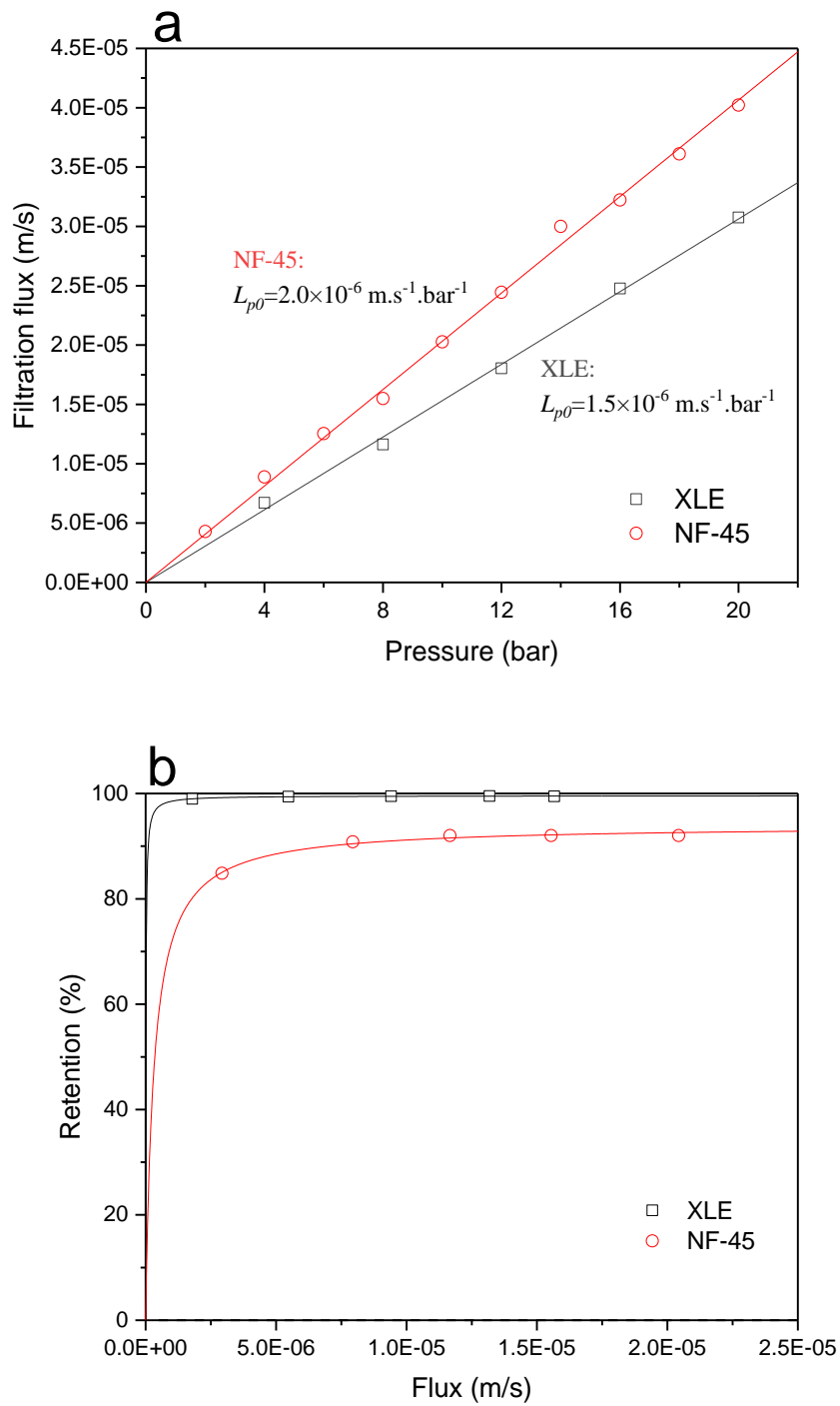


Figure II-1 (a) Pure water permeability and (b) glucose retention of XLE and NF-45 membranes. T= 25 °C.

II.3.2 NF (process) set-up

NF experiments were carried out using a dead-end stirred filtration cell depicted in Figure II-2. The total volume of the cell was 400mL, the dead volume (volume of porous disc and tube) of this system is about 4 cm³. The stirring speed was set at 108 rpm. A piece of NF-45 or XLE membrane was placed at the bottom of the cell, supported by a 316L stainless steel porous disc. The active membrane surface was 30 cm². Pressurized air was used to pressurize the cell. The pressure was controlled manually by a valve.

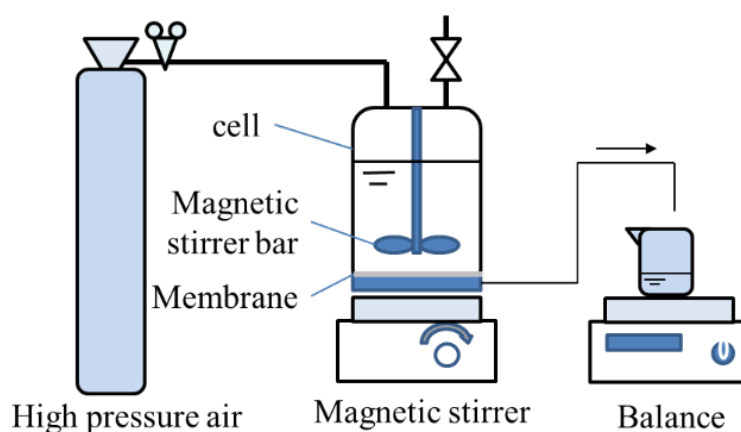


Figure II-2 Schematic diagram of the filtration system

Filtration was operated at room temperature (between 20 and 27°C). For each experiment, 400 mL of solution was initially fed into the cell. Then, the pressure was increased step by step (4, 8, 12, 16, 20 bar). In order to thoroughly rinse the entire system, a volume of 20 cm³ feed was required to pass through the membrane (collected in the beaker) at the initial transmembrane pressure, then 1-2 cm³ of permeate was collected by a disposable polyethylene bottle as a sample. Increase transmembrane pressure to the next pressure value, a volume of 8 cm³ permeate was needed to rinse the membrane and tube before taking a sample for this pressure.

For each transmembrane pressure, 3 cm³ of permeate was collected in the beaker to stabilize the filtration flux, then, from 3 cm³ to 8 cm³, the permeate was timed and measured three times by a timer and an electronic balance, the filtration flux obtained was the average of the three filtration flux calculated from the time and weight records of the permeate.

For each experiment, approximately 60mL of permeate was collected in total. It means that in the worst case, the concentration factor would be equal to 1.15. The feed volume, V_f , permeate

volume, V_p , and retentate volume, V_r , were determined, as well as the concentrations of the feed, C_f , permeate, C_p , and retentate, C_r , using the previously detailed analytical methods. The mass balance, $V_f C_f = V_p C_p + V_r C_r$, was checked, and it was observed that the maximum difference does not exceed 5%.

Membrane conditioning and cleaning procedures are crucial to obtain accurate data. The membrane was first immersed in ultra-pure water for 24 hours. It was then compacted by filtering ultra-pure water at a pressure of 20 bar until the filtration flux, J reaches a constant value, three filtrations and a minimum of 1.5 h are required. The linearity of J versus ΔP was checked and the mean hydraulic permeability L_{p0} was calculated by the slope of $J/\Delta P$. After each NF experiment, the membrane was washed twice by filtering 200 mL of ultra-pure water and pure water permeability was measured to check any membrane fouling or aging.

In addition to pure water permeability, retention of glucose (molecular weight: 180g.mol⁻¹) was used as a reference to detect any membrane modification during the experiments. In this work, once an abnormally pure water permeability was detected (more than 20% difference between two consecutive permeability measurements) or one piece of membrane was used over one month, rejection of Glucose will be tested, to have a reference for membrane damage as well as fouling. Once a membrane sample presents visible mechanical damage or a significant increase or decrease of Glucose rejection (more than 5%), it was being replaced by a new one.

Four pieces of NF-45 membrane and two pieces of XLE membrane are used in this thesis project. No fouling was observed for all the pieces of membranes used, all the membrane changes were due to mechanical damage, contamination, or exposed in the air and completely dried.

For NF-45 membrane, the pure water permeability was between $1.6 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$ and $2.0 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$ for all the four pieces of membrane. The glucose retentions for the four pieces of membranes were within 90% to 93% at a transmembrane pressure of 20 bar. For XLE membrane, the pure water permeability was between $1.5 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$ and $1.9 \times 10^{-6} \text{ m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$, and the glucose retentions were higher than 99.5% at a transmembrane pressure of 20 bar.

II.4 Experimental procedures

The experimental investigation was aimed to reveal the mass transfer mechanism and separation performance of NF process on complex solutions such as fermentation broth contain VFAs.

The experimental investigation was carried with synthetic solutions with increasing complexities, from single and mixed solutions with only VFAs of different compositions at pH 8, mixed solutions with VFAs and inorganic salts of different compositions at pH 8, single and mixed solutions of VFAs at different pH values (from 3 to 8), to synthetic solutions with similar compositions as the real fermentation broths and a real fermentation broth contain VFAs at different pH values (from 5.7 to 8.2).

II.4.1 Nanofiltration of synthetic solutions of VFAs

Nanofiltration of synthetic solutions of VFAs was firstly carried out. Single and mixed VFAs solutions at pH 8 were used to investigate the transfer of individual solutes. The synthetic solutions of VFAs were prepared using sodium acetate, sodium propionate, sodium butyrate dissolved in ultra-pure water.

The feed compositions of single, binary, and ternary solutions of VFAs are summarized in Table II-8. Three total concentrations were investigated (100mM, 200mM and 500mM). The feed compositions are indicated in Figure II-3.

Table II-8 Composition of the synthetic solutions for three total concentrations, 100mM, 200mM and 500mM

Solute	Single solutions (%)			Mixed solutions (%)									
	s1	s2	s3	s4	s5	s6	s7	s8	s9*	s10	s11	s12	
Acetate	100			50	20		50	20	33	60	20	20	
Propionate		100		50	80	50			33	20	60	20	
Butyrate			100				50	50	80	33	20	20	60

* For s9, proportion of Ac:Pr:Bu=33%:33%:33%, two additional total concentrations were also used (300mM, 400mM).

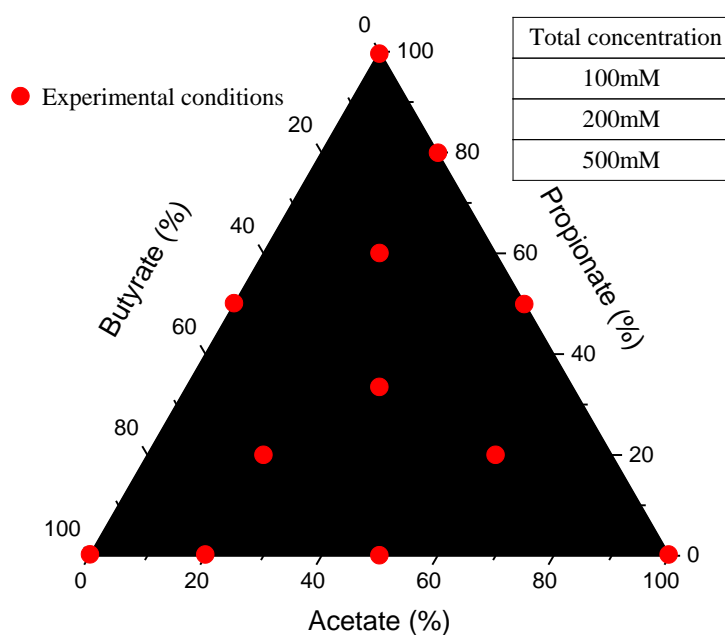


Figure II-3 Composition of the synthetic VFAs solutions

The synthetic solutions from s1 to s12 were filtrated by NF-45 membrane. Then, to verify that if the results obtained with NF-45 membrane were repeatable for another membrane, nanofiltration of solution s9 was also carried out using XLE membrane. The experimental results obtained with these solutions were discussed in Chapter III.

II.4.2 Nanofiltration of synthetic solutions of VFAs: influence of inorganic ions

Synthetic solutions with VFAs sodium salts and three inorganic salts were used to investigate the influence of additionally charged solutes on the mass transfer of VFAs.

Since SO_4^{2-} and Ca^{2+} are divalent ions, the equivalent concentration was used during the investigation of VFAs solutions with inorganic salts. Nanofiltration of single solutions of the three inorganic salts at three ionic concentrations (100mEq.L^{-1} , 200mEq.L^{-1} , and 500mEq.L^{-1}) and mixed solutions containing VFAs and three inorganic salts at two ionic concentrations (200mEq.L^{-1} and 500mEq.L^{-1}) and six proportions (Ac/Bu binary VFAs solutions and Ac/Pr/Bu ternary VFAs solutions with the three salts at ratio of VFAs:salts at 1:1, 2:3, and 1:4 respectively)

were investigated by NF-45 membrane. The compositions of synthetic solutions are summarized in Table II-9.

The results obtained will be discussed and compared in Chapter IV.

Table II-9 Composition of the synthetic solutions for three total concentrations, 100mM, 200mM and 500mM

Solution number	Concentration (mEq.L ⁻¹)	VFAs:salts	Proportion in the feed (%)					
			Ac	Pr	Bu	Na ₂ SO ₄	NaCl	CaCl ₂
s13	100, 200, 500	-				100		
s14	100, 200, 500	-					100	
s15	100, 200, 500	-						100
s16	200	1:1	25		25	50		
s17	200	1:1	17	17	17	50		
s18	500	2:3	20		20	60		
s19	500	2:3	13	13	13	60		
s20	500	1:4	10		10	80		
s21	500	1:4	7	7	7	80		
s22	200	1:1	25		25		50	
s23	200	1:1	17	17	17		50	
s24	500	2:3	20		20		60	
s25	500	2:3	13	13	13		60	
s26	500	1:4	10		10		80	
s27	500	1:4	7	7	7		80	
s28	200	1:1	25		25			50
s29	200	1:1	17	17	17			50
s30	500	2:3	20		20			60
s31	500	2:3	13	13	13			60
s32	500	1:4	10		10			80
s33	500	1:4	7	7	7			80

II.4.3 Influence of the pH on the retention of VFAs

Solution pH influences the dissociation of VFAs as well as the surface charge of the membrane. Synthetic solutions with neutral forms of VFAs (i.e., acetic acid, propionic acid, and butyric acid, pH \approx 3) were used to investigate the influence of solution pH on the retentions of VFAs. The feed compositions of single, binary, and ternary solutions are summarized in Table II-8. Three total concentrations were investigated (100mM, 200mM and 500mM). Each solution was adjusted to different pH values between 3 and 8 using NaOH.

Solutions s34 to s40 were filtrated by NF-45 membrane. The pH values of each solution are listed in Table II-11.

Then, to confirm the results obtained from NF-45 membrane can be extended to another membrane, the filtration of synthetic solutions of s40 was carried out using XLE membrane. The experimental results obtained with these solutions will be discussed in Chapter V.

Table II-10 Composition of the synthetic solutions for three total concentrations (100mM, 200mM, and 500mM) at various solution pH between 3 and 8

Solutes	Single solutions (%)			Mixed solutions (%)			
	s34	s35	s36	s37	s38	s39	s40
Ac	100			50		50	33
Pr		100		50	50		33
Bu			100		50	50	33

Table II-11 pH values of solution s34 to s40

solutions	pH						
	3	4.7	5.3	5.6	6.6	8	
s34	√	√	√	√		√	
s35	√	√	√	√		√	
s36		√	√	√		√	
s37		√	√	√		√	
s38			√	√		√	
s39		√	√	√		√	
s40	√	√	√	√	√	√	

II.4.4 Nanofiltration of synthetic and real fermentation broths containing VFAs

The compositions of a real broth contain VFAs obtained from anaerobic fermentation of municipal solid wastes provided by Toulouse Biotechnology Institute (TBI, previous name LISBP), Université de Toulouse, are listed in Table II-12. The fermentation broth is produced from house hold solid waste via a leaching bed reactor (LBR), operated at a constant pH of 5.5 (diagram of the reactor shown in Figure I-6). The initial pH of the real fermentation broth is 5.7.

The real fermentation broth contain many organic matter/impurities (e.g., ethanol and butanol, as shown in Table II-12), could hinder the following processes. It is impossible and also not necessary to identify the compositions of those organic matter/impurities (OM), the compositions is obtained as the difference of TOC and the theoretical TOC values of the three VFAs obtained from HPLC (i.e., $TOC_{OM}=TOC-TOC_{VFAs}$).

Table II-12 Composition of the real fermentation broth

Organics		Inorganics	
Components	Concentration(mM)	Components	Concentration (mM)
Ac	44.41	Cl ⁻	28.96
Pr	30.76	SO ₄ ²⁻	0.32
Bu	39.96	Na ⁺	46.34
Ethanol	10.17	NH ₄ ⁺	10.96
Butanol	1.72	K ⁺	3.98
		Ca ²⁺	24.09
Total VFAs Concentration (mM)	115.13	Total cations concentration (mEq.L⁻¹)	109.46
TOC (mg.L⁻¹)	4425.17		
TOC_{VFAs} (mg.L⁻¹)	4091.38		
TOC_{OM} (mg.L⁻¹)	333.79		

Experiments were also carried out with synthetic fermentation broths with the similar compositions and pH as the real fermentation previously mentioned, and the real fermentation broth, to investigate if the results previously obtained with synthetic solutions can be extended to a more complex system.

In order to identify the influence of each main component (Cl⁻, Na⁺, Ca²⁺, and Ethanol), synthetic fermentation broths were prepared with only VFAs, with the addition of NaCl, and with the addition of CaCl₂ respectively according to the compositions of the real fermentation broth. Table II-13 summarizes the compositions of the synthetic fermentation broths used for the experimental investigation.

Table II-13 Compositions and pH values of the synthetic fermentation broths

Components	pH 5.7 and 8 (XLE)			pH 5.7 (NF-45)		
	Syn 1	Syn 2	Syn 3	Syn 4	Syn 5	Syn 6
Ac (mM)	39	39	39	45	45	45
Pr (mM)	39	39	39	31	31	31
Bu (mM)	39	39	39	40	40	40
NaCl (mM)		24			24	
CaCl ₂ (mM)			24			24
Total VFAs concentration (mM)	117	117	117	116	116	116

Synthetic broths Syn1, Syn2, and Syn3 at pH 5.7 and pH 8 were filtrated by XLE membrane, while Syn4, Syn5, and Syn6 at pH 5.7 were filtrated by NF-45 membrane.

Then, the experiments were carried out with the real fermentation broth. Nanofiltration using XLE membrane at the initial pH was firstly carried out. The real fermentation both at the initial pH (pH 5.7) used for NF-45 membrane was recycled from the retentate and permeate of the previous filtration using XLE membrane. Then, after the filtration using NF-45 membrane, the permeate and retentate were recycled again. The recycled real fermentation broth was adjusted to pH 6.6 using NaOH solution, and filtration is carried out using the pH adjusted real fermentation broth. Finally, the recycled real fermentation broth was adjusted to pH 8.2 and the last filtration is applied using NF-45 membrane.

The experiments with real fermentation broth using the two membranes are listed in Table II-14.

Table II-14 Filtrations on the pH-adjusted real fermentation broths

Membranes	Real fermentation broth		
	pH 5.7 (initial)	pH 6.6	pH 8.2
XLE	√		
NF-45	√	√	√

The results obtained from synthetic and real fermentation broths by the two membranes will be compered and discussed in Chapter VI.

II.5 Data treatment

The experimental results discussed in this manuscript including filtration flux, solute retention, solute proportion, as well as separation factor, those data were acquired using the following equations.

The filtration flux was calculated via Eq. (II.2).

$$J = \frac{1}{A} \cdot \frac{\Delta V}{\Delta t} \quad (\text{II.2})$$

ΔV , total volume of water and solute permeated through the membrane within time Δt , (m^3 , measured by the weight of the permeate, assuming the density of the permeate equal to $1 \times 10^6 \text{ g} \cdot \text{m}^{-3}$)

A , effective area of the membrane (m^2)

Δt , duration of filtration (s), measured by a timer.

The individual solute retention was calculated from Eq. (II.3).

$$R(\%) = \left(1 - \frac{c_i^p}{c_i^f}\right) \cdot 100\% \quad (\text{II.3})$$

The proportion of individual solute i in the feed and permeate were calculated from Eqs. (II.4) and (II.5) respectively.

$$P_i^f = \frac{c_i^f}{c_{total}^f} = \frac{c_i^f}{\sum_{i=1}^n c_i^f} \quad (\text{II.4})$$

$$P_i^p = \frac{c_i^p}{c_{total}^p} = \frac{c_i^p}{\sum_{i=1}^n c_i^p} \quad (\text{II.5})$$

In a mixed solution contain more than three solutes, the relative proportions of solute i and j , for the couple of two solutes i and j , in the feed and permeate are given in Eqs. (II.6), (II.7), (II.8), and (II.9) respectively.

$$P_{i_i,j}^f = \frac{c_i^f}{c_i^f + c_j^f} \quad (\text{II.6})$$

$$P_{i_i,j}^p = \frac{c_i^p}{c_i^p + c_j^p} \quad (\text{II.7})$$

$$P_{j_i,j}^f = \frac{c_j^f}{c_i^f + c_j^f} = 1 - P_{i_i,j}^f \quad (\text{II.8})$$

$$P_{j-i,j}^p = \frac{c_j^p}{c_i^p + c_j^p} = 1 - P_{j-i,j}^f \quad (\text{II.9})$$

c_i^f, c_j^f concentrations of solutes i, j in the feed (mM)

c_i^p, c_j^p concentrations of solutes i, j in the permeate (mM)

c_{total}^f total concentration in the feed (mM)

c_{total}^p total concentration in the permeate (mM)

P_i^f, P_j^f proportions of solutes i, j in the feed

P_i^p, P_j^p proportions of solutes i, j in the permeate

$P_{i-i,j}^f, P_{j-i,j}^f$ relative proportions of solutes i, j for the couple of i and j in the feed

$P_{i-i,j}^p, P_{j-i,j}^p$ relative proportions of solutes i, j for the couple of i and j in the permeate

Then, the ratio between the proportion of solute i in the permeate and feed was obtained from Eq. (II.10).

$$rT_i = \frac{P_i^p}{P_i^f} \quad (\text{II.10})$$

When $rT_i > 1$, it means that solute i is enriched in the permeate. If $rT_i < 1$, it means that solute i is impoverished in the permeate.

The separation factor ($SF_{i,j}$) defines the separation efficiency between two solutes, i and j , which was calculated according to Eq.(II.11).

$$SF_{i,j} = \frac{c_i^p/c_j^p}{c_i^f/c_j^f} = \frac{p_i^p/p_j^p}{p_i^f/p_j^f} = \frac{rT_i}{rT_j} \quad (\text{II.11})$$

Depends on the values of rT_i and rT_j , the separation factor could be in between 0 to 1 (when $rT_i < rT_j$) or from 1 to ∞ (when $rT_i > rT_j$). In this manuscript, to keep the calculated separation factor between two solutes always higher than 1, the separation factor was calculated using the ratio between proportion in the permeate and feed of the solute which is enriched in the permeate divided by that of the one impoverished in the permeate (i.e., $rT_i > rT_j$).

rT_i and $SF_{i,j}$ calculated from proportion and relative proportions are the same.

rT_i ratio between the proportion of solute i in the permeate and feed

rT_j ratio between the proportion of solute j in the permeate and feed

III.

Chapter III
Nanofiltration of synthetic solutions of
VFAs

This chapter aims to investigate the influence of VFAs composition on the performance of nanofiltration, size and charge effects are discussed for single and mixed solutions.

As previously mentioned (Chapter I), at a neutral solution pH, the NF membrane is negatively charged. Besides the size effect, there are two charge effects on the mass transfer mechanism of charged solutes, i.e., ionic concentration induced screening effect and co-ions competition due to the interactions of more than two ions with the same sign of charge.

For a single solution, there is only the influence of ionic concentration; the solutes and membrane charge are screened when the ionic concentration increases, and then the retention decreases. However, in a mixed solution, besides the screening effect, the individual solutes retentions are also affected by co-ions competition. This phenomenon leads to the retention of the more retained solute increase while the retention of the less retained one decreases [148]. Then, the individual solutes retentions in the mixed solutions at different concentrations are influenced by the combination of screening effect and co-ions competition.

This chapter gives an experimental study, dealing with the influence of the feed composition on nanofiltration of VFAs salts at pH 8, for which VFAs are totally dissociated. The retentions of solutes are measured, proportions of individual VFAs in the permeate of mixed solutions are calculated to discuss the influence of composition on the mass transfer mechanism of single and mixed VFAs solutions. Solution complexity is increased from single VFAs (acetate, propionate, and butyrate) at different concentrations to mixtures of VFAs (binary and ternary solutions) of different compositions. The experiments are carried out using NF-45 membrane for all the conditions, then, a XLE membrane is also used, the results obtained with the two membrane is compared and discussed.

III.1 Retentions of VFAs in single and mixed solutions

III.1.1 Solutes retentions in single solutions

Retentions of VFAs in single solutions (s1-s3, see Chapter II, Table II-8) as a function of filtration flux are represented in Figure III-1a for the different concentrations. One can observe that for any solute, the retention increases with the filtration flux. Moreover, for a given filtration flux, the retention of the individual VFAs continuously decreases for increasing concentrations. The retentions of individual VFAs at various concentrations are compared at a given filtration flux of $2 \times 10^{-6} \text{ m} \cdot \text{s}^{-1}$ in Figure III-1b. The retention of acetate decreases from 65 % to 38 % as its concentration increases from 100mM to 500 mM with an intermediate value of 59 % at 200mM. The same tendencies are obtained for propionate (72%, 68%, and 45%) and butyrate (88%, 73%, and 55%).

At pH 8, the VFAs are in their dissociated form and negatively charged (see pK_a values in Chapter II, Table 2.1). It is known that the retention of charged solutes depends on the combination of steric effects and electrostatic interactions between the charged solutes and the charged membrane. The higher retentions observed at low concentrations are mainly due to electrostatic repulsions since both VFAs and membrane are negatively charged at pH 8. Then, increasing VFAs concentrations result in lower retentions due to the screening effect [139,150].

On the other hand, one can observe that the retentions of VFAs follow a sequence of acetate < propionate < butyrate, in agreement with their molecular weights (acetate, $59 \text{ g} \cdot \text{mol}^{-1}$, propionate, $73 \text{ g} \cdot \text{mol}^{-1}$ and butyrate, $87 \text{ g} \cdot \text{mol}^{-1}$). Comparable result was previously reported with other carboxylic acid salts at the same concentration (100 mM) with the following sequence for the solutes retentions: formate ($45 \text{ g} \cdot \text{mol}^{-1}$) < acetate ($59 \text{ g} \cdot \text{mol}^{-1}$) < lactate ($89 \text{ g} \cdot \text{mol}^{-1}$) [148].

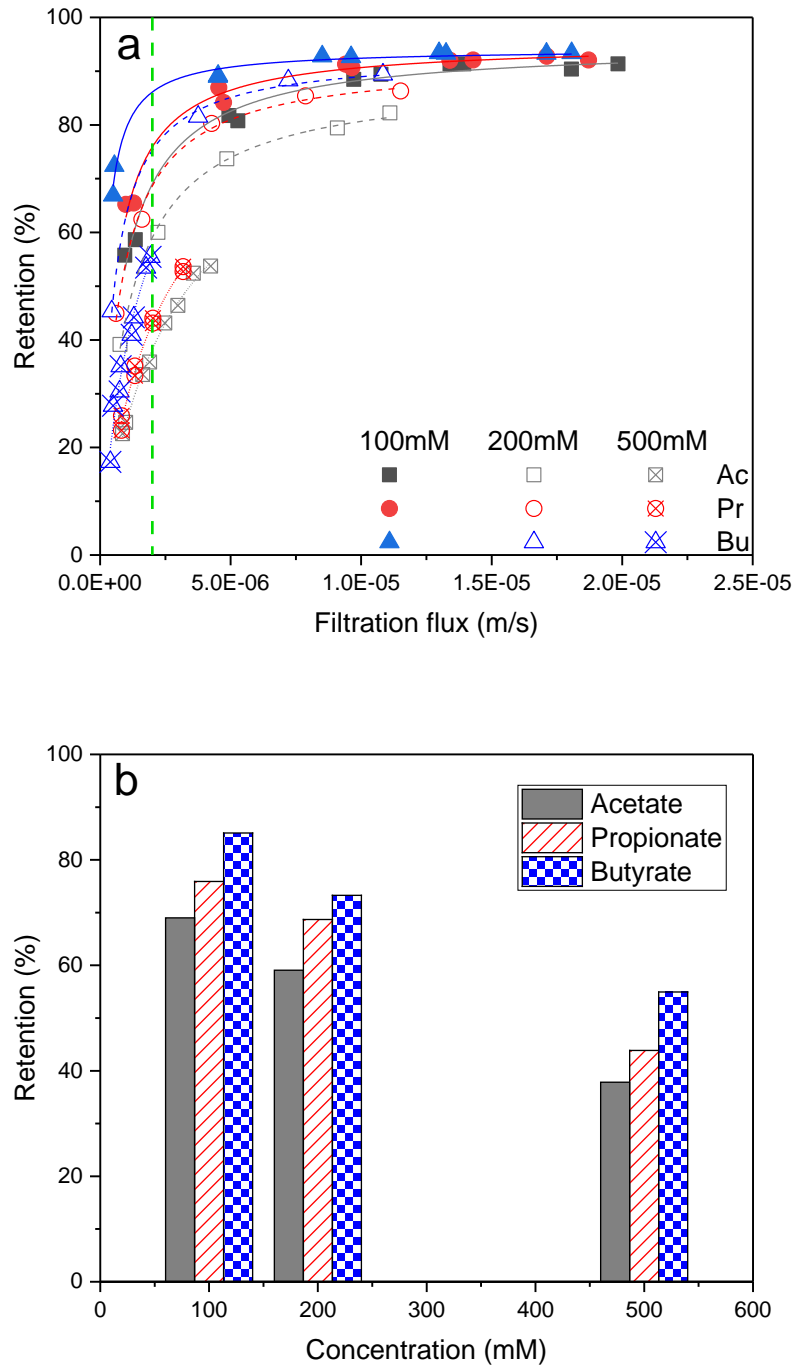


Figure III-1 Retention of VFAs in single solutions for different concentrations (a) retention versus filtration flux (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

III.1.2 Individual solutes retentions in mixed solutions

Binary and ternary solutions containing equal proportions of VFAs are firstly investigated.

The retentions of individual solutes in a binary solution (acetate: propionate=50%: 50%) are plotted in Figure III-2a versus filtration flux for increasing total concentrations. As observed with single solutions, the solutes' retentions increase with filtration flux. Figure III-2b shows the individual solutes retentions for different concentrations at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$. Retentions of acetate and propionate decrease from 74% and 82%, for a total concentration of 100 mM, to 51% and 68%, at 200 mM, and to 30% and 50% respectively for a total concentration of 500 mM. As previously mentioned for single solutions, the influence of the total concentration on individual solutes retentions is due to the screening effect. Then, one can notice that the retention of propionate is higher than that of acetate, following the molecular weight, for any total concentration and that the retention difference between acetate and propionate increases with the total concentration.

The same trends are observed with binary solutions of acetate and butyrate (acetate: butyrate=50%: 50%) (Figure III-3) and ternary solutions (acetate: propionate: butyrate=33%: 33%: 33%) (Figure III-4). For the given filtration flux aforementioned, retentions of acetate and butyrate in binary mixture decrease from 72% and 86% at 100mM, to 58% and 80% at 200mM, then decline to 24% and 60% respectively for the total concentration of 500mM (Figure III-3b). For ternary solutions, the retentions of acetate, propionate and butyrate are 68%, 79% and 86% at 100mM, 49%, 68% and 77% at 200mM, and go down to 24%, 43%, and 58% at 500mM (Figure III-4b). From these results, a general trend can be drawn. Indeed, for any composition and filtration flux, the same retention sequence is observed, i.e., acetate < propionate < butyrate. This sequence, already observed with single solutions, follows the VFAs molecular weights.

For mixed solutions with different concentrations and proportions, i.e., Ac: Pr = 20% :80% (Figure III-5), Ac: Bu = 20% :80% (Figure III-6), Ac: Pr: Bu = 60%: 20% :20% (Figure III-7), Ac: Pr: Bu = 20%: 60% :20% (Figure III-8), and Ac: Pr: Bu = 20%: 20% :60% (Figure III-9), the same tendencies (i.e., Ac < Pr < Bu) can be also observed.

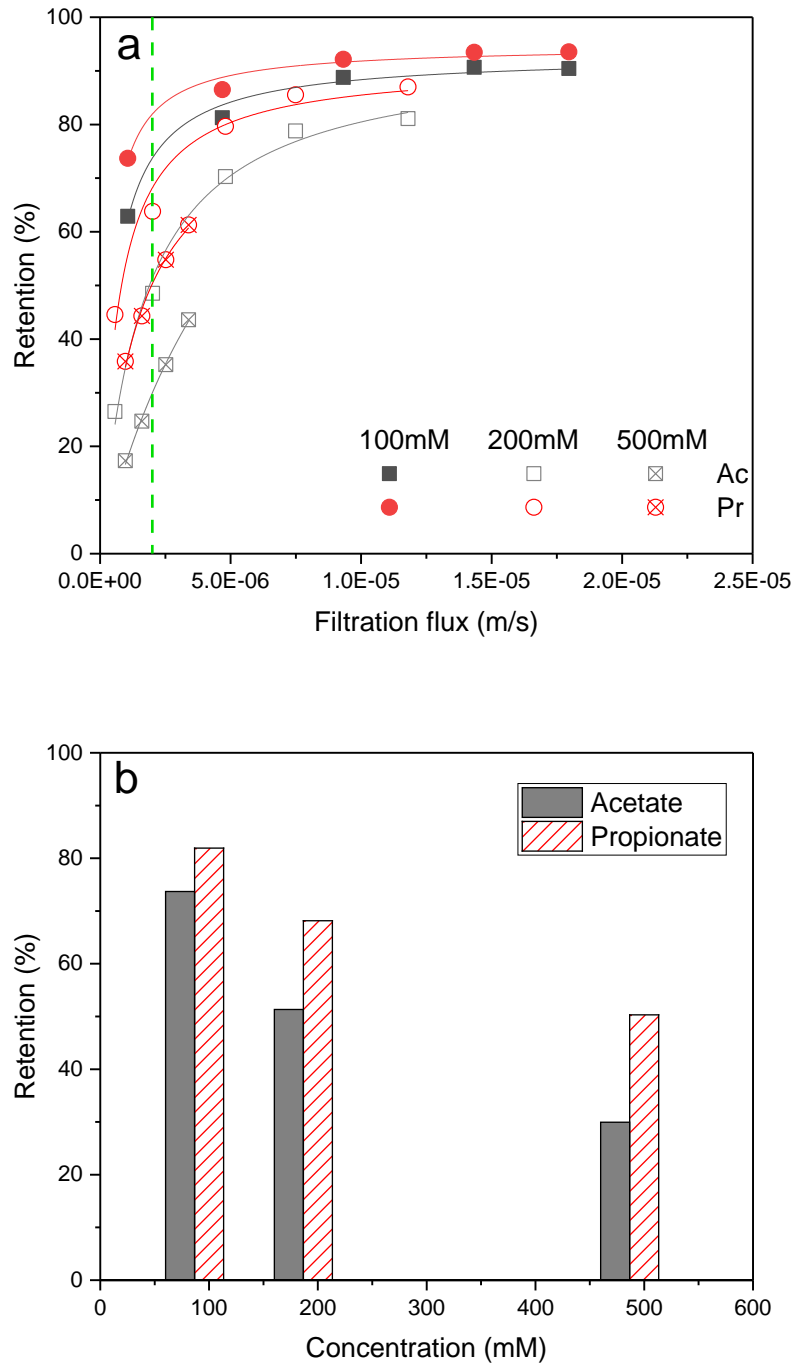


Figure III-2 Individual VFAs retention in binary (acetate: propionate=50%:50%) solutions (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

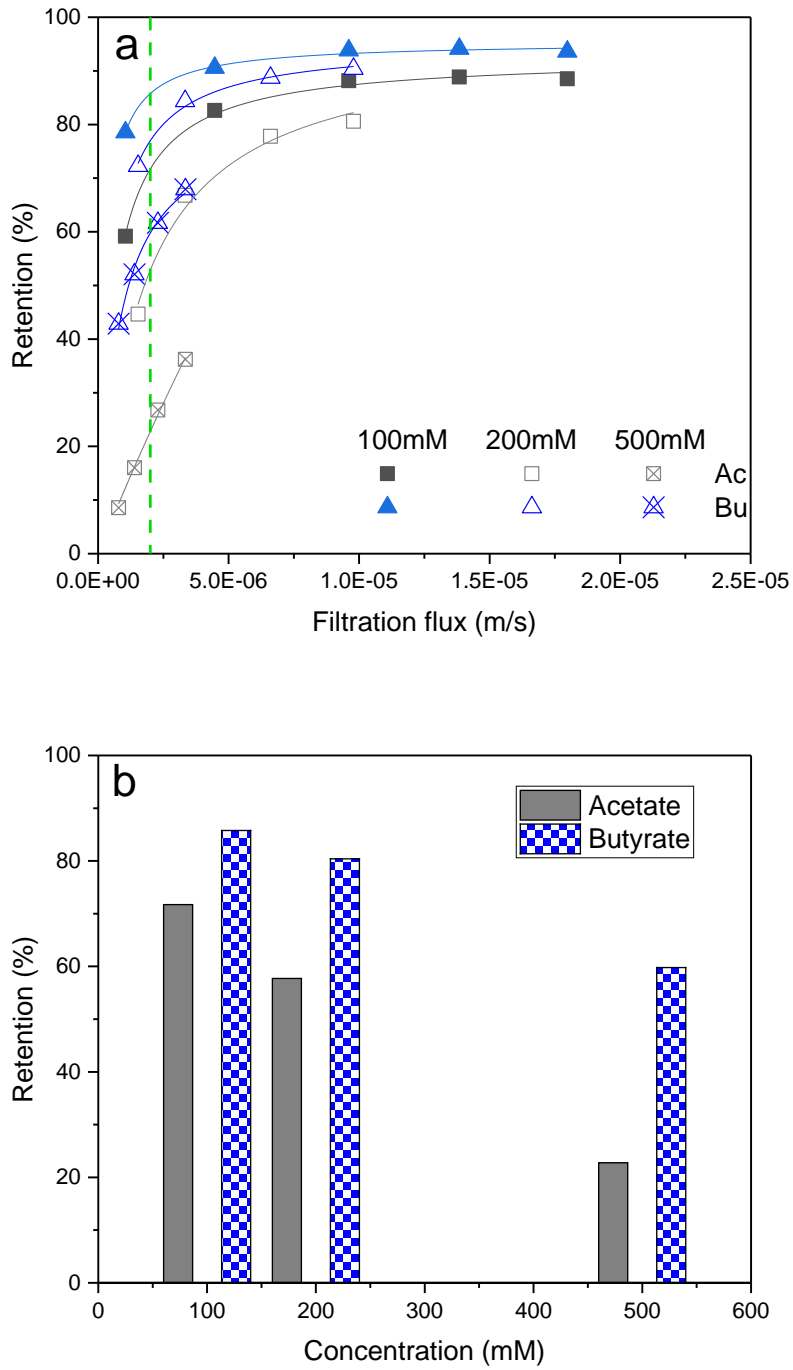


Figure III-3 Individual VFAs retention in binary (acetate: butyrate=50%:50%) solution (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

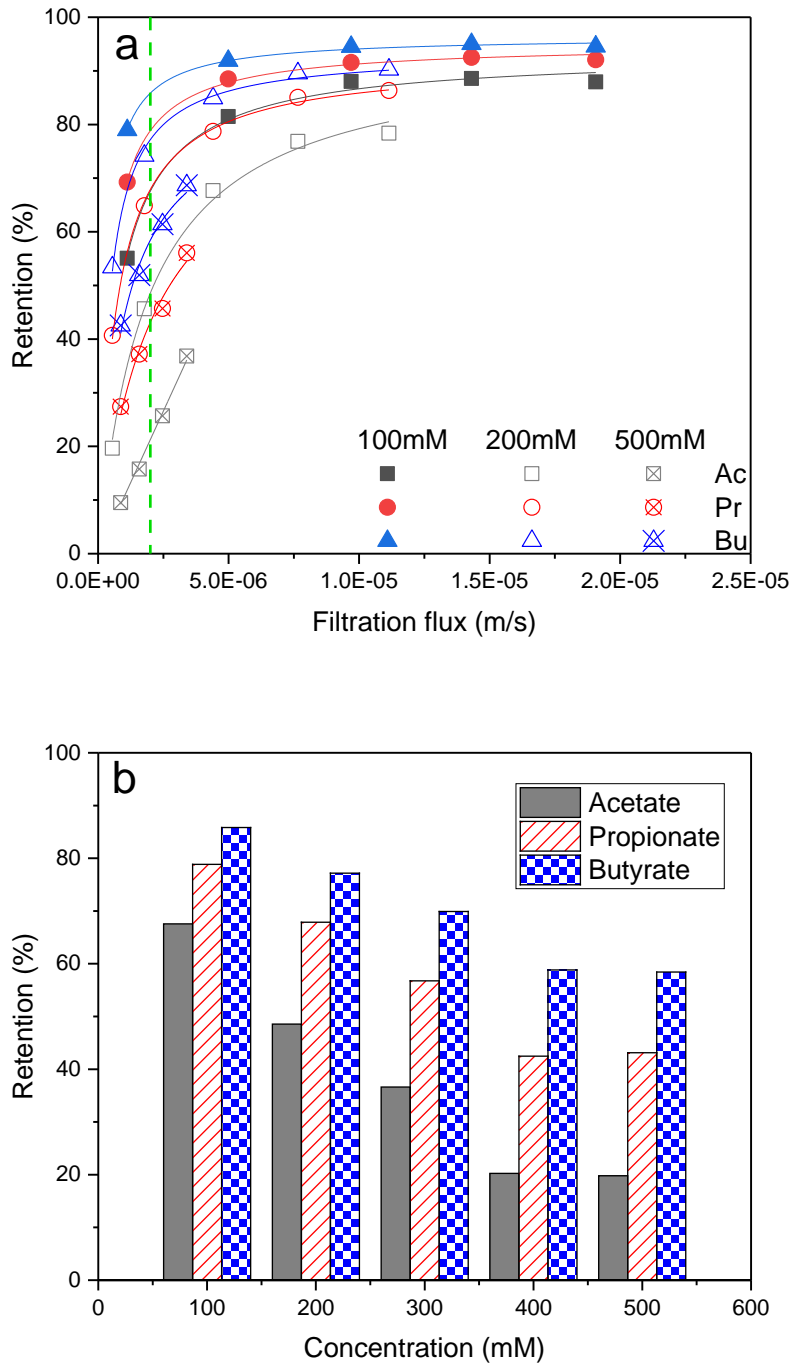


Figure III-4 Individual VFAs retention in ternary (acetate: propionate: butyrate=33%:33%:33%) solution (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

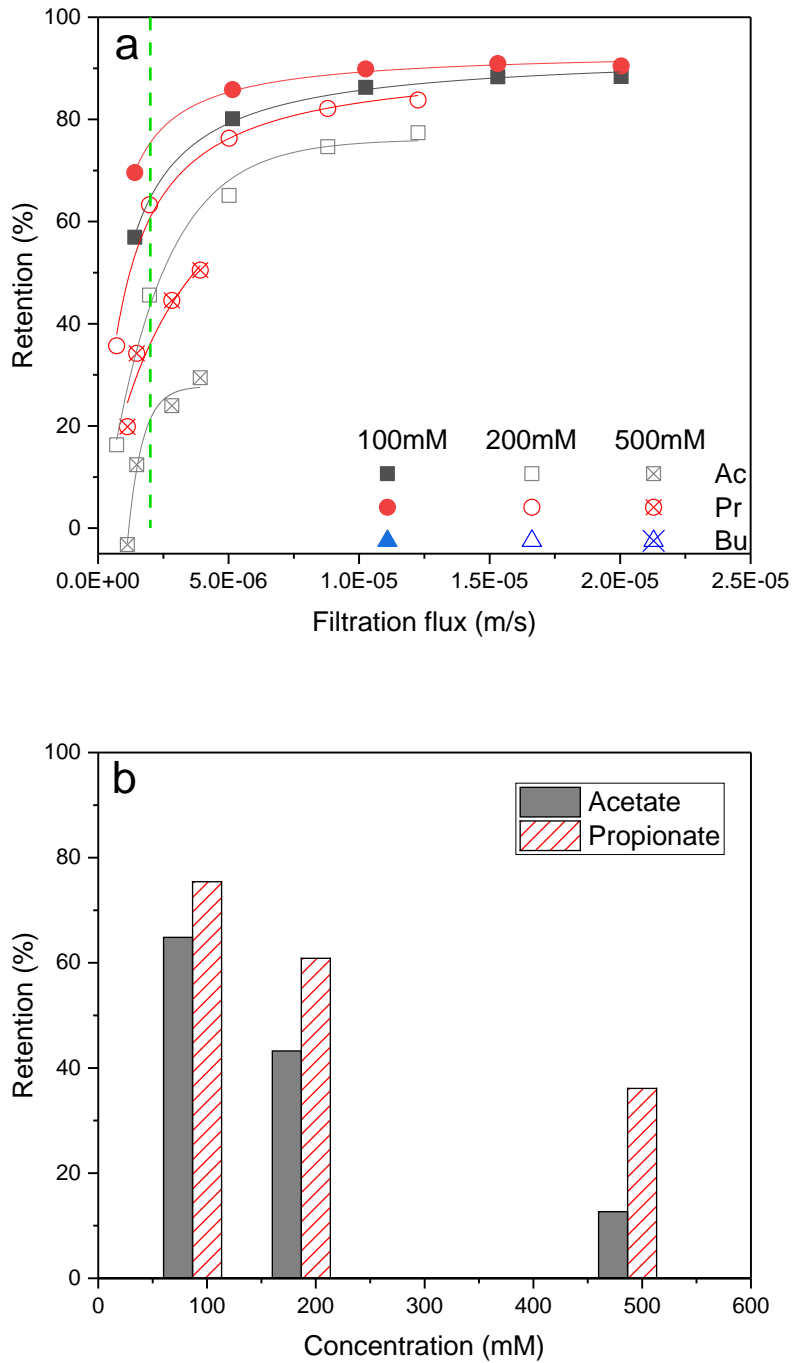


Figure III-5 Individual VFAs retention in binary (acetate: propionate =20%:80%) solutions (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

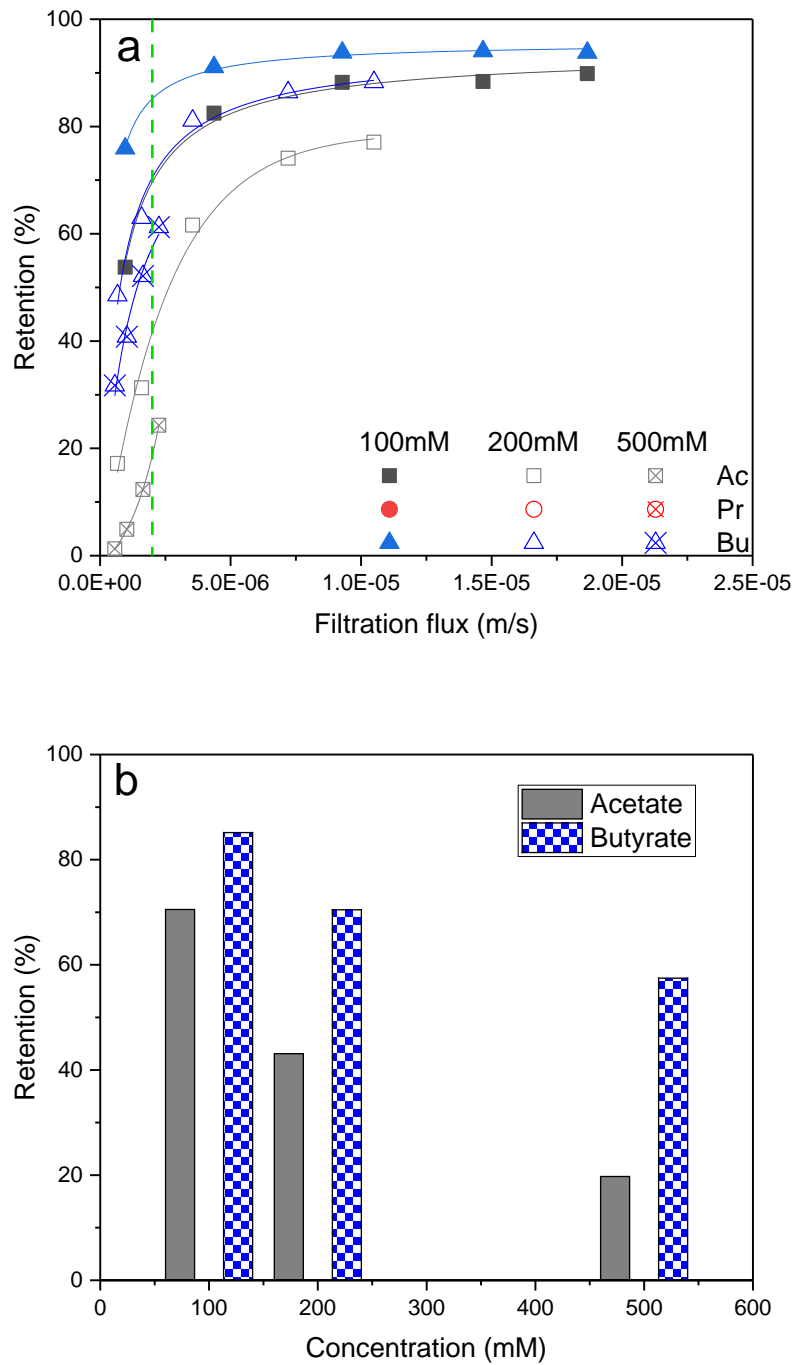


Figure III-6 Individual VFAs retention in binary (acetate: butyrate=20%:80%) solutions (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

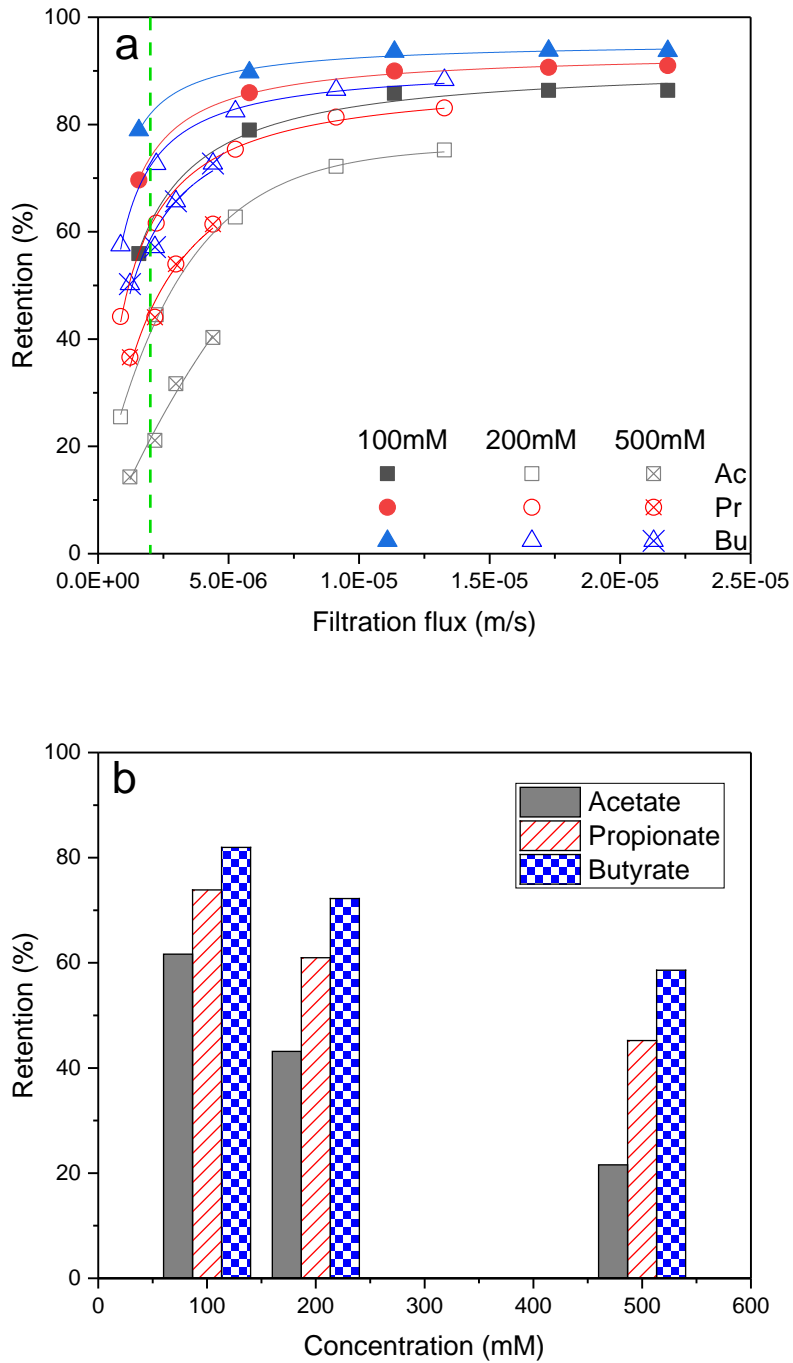


Figure III-7 Individual VFAs retention in ternary (acetate: propionate: butyrate=60%:20%:20%) solution (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

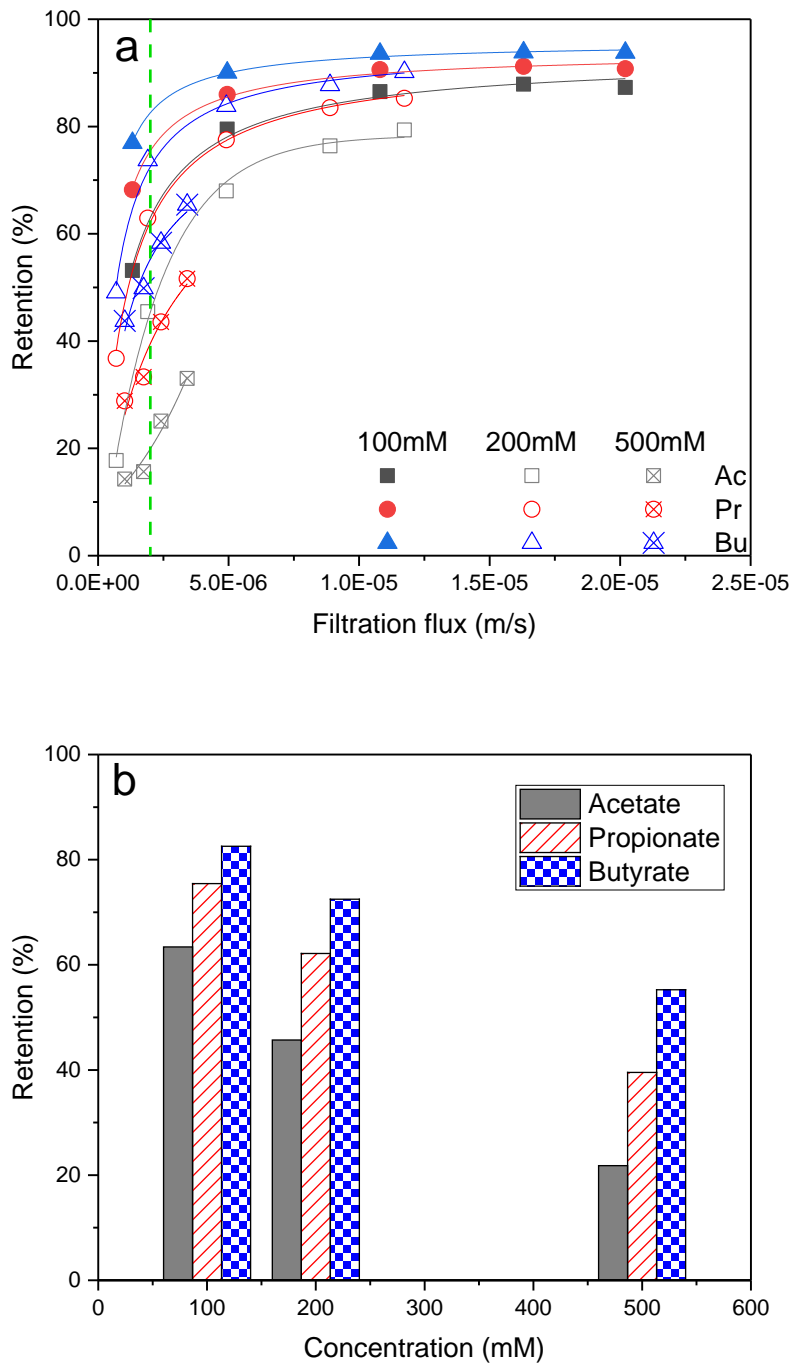


Figure III-8 Individual VFAs retention in ternary (acetate: propionate: butyrate=20%:60%:20%) solutions (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

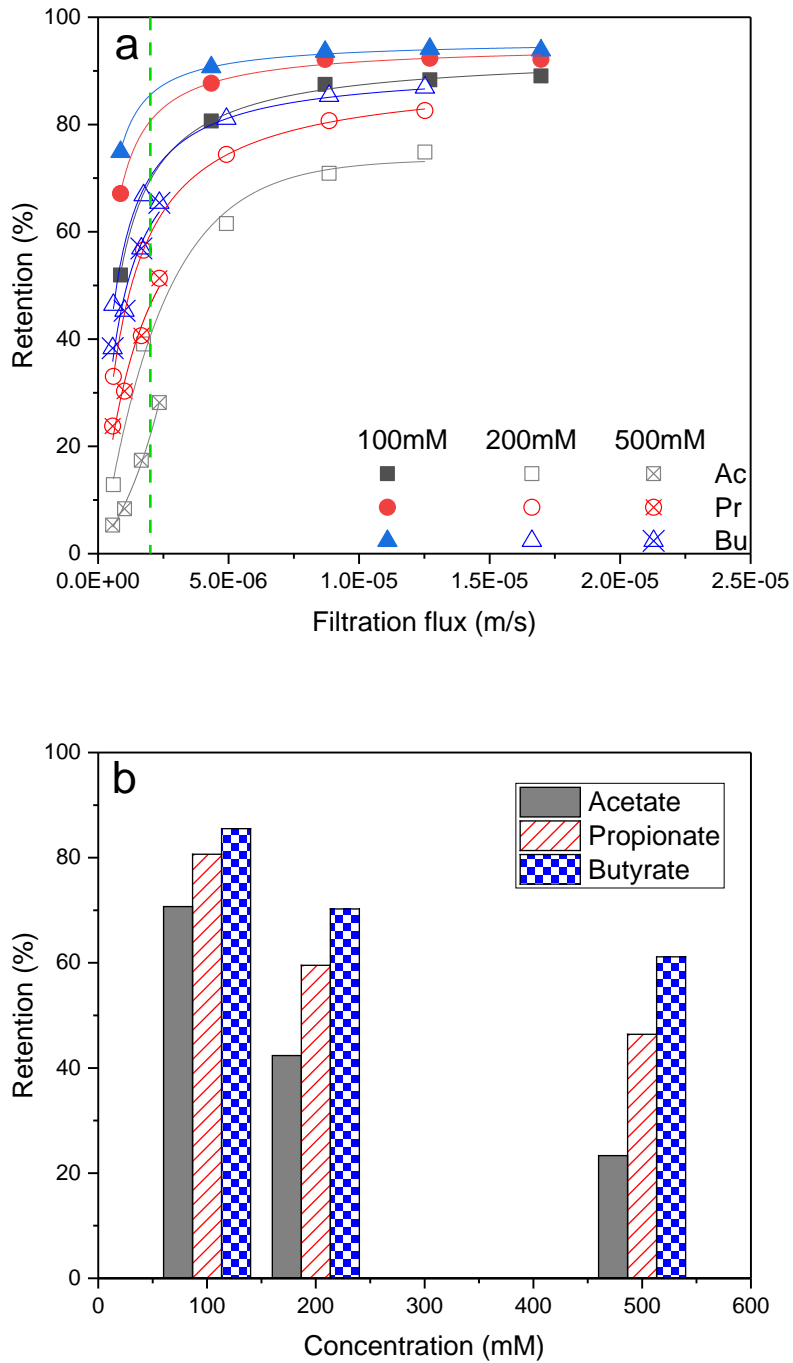


Figure III-9 Individual VFAs retention in ternary (acetate: propionate: butyrate=20%:20%:60%) solutions (a) retention versus filtration flux at different concentrations (b) retention versus concentration at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, using NF-45 membrane, at pH 8.

Since the retention mechanism of nanofiltration is a combination of size and charge, it is expected that the retention of solutes with the same charge decreases for increasing molecular weight. Indeed, this was previously observed during NF of single solutions of formate (46.03 g.mol^{-1}), acetate (60.05 g.mol^{-1}), and lactate (90.08 g.mol^{-1}) at a given concentration, with various membranes, NF1, NF2 and NF270 [186]. However, contradictory results have also been reported for different membranes and more complex solutions. For instance, for given operating conditions (dead-end nanofiltration, transmembrane pressure 15 bar, total concentration 50mM and pH 8.25), it was observed that with HL and NF270 membranes the retention of acetate is lower than that of butyrate, whereas the reverse is obtained with DK, DL, and LF10 membranes [174]. The retentions of carboxylic acids contained in a real digestion liquor, a more complexed solution, during cross-flow nanofiltration using DL and DK membranes were also reported. They were compared with the retentions obtained with single or mixed synthetic solutions. It was observed that the retention of butyric acid during NF of the digestion liquor was much higher (close to 100%) than that observed with synthetic solutions. On the other hand, on the contrary to the molecular weight sequence, higher retention of acetate was obtained compared to that of propionate (at pH 7). However, the explanation was not identified [6].

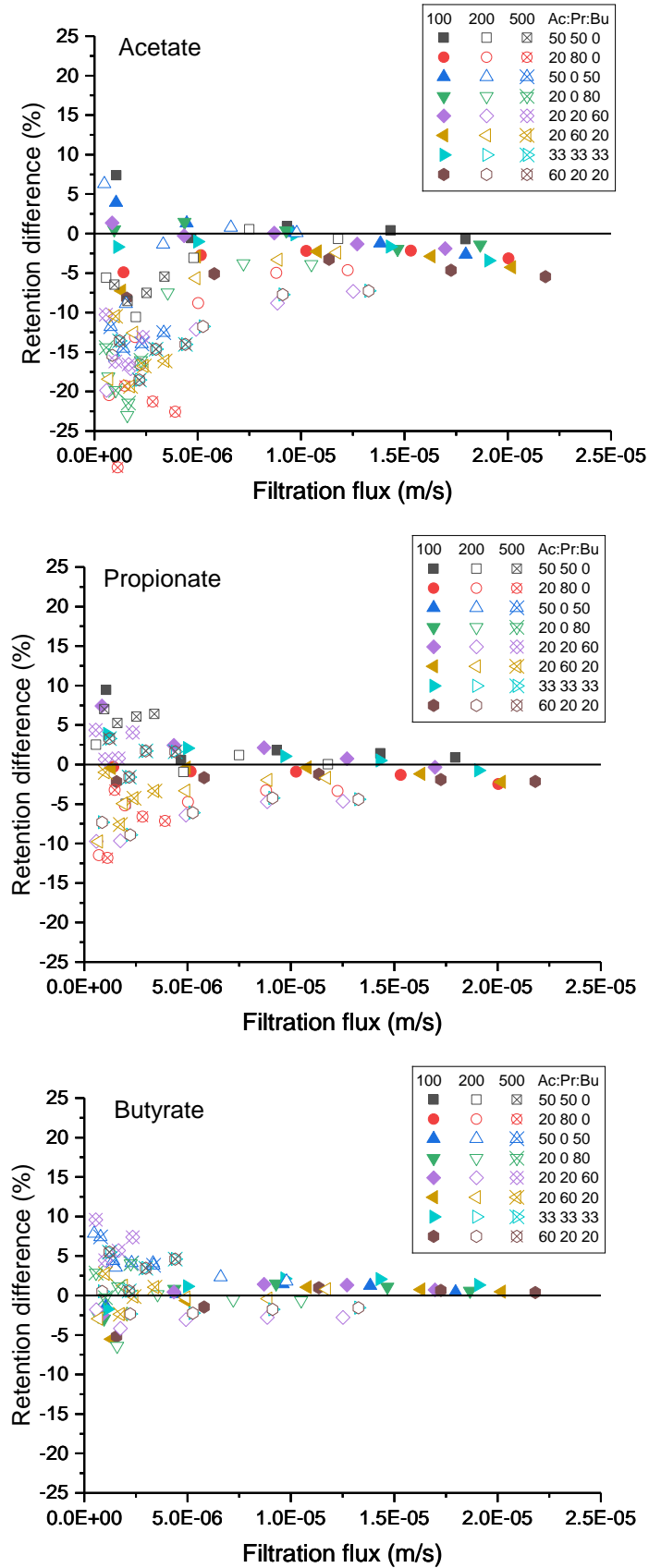


Figure III-10 Comparison of Individual VFAs retentions between mixtures and single solutions ($\text{Retention difference} = R_{mix}^{VFA} - R_{sgl}^{VFA}$) for all the conditions investigated using NF-45 membrane, at pH 8.

The differences between individual solutes retention in mixed solutions and single solutions (Retention difference = $R_{mix}^{VFA} - R_{sgl}^{VFA}$) are shown in Figure III-10. The experimental VFAs retentions in the mixed solutions are compared with the individual VFAs retentions in single solutions at the same filtration flux via fitting, as explained in Chapter II.

Firstly, one can observe that the retention differences between individual VFAs in mixed and single solutions decrease when the filtration flux increases. The retentions in mixtures (binary and ternary solutions) are different from those obtained with single solutions. Indeed, for most of the cases, it seems that the retention of the less retained solute (Ac) in the mixture decreases compared to that in a single solution, while the retention of the more retained solute (Bu) increases compared to that in a single solution. Furthermore, the increase and decrease are more significant at high concentrations and low filtration flux. For Pr, the VFA has retention in-between of Ac and Bu, its retention can be either higher or lower compared to single solution. No clear trend at different compositions can be drawn.

These results are in agreement with previous ones concerning the retention of monovalent and divalent organic acid salts of various molecular weight in single solutions and mixtures (formate, acetate, lactate, and succinate). Indeed, it was also reported that the retention of the most retained solute, succinate, was higher in the binary mixtures than in the single solutions. Meanwhile, the retentions of the less retained acid salts, formate, acetate, and lactate, decreased significantly in the presence of succinate and even reached negative values under certain conditions. The extent of decline of monovalent acid salt retentions followed the sequence: formate>acetate>lactate [148]. This trend, i.e., increase of the retention of the more retained solute and decrease of the less retained solute, was mentioned as “distribution effect” [148] or “co-ions competition” [142,187].

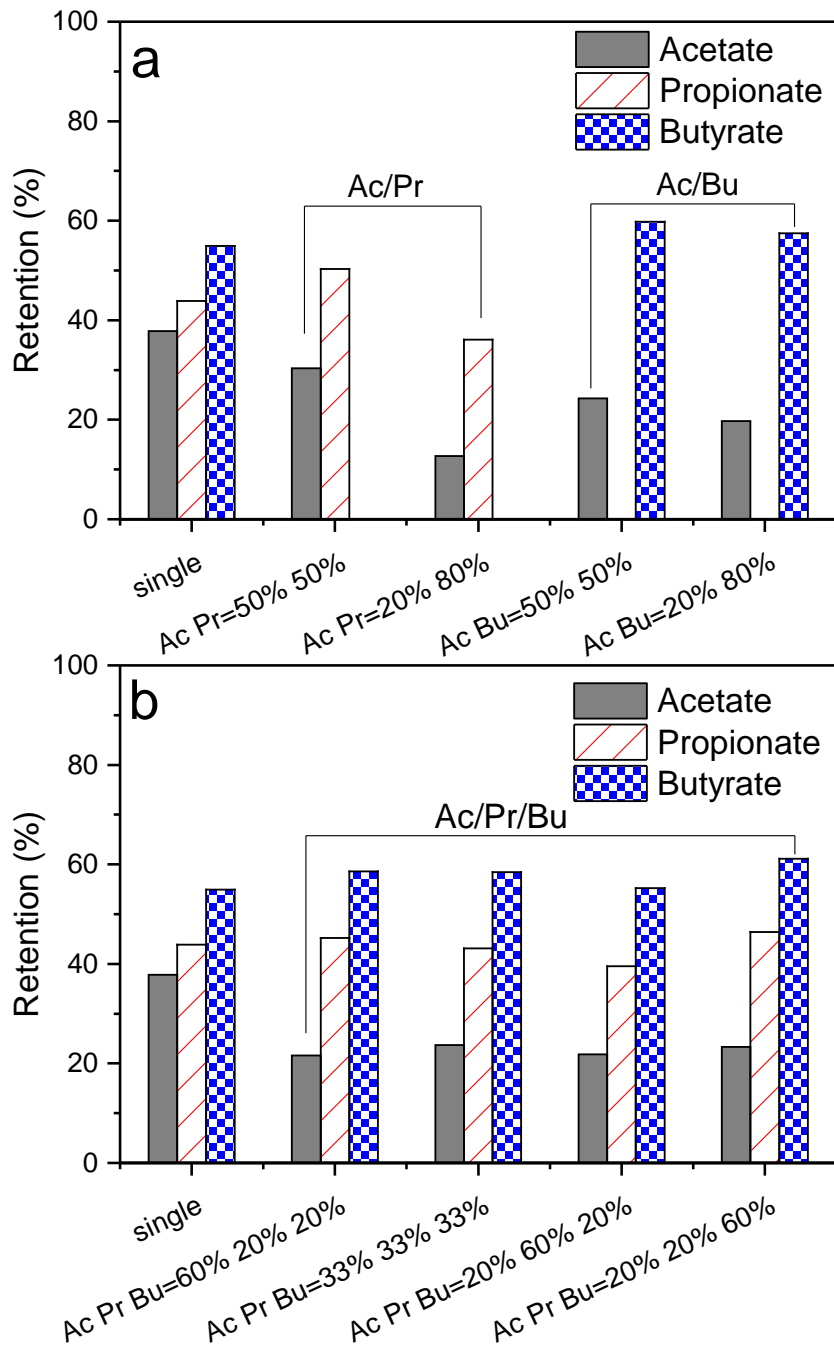


Figure III-11 Comparison of individual VFAs retentions in single and mixed solutions with different proportions at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$ and the total concentration of 500mM (a) Binary solutions (b) Ternary solutions using NF-45 membrane, at pH 8.

Figure III-11 shows the individual VFAs retentions at a given filtration flux in binary and ternary solutions with different proportions of VFAs, at a total concentration of 500 mM. This condition is in the region of low filtration flux and high concentration, in which the retention difference between VFAs in single and mixed solutions is more pronounced than high filtration flux and low concentrations (which is shown in Figure III-10). The retentions in single solutions at the same concentration are given for comparison. As observed previously, the retention of the less retained solute decreases and that of the more retained one increases compared to those observed in single solutions (except for the retention of propionate in the binary solution with the proportion of Ac: Pr = 20%: 80%). In addition, the extent of retention decrease of the less retained solute (Ac) is larger than the extent of the retention increase of the more retained solutes (Pr and Bu).

For binary solutions of Ac/Pr and Ac/Bu, one can observe that when the proportion of the less retained solute (acetate) decreases from 50% to 20%, the retentions of both VFAs tend to decrease. This decrease is more pronounced for the binary solution of Ac/Pr than for that of Ac/Bu (Figure III-11a).

Different authors suggested that the concentration ratio between the co-ions is one of the major factors influencing the retention decrease of the less retained solute [128,150]. For instance, during nanofiltration of a mixed solution of Na_2SO_4 and NaNO_3 , a decrease of the NO_3^- retention was observed for an increasing concentration ratio of $\text{SO}_4^{2-}/\text{NO}_3^-$ in the feed [136]. Similar results were observed for the retention of acetate in a succinate/acetate binary solution, i.e. a decrease of acetate retention for increasing succinate/acetate ratio[128].

As previously explained, this phenomenon, called “co-ions competition” [142] or “distribution effect” [148], is due to the “competition” or “distribution” of the co-ions.

Current observation at high concentration and low filtration flux is in agreement with previous research, showing that for binary mixtures increase the proportion of more retained solute (or decrease the proportion of less retained one) makes the retention of the less retained solute decrease [128,136,139,148,188].

However, for ternary mixtures, no clear trend is observed for the retentions of individual VFAs obtained with mixtures of different proportions (Figure III-11b).

III.2 Solute transfer in mixed solutions

III.2.1 Proportions of VFAs in the permeate

The aim of NF process on VFAs separation is to change the VFAs proportion between the feed and permeate. Therefore, the comparison of VFAs proportion in the permeate at different compositions and operating conditions can give guidance for further separation.

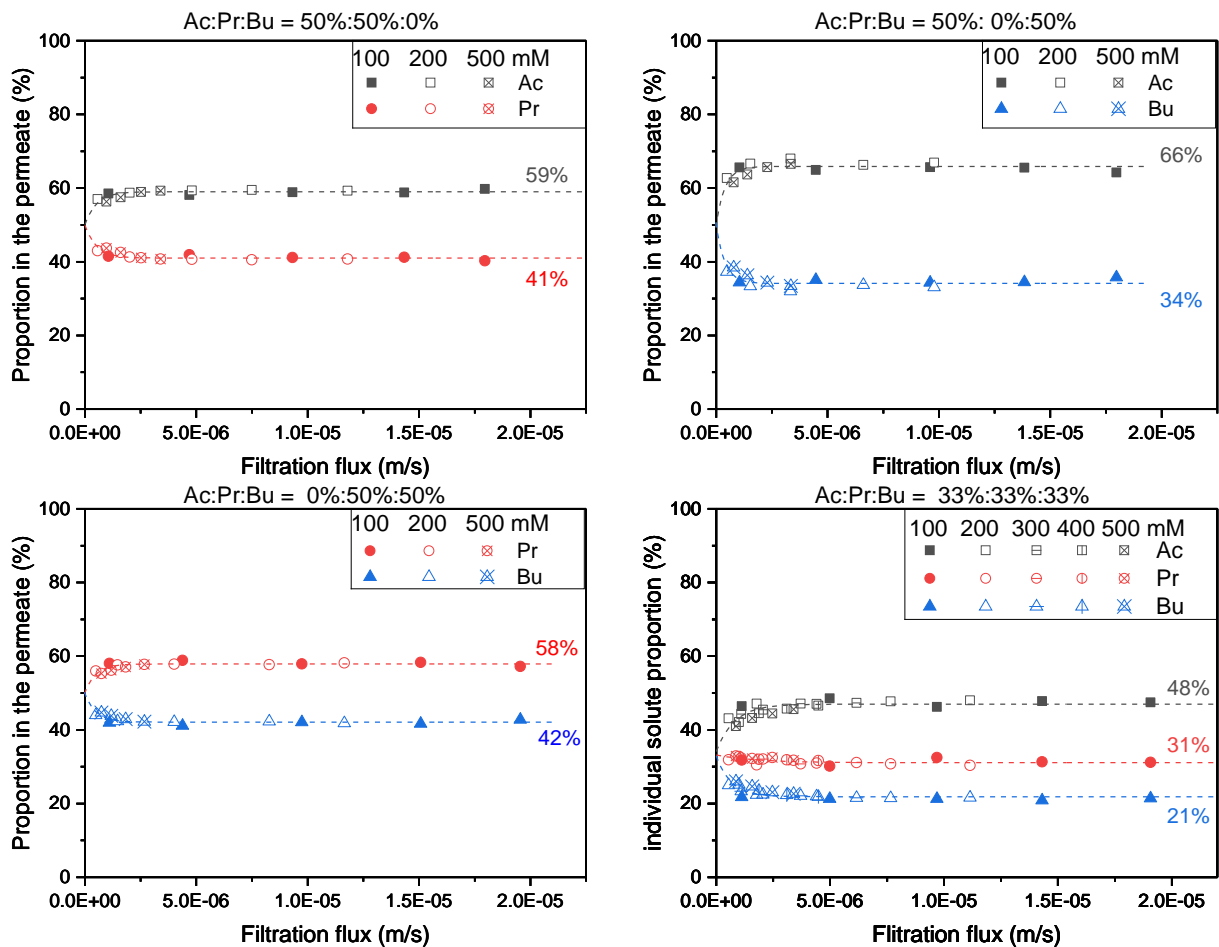


Figure III-12 Individual VFAs proportions in the permeate for Binary (Ac/Pr, Ac/Bu, Pr/Bu) and ternary (Ac/Pr/Bu) solutions at different concentrations with equal VFAs proportion (50% or 33%) in the feed, using NF-45 membrane, at pH 8.

Figure III-12 shows the individual VFAs proportions in the permeate versus filtration flux for binary and ternary solutions at different concentrations with an identical proportion of VFAs in the feed.

For all the concentrations investigated, one can observe that the proportion of the less retained solute in the permeate increases when the filtration flux increases, and reaches a plateau (namely P_i^*) when the filtration flux is higher than a certain value. This is the case for Ac in Ac/Pr, Ac/Bu, and Ac/Pr/Bu mixtures and for Pr in Pr/Bu mixture. At the same time, the proportion of the more retained solute decreases as the filtration flux increases, then remains nearly constant at high filtration flux. This is the case for Pr in Ac/Pr mixture and Bu in Ac/Bu, Pr/Bu, and Ac/Pr/Bu mixtures. For the ternary mixture Ac/Pr/Bu, the proportion of Pr, which has a retention between the ones of acetate and butyrate, decreases slightly compared to that in the feed (from 33% to 31%).

Then, comparing the results obtained with binary and ternary solutions, the proportion of Ac increases 9%, 16%, and 15% in Ac/Pr, Ac/Bu and Ac/Pr/Bu solutions respectively, the proportion of Bu decreases 16%, 8%, and 12% in Ac/Bu, Pr/Bu and Ac/Pr/Bu solutions respectively. This observation indicates that the existence of other co-ions has a significant influence on the ionic proportions in the permeate. Thus, the higher the difference between solutes' retentions in single solutions, the higher the difference between solutes proportions in the permeates of mixtures.

For mixed solutions with different proportions (Ac: Pr = 20% :80%, Ac: Bu = 20% :80%, Ac: Pr: Bu = 20%: 20% :60%, Ac: Pr: Bu = 20%: 60% :20%, and Ac: Pr: Bu = 60%: 20% :20%), the same tendencies can be also observed (shown in Figure III-13).

Those results indicate that, for a given proportion in the feed, regardless of the concentration, one fixed solute proportion (P_i^{p*}) is found in the permeate when the filtration flux is higher than a certain value.

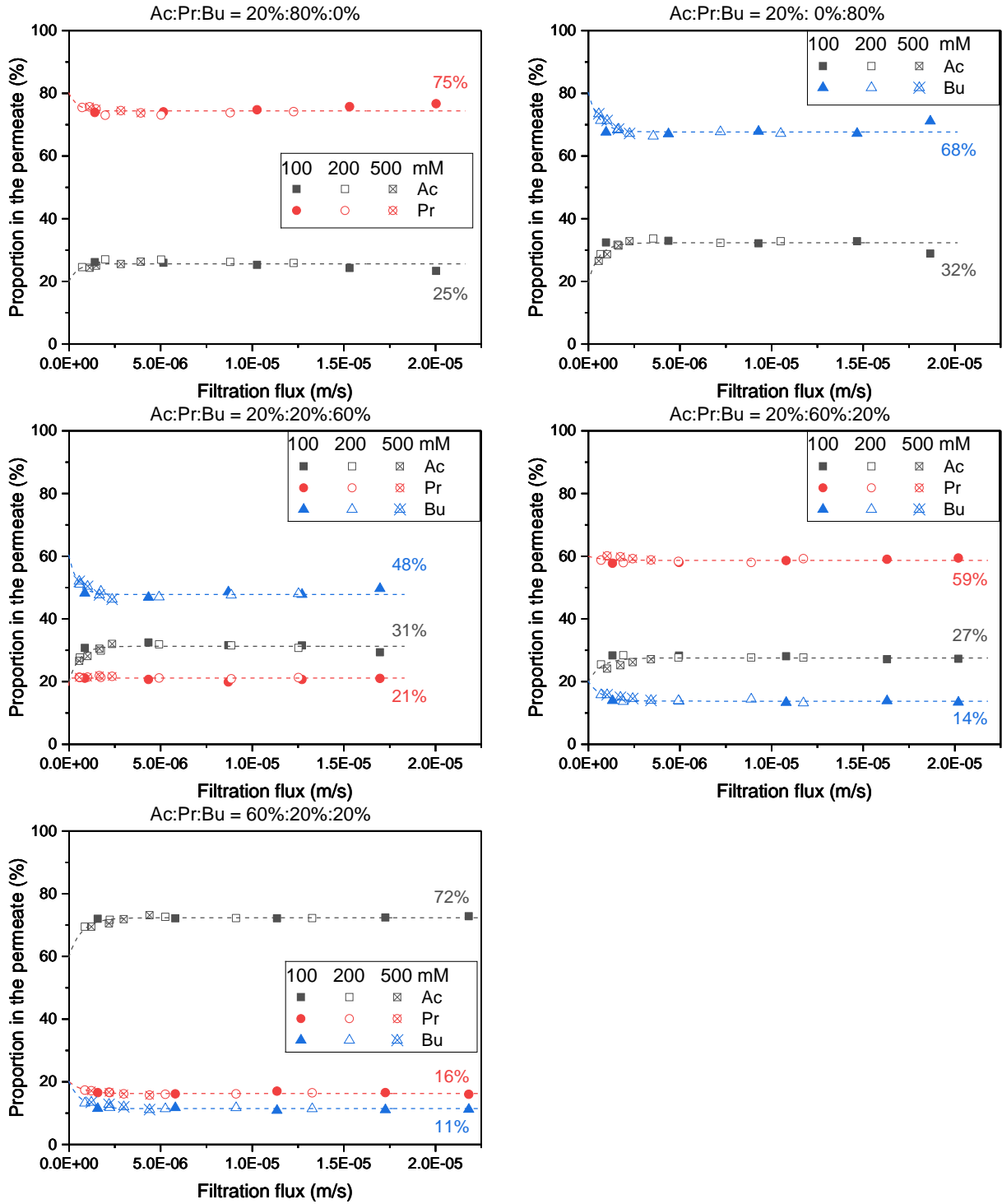


Figure III-13 Individual VFAs proportions in the permeate for binary (Ac/Pr, Ac/Bu) and ternary solutions (Ac/Pr/Bu) at various proportions, using NF-45 membrane, at pH 8.

The previous results show that the proportion of VFA in the permeate at low filtration flux is not the same as that obtained at high filtration flux.

As an example, the proportion differences of Ac and Bu to the constant values ($P_i^{p^*} - P_i^p$) for ternary solutions (Ac:Pr:Bu=33%:33:33%) at a total concentration of 100, 200, and 500 mM is given in Figure III-14. Results for Pr are not shown due to that the difference is too small (from 33% in the feed to 31% in the permeate at the plateau value).

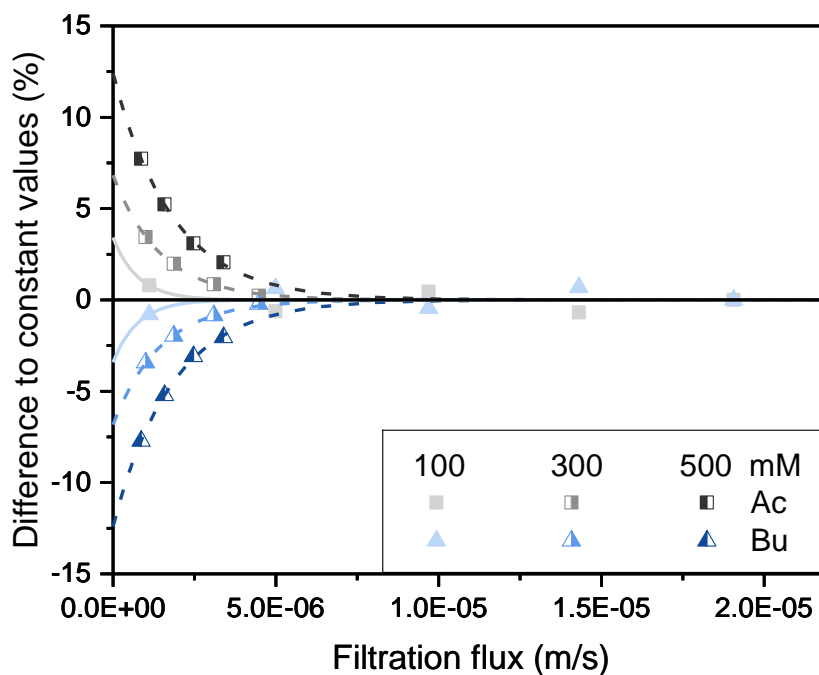


Figure III-14 The proportion difference to the constant values (proportion difference = $P_i^{p^*} - P_i^p$) for ternary solutions (Ac:Pr:Bu=33%:33:33%) at total concentration of 100, 300, and 500 mM, using NF-45 membrane, at pH 8.

It is shown that the total concentration has an influence on the proportion of VFAs in the permeate at low filtration flux. One can also observe that the higher the concentration, the higher the filtration flux required to obtain constant proportions of VFAs in the permeate. Similar observation is found for other conditions (Figure III-15).

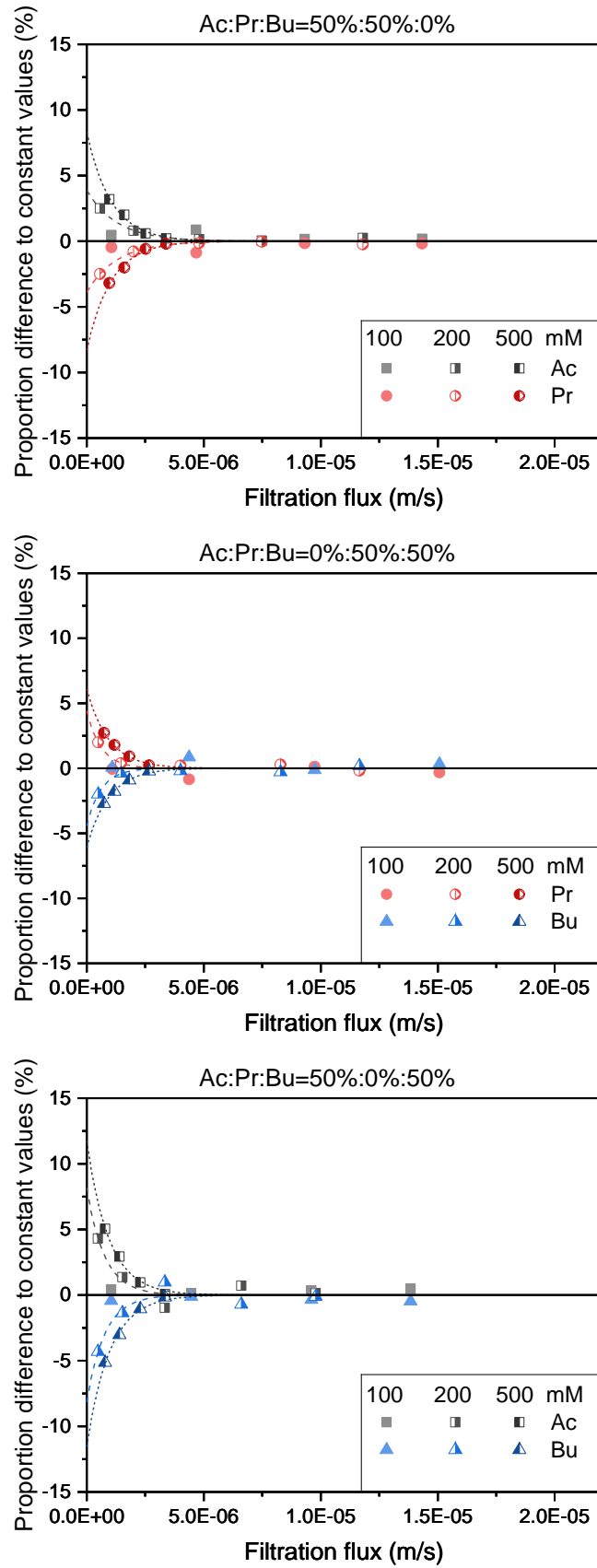


Figure III-15 The proportion difference to the constant values (proportion difference = $P_i^{p*} - P_i^p$) for binary solutions of Ac/Pr, Pr/Bu and Ac/Bu with identical proportions at total concentration of 100, 200, and 500 mM, using NF-45 membrane, at pH 8.

The proportions in the feed and the proportion in the permeate obtained for high filtration flux (the plateau values, P_i^{p*}) are given to compare the separation performance. The ratio between proportion in the permeate and feed is calculated for each VFA, then the separation factors between every two VFAs are determined (as defined in Chapter II). In fact, the separation factor between two VFAs is the ratio of the two VFAs in the permeate divided by the ratio of the two VFAs in the feed. The results for all the feed proportions are listed in Table III-1.

Table III-1 VFAs proportions in the feed and permeate and corresponding separation factor for all the conditions investigated, using NF-45 membrane, at pH 8.

Feed proportion			Permeate proportion (P_i^{p*})			Permeate/Feed			Separation factor		
Ac	Pr	Bu	Ac	Pr	Bu	Ac	Pr	Bu	Ac/Pr	Pr/Bu	Ac/Bu
1.00			1.00			1.00					
	1.00			1.00			1.00				
		1.00			1.00			1.00			
0.50	0.50		0.59	0.41		1.18	0.82		1.45		
0.20	0.80		0.25	0.75		1.27	0.93		1.37		
0.50		0.50	0.66		0.34	1.32		0.68			1.95
0.20		0.80	0.32		0.68	1.60		0.85			1.89
0.00	0.50	0.50		0.58	0.42		1.15	0.85		1.37	
0.20	0.20	0.60	0.31	0.21	0.48	1.56	1.05	0.80	1.48	1.32	1.95
0.20	0.60	0.20	0.27	0.59	0.14	1.37	0.98	0.69	1.39	1.42	1.98
0.33	0.33	0.33	0.47	0.31	0.22	1.41	0.94	0.65	1.51	1.44	2.17
0.60	0.20	0.20	0.72	0.16	0.11	1.21	0.81	0.57	1.49	1.43	2.13

The comparison of the results in Table III-1 with three solutes is complicated. Ternary figures are drawn to visualize the results and see if a general trend can be drawn.

Figure III-16a shows the ternary contour graphs of the VFAs proportions in the permeates of single and mixed solutions for all the proportions investigated. Those plots use the proportion of Ac, Pr, and Bu in the feed as three coordinates, and color from dark blue to deep red to represent the proportion of corresponding VFA in the permeate from 0 to 1 (with contour lines at 0.20, 0.40, 0.60, and 0.80 indicated). The red points correspond to the proportion of the solutions used for the experimental study, and the color and contour lines filling the space between those points represent the proportion of VFAs in the permeate at corresponding feed proportion obtained by linear interpolation of the experimental values. For each axis, the scale represents the proportion of one VFA in the feed from 0% to 100%; three vertices correspond to single solutions of VFAs, points

on the three edges of the triangle correspond to binary mixtures while points inside the triangle correspond to ternary mixtures.

For Ac, it is observed that the contour lines representing the Ac proportion in the feed (grey dashed lines parallel to the axis of Bu) are always lower than the contour lines representing the Ac proportion in the permeate (solid black lines). This indicates that the proportion of Ac in the permeate is always higher than the proportion of Ac in the feed. Moreover, the contour lines representing the Ac proportions in the feed and permeate are not parallel, the more difference being obtained at the Ac axis, while the less difference is obtained at the Pr axis. This means that for a given Ac feed proportion, the presence of Bu makes the proportion of Ac in the permeate decrease more than the presence of Pr.

For Bu, the contour lines representing the Bu proportion in the feed (grey dashed lines parallel to the axis of Pr) are always higher than the contour lines representing the Bu proportion in the permeate (solid black lines). This indicates that the proportion of Bu in the permeate is always lower than that in the feed. Again, the contour lines represent the proportions in the feed and permeate are not parallel, the two types of contour lines show more difference at the Ac axis, while show less difference between each other at the Bu axis. This means that for a given Bu feed proportion, the presence of Ac make the proportion of Bu in the permeate increase more than the presence of Pr.

However, for Pr, the contour lines representing the Pr proportion in the feed (grey dashed lines parallel to the axis of Ac) crossover the contour lines representing the Pr proportion in the permeate (solid black lines). This indicates that the proportion of Pr in the permeate is lower than that in the feed on the right side of the triangle, while it is higher than that in the feed on the left side of the triangle. The conditions for which observe the permeate proportions equals to the feed proportions are shown on the purple dashed line.

Figure III-16b shows the separation factors between Ac/Pr, Pr/Bu, and Ac/Bu in binary and ternary solutions. The color from dark blue to deep red represents the separation factors from the minimum to the maximum, 1.37 to 1.51 for Ac/Pr, 1.32 to 1.44 for Pr/Bu, and 1.89 to 2.17 for Ac/Bu.

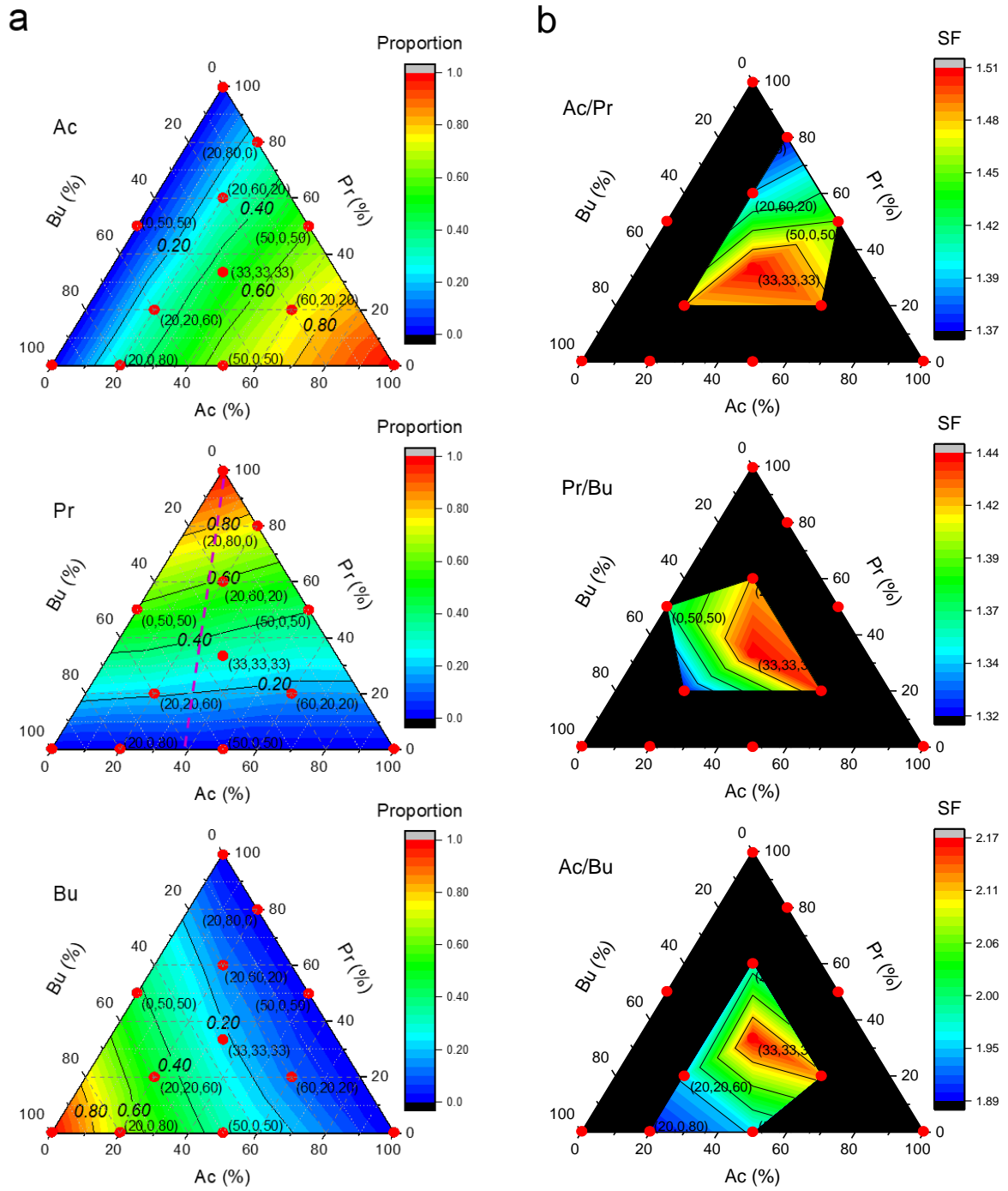


Figure III-16 (a) VFAs proportions in the permeate, and (b) separation factors between VFAs, at all the compositions in the feed investigated, using NF-45 membrane, at pH 8.

One can observe that the highest values of the separation factors for Ac/Pr, Pr/Bu, and Ac/Bu occur for the ternary solution with identical proportions in the feed (Ac:Pr:Bu=33%:33%:33%). It decreases the more as the proportions are different. For binary solutions (Ac/Pr and Ac/Bu), the same trend is observed, the higher separation factors are observed for the solutions with identical proportions (Ac:Pr=50%:50% and Ac:Bu=50%:50%).

This result indicates that when the proportion differ from equal proportion condition, the separation performance decreases.

III.2.2 Solute transfer in mixed solutions

The proportion of solute i in the permeate is defined as Eq. (III.1).

$$P_i = \frac{c_i^p}{c_s^p} = \frac{c_i^p}{\sum(c_i^p)} \quad (\text{III.1})$$

The individual solute flux is defined as Eq. (III.2).

$$J_i = J_w c_i^p \quad (\text{III.2})$$

The total solute flux is the sum of all the solute flux in the mixture, shown in Eq. (III.3).

$$J_s = J_w c_s^p = \sum J_i = \sum (J_w c_i^p) \quad (\text{III.3})$$

Then, Eq. (III.1) can be rewritten as Eq. (III.4).

$$P_i = \frac{c_i^p}{c_s^p} = \frac{c_i^p}{\sum(c_i^p)} = \frac{J_w c_i^p}{\sum(J_w c_i^p)} = \frac{J_i}{J_s} \quad (\text{III.4})$$

Therefore, the proportion of solute i in the permeate also represents the contribution of solute i to the total solute transfer.

For electrolyte solutions, J_s represents the total amount of charge transferred through the membrane, P_i represents the contribution of ion i to the charge transfer.

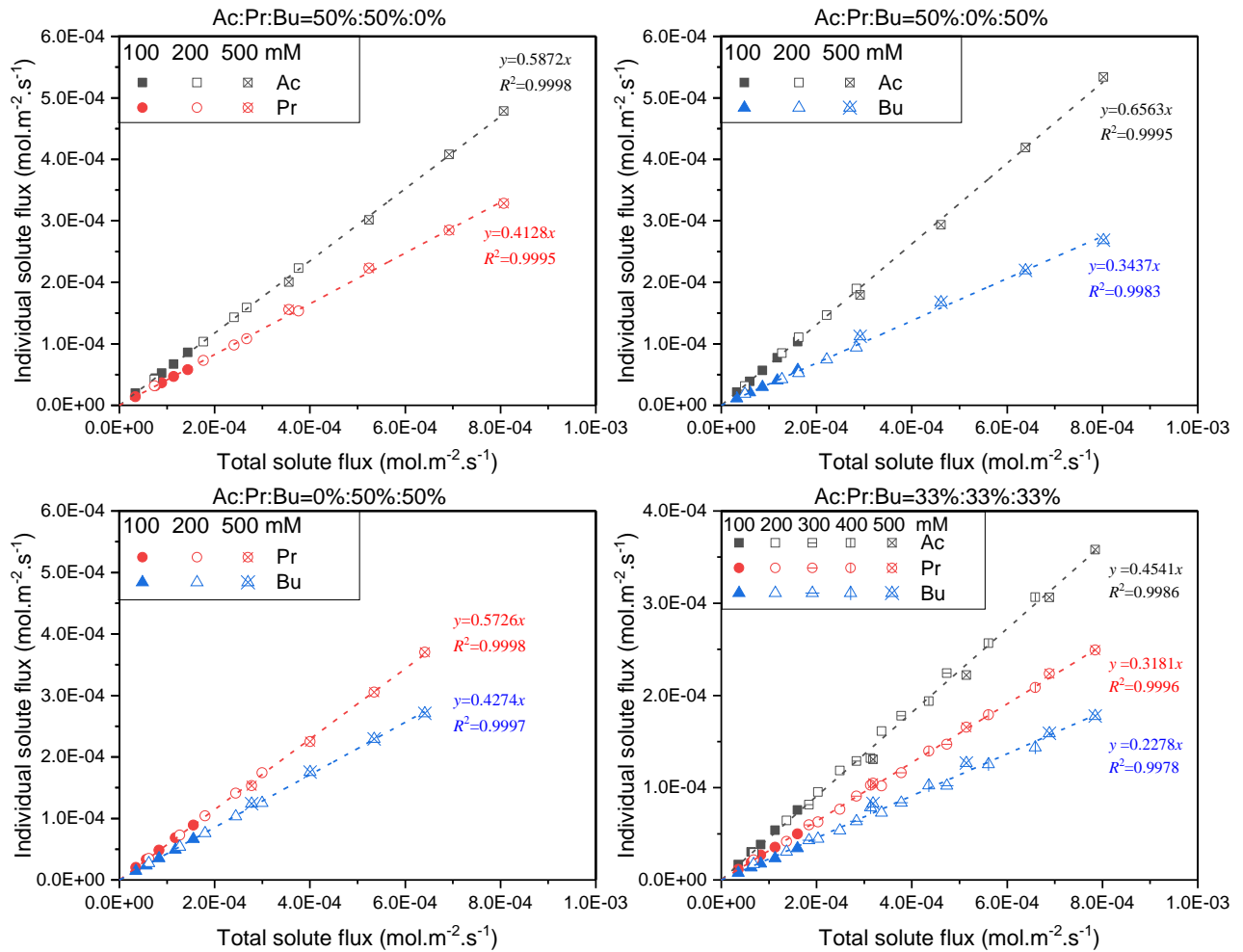


Figure III-17 Individual solute flux as a function of total solute flux, for binary (Ac/Pr, Ac/Bu, Pr/Bu) and ternary (Ac/Pr/Bu) solutions at different concentrations with the equal VFAs proportion (50% or 33%), NF-45 membrane, at pH 8.

Figure III-17 shows the individual solute flux versus total solute flux, for binary and ternary solutions (Ac/Pr, Ac/Bu, Pr/Bu, and Ac/Pr/Bu) at different concentrations with identical proportion of VFAs.

It is shown that whatever the conditions, the individual solute flux increases with the total solute flux and that this variation is linear, the coefficient of determination (R^2) of the linear approach is higher than 0.997.

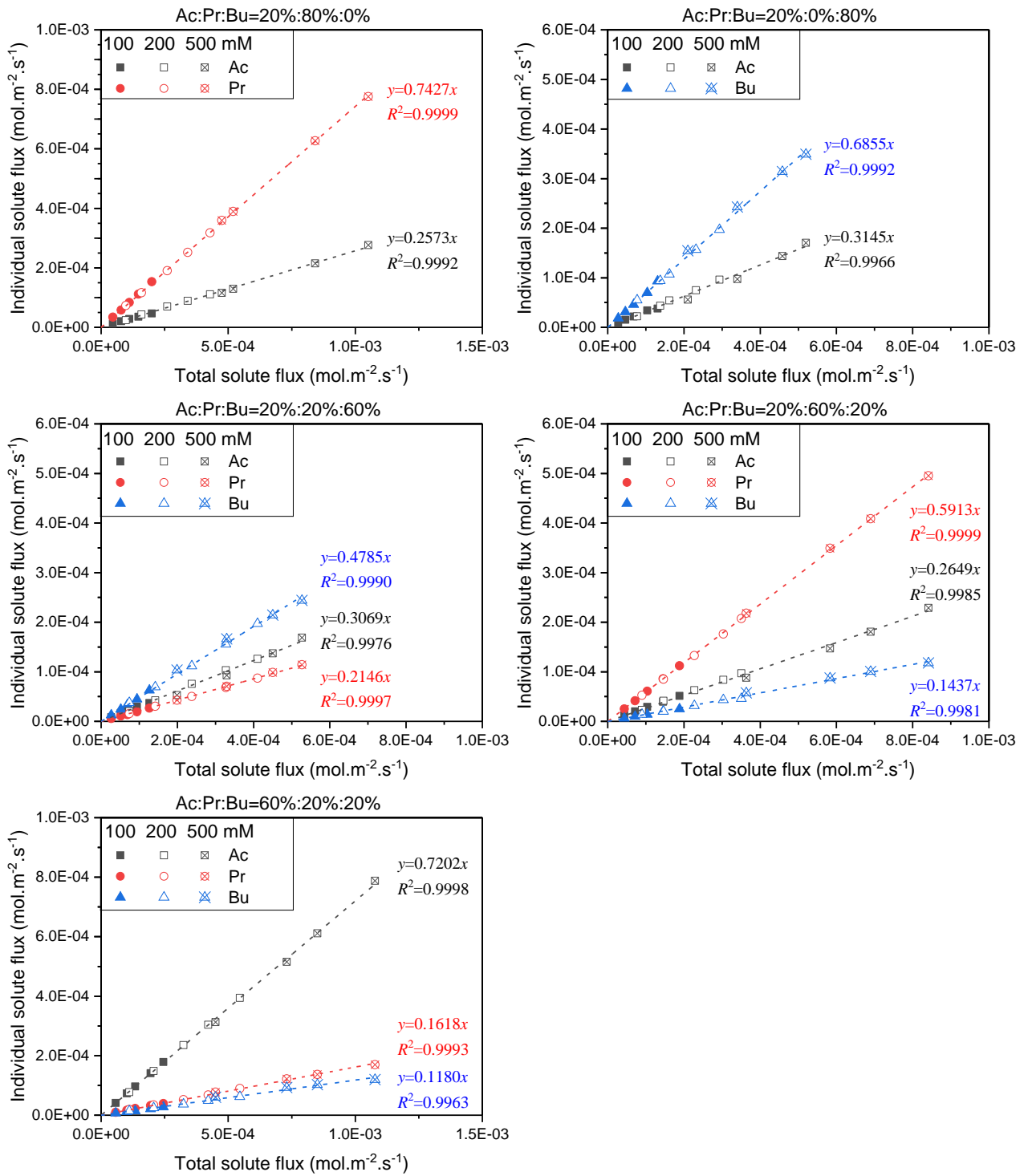


Figure III-18 Individual solute flux as a function of total solute flux, for binary (Ac/Pr, Ac/Bu, Pr/Bu) and ternary (Ac/Pr/Bu) solutions at various concentrations and proportions, using NF-45 membrane, at pH 8.

The individual solute flux versus total solute flux for mixtures at different concentrations and proportions are given in Figure III-18. For all the conditions investigated, the coefficient of determination (R^2) of a linear approach is higher than 0.996.

According to Eq. (III.4), the slope of each linear fitting represents the contribution of one given solute to the total solute transfer, that is the proportion of the given solute in the permeate.

For binary solutions with identical proportion in the feed, on the one hand, Ac contributes 59% to the total solute transfer in the presence of Pr, increases to 66% when coupled with Bu. On the other hand, Bu contributes only 34% to the total solute transfer when Ac is present, this contribution increases to 43% when coupled with Pr. The contribution of Pr to the total solutes transfer increases from 41% in the presence of Ac to 57% in the presence of Bu.

For binary solutions with different proportions, for instance, Ac/Pr binary solutions with Ac:Pr at 50%:50% and 20%:80%, increasing the feed proportion of Pr from 50% to 80%, the contribution of Ac to the total solutes transfer decreases from 59% to 26%. The same tendency can be found for Ac/Bu binary solutions with Ac:Bu at 50%:50% and 20%:80%. Increasing the feed proportion of Bu from 50% to 80% leads to the decrease of Ac contribution to the total solute transfer from 66% to 31%.

For ternary solutions, the contribution of Ac to the total solute transfer increases from 26% for Ac:Pr:Bu=20%:60%:20%, 31% for Ac:Pr:Bu=20%:20%:60%, 45% for Ac:Pr:Bu=33%:33%:33%, to 72% for Ac:Pr:Bu=60%:20%:20%.

In general, for binary solutions, one can observe that the contribution of Ac to the total solute flux (i.e., the proportion in the permeate) is higher than its proportion in the feed, and that the contribution of Bu for the transfer of the total solutes is lower than its proportion in the feed. The contribution of Pr for the mass transfer is depended on the existence of the other VFAs. When coupled with Ac, the least retained VFA, the contribution of Pr decreases, and in the presence of Bu, the most retained VFA, the contribution of Pr increases, compared to its proportion in the feed. In the ternary solution, when both Ac and Bu are present, the contribution of Pr for the transfer of the total solutes shows a slight decrease compared to its proportion in the feed except for Ac:Pr:Bu=20%:20%:60%.

The individual contributions of VFAs to the total solutes transfer through the membrane at different feed proportions show the mechanism of co-ions competition. Indeed, in a binary solution with two co-ions, for a given charge flux, the less retained co-ion contributes more to the

charge flux, while the more retained one contributes less to the charge flux. The contribution of each co-ions, which represents its proportion in the permeate, depends on their proportions in the feed. When the feed proportion of the more retained co-ion increases, the contribution of the less retained one needs to decrease in order to maintain the same total amount of charge transfer, and vice versa.

The co-ions competition phenomenon in a ternary solution is more complicated. The least retained co-ion always contributes more to the charge flux, while the most retained co-ion always contributes less to the charge flux, compared to their contributions to the feed (i.e., feed proportions). The co-ion having an intermediate retention behaves differently according to the contributions of the least and most retained co-ions in the feed, as shown with Pr in Figure III-16a.

III.2.3 Solute transfer with XLE membrane

It was previously observed that despite the change in concentration, the proportion of VFAs in the permeate remains the same for a given feed proportion when the filtration flux is higher than a specific value. This finding could be unique for the NF-45 membrane or universal for different NF membranes. Then, an additional membrane, XLE membrane is tested to verify the finding previously mentioned.

III.2.3.1 Individual solutes retentions in ternary solutions

The retentions of VFAs ternary solutions (Ac:Pr:Bu=33%:33%:33%) at three total concentrations (100, 200, and 250mM) by XLE membrane are given in Figure III-19. The result at 500mM is not obtained due to a too low filtration flux, then, instead of 500mM, the total concentration of 250mM is used.

It is observed that the retentions of VFAs at different total concentrations observed similar retention at the same filtration flux. when the filtration flux is higher than $0.25 \times 10^{-5} \text{ m.s}^{-1}$, the retentions of all the VFAs are higher than 97%. Even though the differences of VFAs retentions are very small, one can observe that the retention sequence is Ac<Pr<Bu, following their MWs. This observation is in agreement with the result observed using NF-45 membrane.

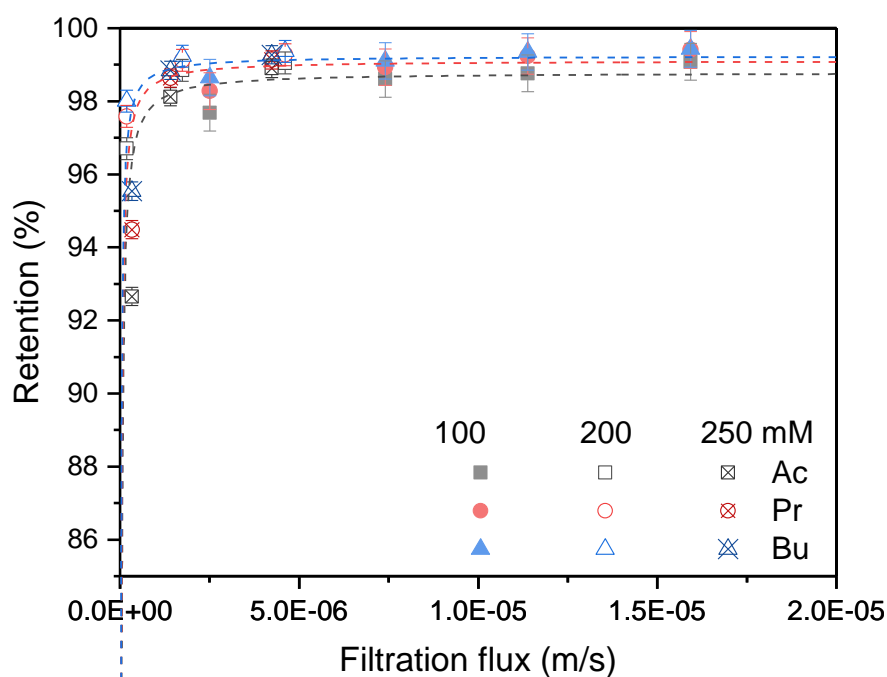


Figure III-19 Retention of VFAs ternary solutions (Ac:Pr:Bu=33%:33%:33%) at various total concentrations, using XLE membrane, at pH 8.

III.2.3.2 Solutes transfer in ternary solutions

The solutes proportions in the permeate versus filtration flux for VFAs ternary solutions (Ac:Pr:Bu=33%:33%:33%) at various concentrations are given in Figure III-20a. As shown in Figure III-19, the retention of XLE membrane for VFAs ternary solution at pH 8 is higher than 97%, the permeate concentration is about 0.2 to 3 mM for the lowest feed concentration. The precision of HPLC using UV detector is about 0.05mM, the error bar shows the precision of the analysis.

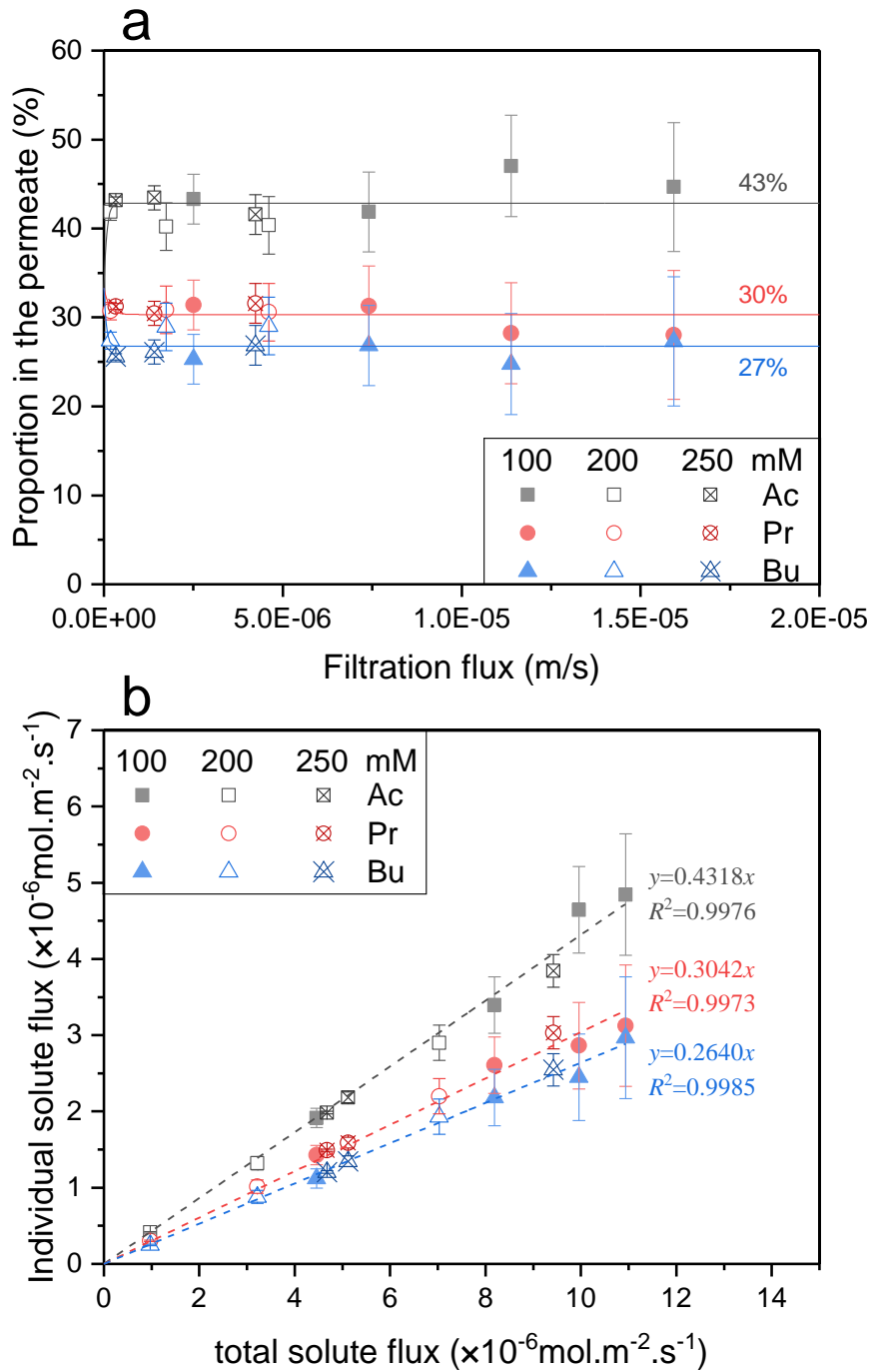


Figure III-20 (a) Solutes proportions in the permeate versus filtration flux and (b) individual solute flux versus total solute flux for VFAs ternary solutions (Ac:Pr:Bu=33%:33%:33%) at various concentrations using XLE membrane, at pH 8. The error bar represent the error of the analysis.

Despite that the solute concentration in the permeate of XLE membrane is very low, one can still observe that, when the filtration flux increases, the proportion of Ac in the permeate increases while the proportion of Bu decreases, reach a plateau at 43% and 27% respectively when the filtration flux is higher than a certain value. The permeate proportion of Pr slightly decreases from 33% to 30%.

Furthermore, it is shown that this filtration flux required for the permeate proportion to reach constant value (lower than $0.1 \times 10^{-5} \text{ m.s}^{-1}$) is much lower than that observed for NF-45 membrane (about $0.5 \times 10^{-5} \text{ m.s}^{-1}$). It seems that concentration does not have a significant influence on the filtration flux required to reach the constant proportion for XLE membrane.

The individual solutes flux versus total solute flux for VFAs ternary solutions at three concentrations are shown in Figure III-20b.

One can observe that the individual solutes flux increase linearly when the total solute flux increases, the coefficient of determination (R^2) of the linear approach is higher than 0.997.

In general, the experimental results observed for XLE membrane are in agreement with that are obtained using NF-45 membrane. It is also noticed that, even for a tight membrane that has a VFAs retention much higher NF-45 membrane, for the same feed proportion (Ac:Pr:Bu=33%:33%:33%), the permeate observed similar proportions (Ac:Pr:Bu at 48%:31%:22% and 43%:30%:27% using NF-45 and XLE membrane respectively), as showed in Figure III-21. This finding deserved further investigation.

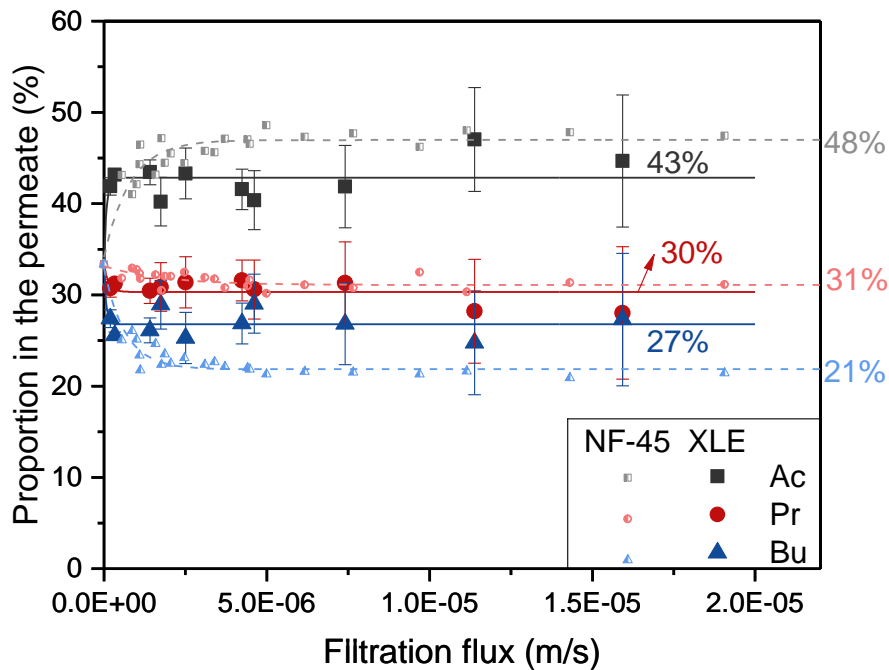


Figure III-21 Comparison of the solute proportions in the permeate versus filtration flux for VFAs ternary solutions (Ac:Pr:Bu=33%:33%:33%) at various concentrations using XLE and NF-45 membranes, at pH 8. The error bar represent the error of the analysis.

III.3 Conclusion

The understanding of the mass transfer mechanism of complex solutions (i.e., solutions having more than 2 co-ions) was pointed out as one of the most important prospects for the application of NF process [116]. The co-ions competition phenomenon is frequently observed during the nanofiltration of mixed electrolyte solutions. Some trends were reported, showing that the solution concentration, as well as solutes proportions, can influence the individual solute retention. However, the mechanism was not clear.

In this Chapter, it was observed that the retention of the more retained solute increases compared to that in single solution, while that of the less retained one decreases. This is in agreement with previous reported results.

A general trend was observed regarding the variation of the VFAs proportions in the permeate versus filtration flux. When the filtration flux is higher than a specific value, the proportion of solutes in the permeate remains constant, regardless the change in total concentration. However, the filtration flux required to reach this plateau value depends on the total concentration.

Moreover, it was found that in the mixed solutions, the individual solute transfer is controlled by the total amount of charge transferred through the membrane. Indeed, it was pointed out that the individual solute flux increases linearly with the total solute flux and does not depend on the total concentration but only on the VFAs proportions in the feed. The general trend obtained using NF-45 membrane is further checked with a second membrane (XLE membrane), and the conclusions are the same.

Furthermore, it is found that the proportion in the feed influences the separation factor between solutes. For binary solutions, the higher separation factors between Ac/Pr and Ac/Bu are observed for solutions with identical proportions (Ac:Pr=50%:50%, and Ac:Bu=50%:50% respectively). For ternary solutions, the highest separation factors between Ac/Pr, Pr/Bu, and Ac/Bu are also obtained for solutions with identical proportions (Ac:Pr:Bu=33%:33%:33%). Moreover, the results observed for ternary solutions with identical VFAs proportion are also the highest among all the conditions (Binary and ternary solutions) investigated. This observation indicates that for mixed solutions with identical proportions, the more solutes in the solutions, the higher the separation factor between each couple of solutes.

IV.

Chapter IV
Nanofiltration of synthetic solutions of
VFAs: influence of inorganic ions

This chapter aims to extend the investigation of solutes composition from VFAs solutions to solutions with VFAs and inorganic salts.

In the previous discussion (Chapter III), a general trend is observed for individual VFAs proportions in the permeate of mixed solutions at different concentrations and proportions. That is, the proportion of the least retained solute (Ac) in the permeate is higher than that in the feed, while the proportion of the most retained solute (Bu) in the permeate is lower than the proportion of Bu in the feed. The permeate proportion of the VFA, which has the retention in-between the two (i.e. Pr), can be either higher (with more Ac in the solution) or lower (with more Bu in the mixture) depends on the proportion.

In the current chapter, more complex solutions, containing VFAs sodium salts (acetate, propionate, and butyrate) and inorganic salts (Na_2SO_4 , NaCl , and CaCl_2) are investigated. Synthetic solutions from single solutions of each solute at different concentrations to mixed solutions of two (Ac/Bu) or three (Ac/Pr/Bu) VFAs with inorganic salts at the ratio of VFAs: salts = 1:1, 2:3, to 1:4 at a different total concentrations are investigated. The general trend obtained in Chapter III is verified with the more complex solutions, and the influence of additional inorganic salts on the mass transfer of VFAs is explored.

In this chapter, the retentions of individual solutes in single and mixed solutions are firstly discussed. Then, the mass transfer of anions and cations is investigated, the influence of co-ions (SO_4^{2-} , Cl^-) and counter-ions (Na^+ , Ca^{2+}) on individual solute transfer is investigated. Furthermore, the separation of VFAs at different compositions with different inorganic salts is also discussed.

All the results discussed in the current chapter are obtained using NF-45 membrane at pH 8.

IV.1 Individual solutes retention in single solutions

Retentions of VFAs sodium salts and three inorganic salts, namely Na_2SO_4 , NaCl , and CaCl_2 , at three concentrations are given in Figure IV-1. The fitting curves are plotted and the solutes retentions at a given filtration flux are calculated based on the model proposed by Timmer et al. [143], as introduced in Chapter II. Figure IV-2 shows the retentions of the three VFAs and three inorganic salts at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$ versus concentrations. Then we can compare the retentions of the six solutes at given filtration flux.

Figure IV-1 and Figure IV-2 show that the retentions of all the solutes in single solutions decrease when the concentration increases. However, one can observe that the influence of concentration is more pronounced for NaCl , and less significant for Na_2SO_4 , the influence of concentration on the retentions of VFAs and CaCl_2 is in-between of NaCl and Na_2SO_4 . As already observed in Chapter III, the retention sequence of VFAs is $\text{Ac} < \text{Pr} < \text{Bu}$. Then, it is observed that the retention sequence for the three inorganic salts is $\text{NaCl} < \text{CaCl}_2 < \text{Na}_2\text{SO}_4$. Put the six solutes together, the retention of Na_2SO_4 is higher than the retentions of VFAs, especially at high concentrations; the retentions of CaCl_2 and NaCl are lower than the retentions of VFAs. Thus, for the five anions with sodium as counter-ions, the retention sequence is $\text{Cl}^- < \text{Ac}^- < \text{Pr}^- < \text{Bu}^- < \text{SO}_4^{2-}$.

As discussed in Chapter I, the retention mechanism of NF is a combination of size and charge effects. On the one hand, the retention sequence of solutes with the same charge and counter-ions is expected to follow their sizes (which are related to their MWs and hydration). As already mentioned in Chapter III, the retention sequence of organic salts followed their MWs, for instance, it is reported that the retention sequence of three carboxylic acid sodium salts (formate (45 g.mol^{-1}), acetate (59 g.mol^{-1}), and lactate (89 g.mol^{-1})) follows their molecular weights (MWs) [148]. On the other hand, charge repulsion can also play a role in the retention of ions. Retention of symmetric salts like NaCl is governed by ions with the same sign of charge as the membrane (namely, co-ions), while the retention of asymmetric salts (i.e., CaCl_2 and Na_2SO_4) is dominated by the ions having higher valence [142]. In addition, the charge effect is influenced by ionic concentration. The increase of ionic concentration screens the electrostatic interactions between membrane and ions, then the charge repulsion is weakened, and the retention of ions decreases. This phenomenon is reported as screening effect [128,139].

The retention sequence found for VFAs follows their MWs. However, the retention sequence of inorganic salts with different counter-ions is more complicated. Indeed, different sequences were reported with NaCl , CaCl_2 , and Na_2SO_4 for various NF membranes [125]. Except for

positively charged membranes, retention of Na_2SO_4 is always the highest among the three. Then, for negatively charged membranes, the retention sequences of NaCl and CaCl_2 are different for different membranes [125]. Thereafter, further investigation showed that the retention sequence of these three salts is concentration-dependent. It is reported that the retention sequence of the two salts at 10mM is $\text{CaCl}_2 < \text{NaCl}$, then changed to $\text{NaCl} < \text{CaCl}_2$ when concentration increases to 100mM for an ESNA 1 (Nitto Denko, Japan) membrane [141]. Similar observations are reported for other polymeric membranes. For instance, retention sequence is $\text{CaCl}_2 < \text{NaCl}$ for TFCS membrane [189], NF-45 membrane [125], DF 10 membrane [190], and NF270 membrane [191] when concentration is within the range of 1~10 mM. The retention sequence changes as $\text{NaCl} < \text{CaCl}_2$ for Desal DK-5 membrane [192,193], and retention sequence of $\text{NaCl} < \text{MgCl}_2$ is found for NF-45 and SU 200 membranes [194], at concentration of 100mM. In those investigations, retention of Na_2SO_4 remains the highest among the three salts.

The present results are obtained at an ionic concentration higher than 100mM, then the result agrees with the trend previously mentioned ($\text{NaCl} < \text{CaCl}_2 < \text{Na}_2\text{SO}_4$).

Based on the previously reported results, there could two possible explanations for the alteration of the retention sequence of NaCl and CaCl_2 (i.e., $\text{CaCl}_2 < \text{NaCl}$ at concentration lower than 10 mM and $\text{NaCl} < \text{CaCl}_2$ at concentration higher than 100 mM). On the one hand, the membrane polymers could capture/adsorb the counter-ions, especially for alkaline-earth metal ions at the second group, for instance, Mg^{2+} and Ca^{2+} , reducing the negative membrane charge that could even become positive [190,195,196]. Then when there are only trace amounts of ions in the solution, the charge interactions between Cl^- in CaCl_2 and membrane could be weaker than the charge interactions between Cl^- in NaCl and membrane, due to weaker membrane charge in the presence of Ca^{2+} . Therefore, lower retention of CaCl_2 compared to the retention of NaCl is observed. On the other hand, Ca^{2+} has much higher hydration free energy ($-1650 \text{ kJ}\cdot\text{mol}^{-1}$) than Na^+ ($-365 \text{ kJ}\cdot\text{mol}^{-1}$) and Cl^- ($-340 \text{ kJ}\cdot\text{mol}^{-1}$), the hydration radius of Ca^{2+} (0.412-0.420 nm) is bigger than that of Na^+ (0.276-0.360 nm) and Cl^- (0.324-0.332 nm) [197]. Then, at high concentration, when the charge effect is weakened, the retention of CaCl_2 could be higher than the retention of NaCl due to a bigger size [197].

In addition, the size of SO_4^{2-} is bigger than that of Cl^- own to both higher MW and larger hydration shell [198], then higher retention of Na_2SO_4 at high concentration than retention of NaCl is observed. Thus, when the concentration increases, the decrease of Na_2SO_4 retention is less

significant than the decrease of NaCl retention. Similar results are also reported by other authors [198,199].

In conclusion, for ions having the same valence, the retention is fixed by the co-ions whereas for ions of different valences, the retention is fixed by the ion having the highest retention [142].

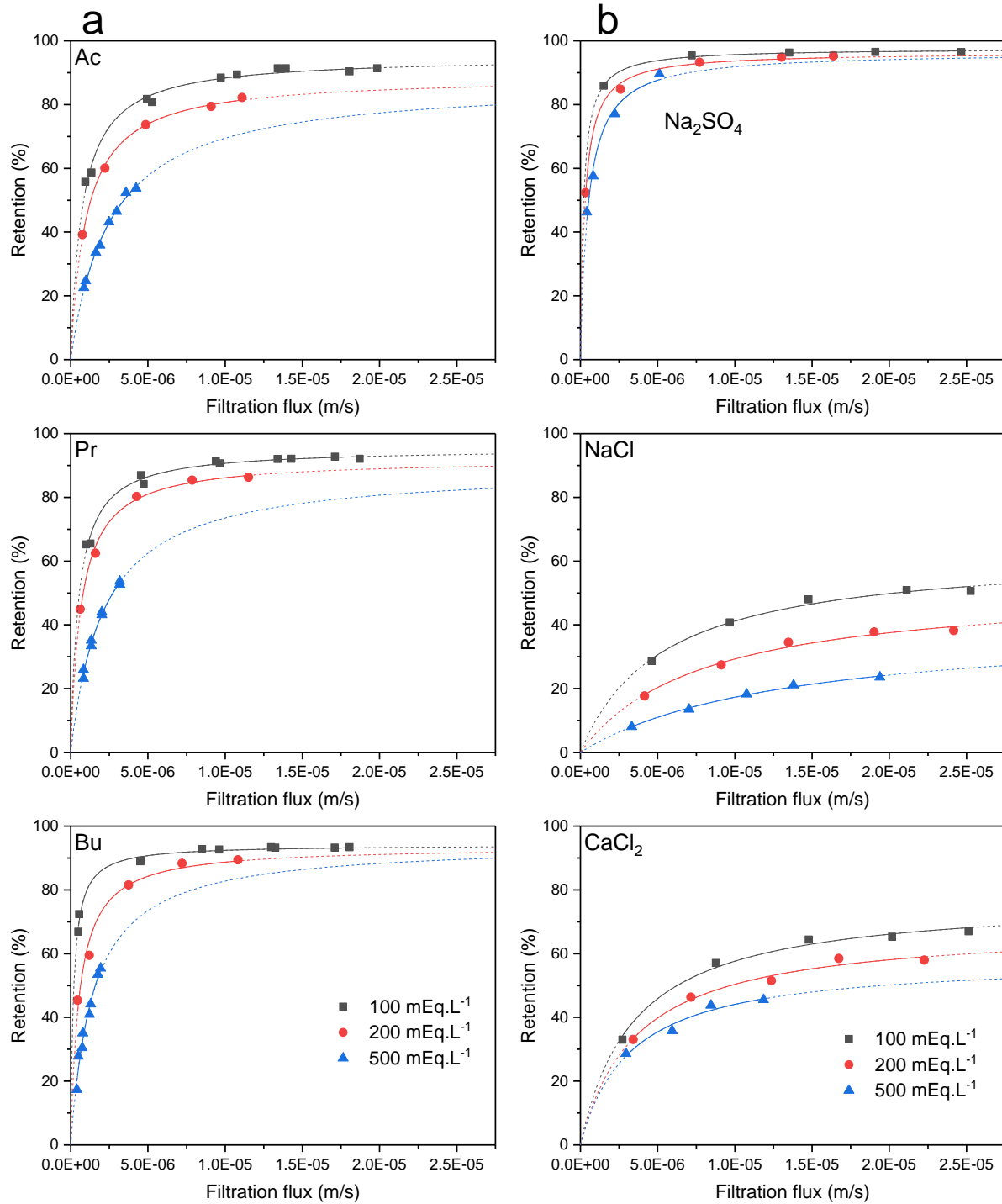


Figure IV-1 Retentions of (a) VFAs (acetate, propionate, and butyrate) and (b) salts (Na_2SO_4 , NaCl and CaCl_2) in single solutions at different concentration, using NF-45 membrane.

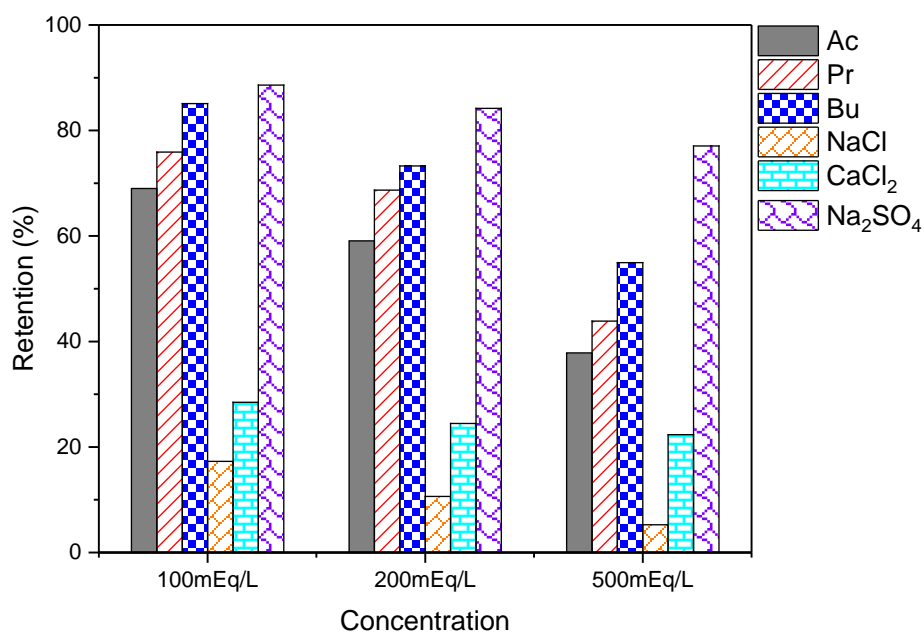


Figure IV-2 Retentions of VFAs (acetate, propionate, and butyrate) and inorganic salts (Na_2SO_4 , NaCl and CaCl_2) in single solutions at a filtration flux of $2 \times 10^{-6} \text{ m.s}^{-1}$, for different concentrations, using NF-45 membrane.

IV.2 Individual solutes retention in mixed solutions

IV.2.1 Influence of VFAs co-ions (SO_4^{2-} and Cl^-) on individual solutes retentions

Figure IV-3 shows the retentions of all the anions in binary solutions of Ac/Bu (Ac : Bu = 50% : 50%), and ternary solutions of Ac/Pr/Bu (Ac : Pr : Bu = 33% : 33% : 33%) at different total concentrations with addition of Na_2SO_4 . The concentration ratio of VFAs: salt in the feed solution is 1:1 for 200 mEq/L, then decrease to 2:3 and 1:4 for the concentration of 500 mEq/L. Retentions in single solutions of NaAc, NaPr, NaBu, and Na_2SO_4 at the same ionic concentration, obtained from fitted curves as previously explained, are given as references. It is shown that when the concentration increases, retentions of all the anions in single and mixed solutions decrease, which is due to the screening of electrostatic interactions. Then, one can observe that the retention sequence of individual anions in mixed solutions is $\text{Ac}^- < \text{Pr}^- < \text{Bu}^- < \text{SO}_4^{2-}$, the same as that in single solutions, for all the compositions investigated.

It is noticed that the retentions of SO_4^{2-} in mixed solutions are nearly equal to that in single solutions. The retention curves of individual VFA show different behaviors at different compositions: the least retained VFA, Ac, decreases the most with the presence of Na_2SO_4 , followed by Pr, which is intermediately retained, and then the retention of the most retained VFA, Bu, slightly decreases compared to that in single solutions. Furthermore, with the addition of SO_4^{2-} , it seems that the retention of Ac in Ac/Pr/Bu ternary solutions decreases more than in Ac/Bu binary solutions for VFAs : salts at 1:1 and 1:4. However, at conditions that VFAs : salts=2 : 3, this result is not observed.

In addition, negative retentions of Ac^- are obtained with VFAs : $\text{Na}_2\text{SO}_4 = 2 : 3$ at an ionic concentration of 500 mEq.L^{-1} , both in binary and ternary solutions. When the ratio of VFAs : Na_2SO_4 decreases to 1 : 4, the retention of Ac^- decreases more and the retention of Pr^- is also negative at low filtration flux. This result indicates that the retention difference between VFAs and SO_4^{2-} increases when decreasing the concentration ratio between VFAs (the less retained solutes) and SO_4^{2-} (the more retained solute).

As discussed in Chapter III, the retentions of ions in mixed solutions differ from those in single solutions. In the mixed solution containing two ions with the same sign of charge, the retention of the more retained ion tends to increase while that of the less retained one decreases. A decrease of the retention of the less retained solute is observed when the concentration ratio between the less and more retained solutes decreases. This phenomenon is called “distribution effect” [148] or “co-ions competition” [142,187].

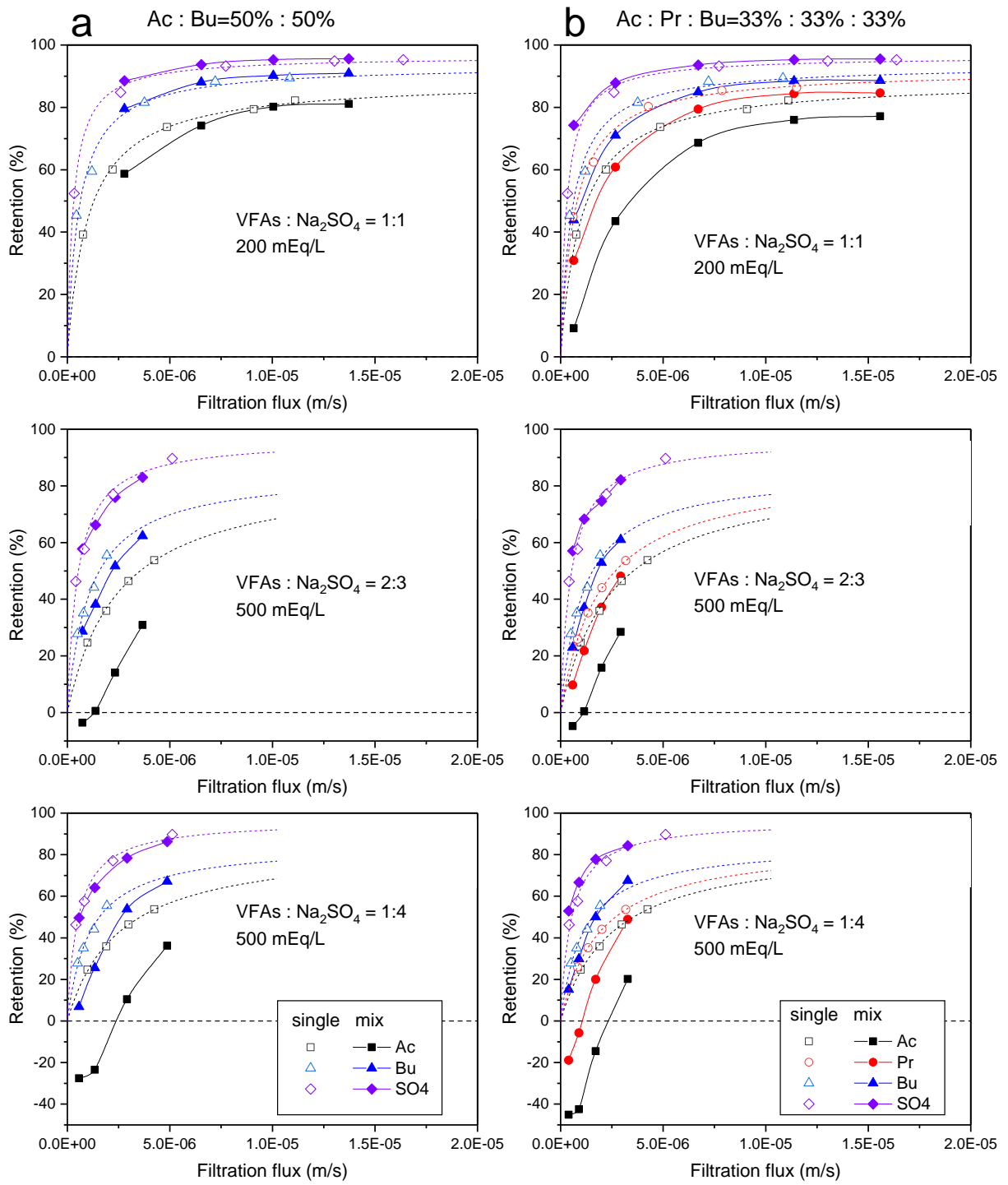


Figure IV-3 Retention of individual anions at different compositions: (a) Ac/Bu binary solution with Na_2SO_4 , (b) Ac/Pr/Bu ternary solution with Na_2SO_4 , using NF-45 membrane.

In current work, SO_4^{2-} is the most retained ion. The retentions of VFAs are lower than that of SO_4^{2-} and follow their MWs ($\text{Ac} < \text{Pr} < \text{Bu}$). Then, retentions of VFAs decrease in the mixture compared to their retentions in single solutions, and the trend of decline is $\text{Bu}^- < \text{Pr}^- < \text{Ac}^-$, which is the reverse of their MWs sequence. However, the retention of SO_4^{2-} does not increase in the mixed solutions.

Figure IV-4 shows the anions retentions in binary solutions of Ac/Bu and ternary solutions of Ac/Pr/Bu with the addition of NaCl. The concentration ratio between VFAs and NaCl in the feed is controlled as the same as that in the VFAs+ Na_2SO_4 systems. The retentions of Ac, Pr, Bu, and NaCl in single solutions as well as the fitted retention curves at the corresponding total ionic concentration as the mixture are given as references.

One can observe that the retention sequence in the mixed solutions is $\text{Cl}^- < \text{Ac}^- < \text{Pr}^- < \text{Bu}^-$, the same as that in single solutions, for all the compositions investigated. Then, it is observed that the retentions of Cl^- , the least retained solute, decrease in the mixtures compared to those in single solutions and even reach negative values for some conditions. For the retentions of VFAs, it is observed that their retentions in the mixtures at the conditions that VFAs: salts = 1:1 are similar to those in single solutions. When the total concentration increases to 500 mEq.L^{-1} , despite the fact that the retentions of individual VFAs in single and mixed solutions are not obtained at the same filtration flux, it seems that one single curve can represent the results obtained in single and mixed solutions.

Moreover, the decreasing trend of Cl^- retention is related to the ratio between VFAs and NaCl. Indeed, when the ratio between VFAs and NaCl decreases from 1:1, 2:3, to 1:4, the decrease of Cl^- retention becomes less and less pronounced. On the other hand, it seems that the increase of Pr^- retentions in the mixed solutions compared to those in single solutions for VFAs: salt = 2:3 are more significant than at VFAs: salts = 1:1.

In $\text{Ac}^-/\text{Pr}^-/\text{Bu}^-/\text{Cl}^-$ system, Cl^- is the least retained anion and Bu^- is the most retained one. Then, as previously reported, retentions of Cl^- in mixed solutions are expected to be lower than those in single solutions, while retentions of Bu^- in the mixtures are expected to increase compared to single solutions. However, while the decrease of Cl^- retention compared to that in single solutions is observed, the increase of Bu^- retention compared to that in single solutions is not clear. This observation is the same as that previously reported for VFAs+ Na_2SO_4 systems.

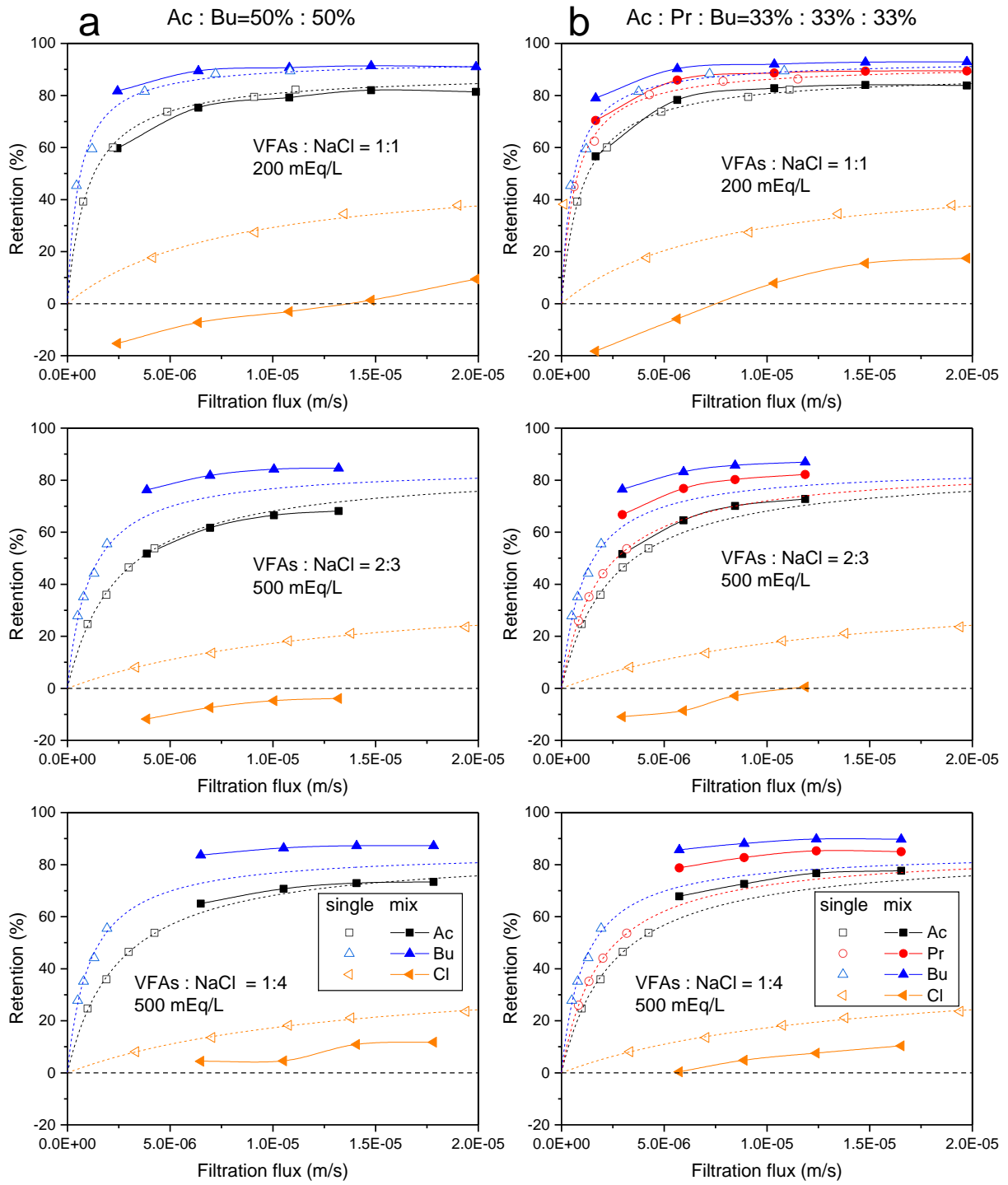


Figure IV-4 Retention of individual anions at different compositions: (a) Ac/Bu binary solution with NaCl, (b) Ac/Pr/Bu ternary solution with NaCl, using NF-45 membrane.

The co-ions competition phenomenon is generally observed as the decrease of the retention of the less retained co-ions [128,136,139,148,188]. The increase of the more retained co-ions in the mixed solution compared to that in single solution is only reported by a few works [146,148]. In the conditions we investigated, the decrease of the less retained co-ions is observed for VFAs+Na₂SO₄ and VFAs+NaCl systems. However, no significant increase of the more retained co-ions is observed. This observation is probably due to the definition of retention. Indeed, by definition, the retention of any ions is lower than 100%; when the retention of one solute approaches 100%, any increase is no more significant. However, retention of the less retained solute can reach negative value with no limit reported yet. Therefore, the increase in retention of more retained solute is less significant and harder to observe, while the decrease in retention of less retained solute is more significant and easier to observe.

IV.2.2 Influence of VFA counter-ions (Na⁺ and Ca²⁺) on individual solutes retentions

Figure IV-5 shows the anions retentions in binary solutions of Ac/Bu and ternary solutions of Ac/Pr/Bu with the addition of CaCl₂. The ratio between VFAs and CaCl₂ in the feed is controlled as the same as that in VFAs+Na₂SO₄ and VFAs+NaCl systems. The retentions of VFAs as well as Cl⁻ in VFAs+NaCl system at corresponding concentrations and proportions are given as references. In these two systems, VFAs sodium salts were combined with NaCl and CaCl₂. Therefore, the only difference between the two systems is that one part of the counter-ions, Na⁺, is replaced by the same amount of Ca²⁺.

As for the VFAs+NaCl system, the retention sequence of anions is Cl⁻ < Ac⁻ < Pr⁻ < Bu⁻, in single and mixed solutions for all the compositions investigated. One can observe that the retentions of VFAs in NaVFAs+ CaCl₂ system seem slightly lower than in VFAs+NaCl system, especially for ternary Ac/Pr/Bu solutions. On the other hand, the retentions of Cl⁻ in the NaVFAs+ CaCl₂ system are significantly higher than the retention of Cl⁻ with NaCl. When the concentration ratio of VFAs: salts decreases from 1:1, 2:3 to 1:4, the differences between the Cl⁻ retentions in the two systems gradually enlarged.

Current results indicate that the counter-ions can significantly influence the retention of ions in mixed solutions. When one part of the counter-ions was changed from Na⁺ to Ca²⁺, the retention difference between VFAs and Cl⁻ decreased, showing that the co-ions competition between VFAs

and Cl^- decreases in the presence of Ca^{2+} . Moreover, when the proportion of Ca^{2+} increases, the co-ions competition decreases.

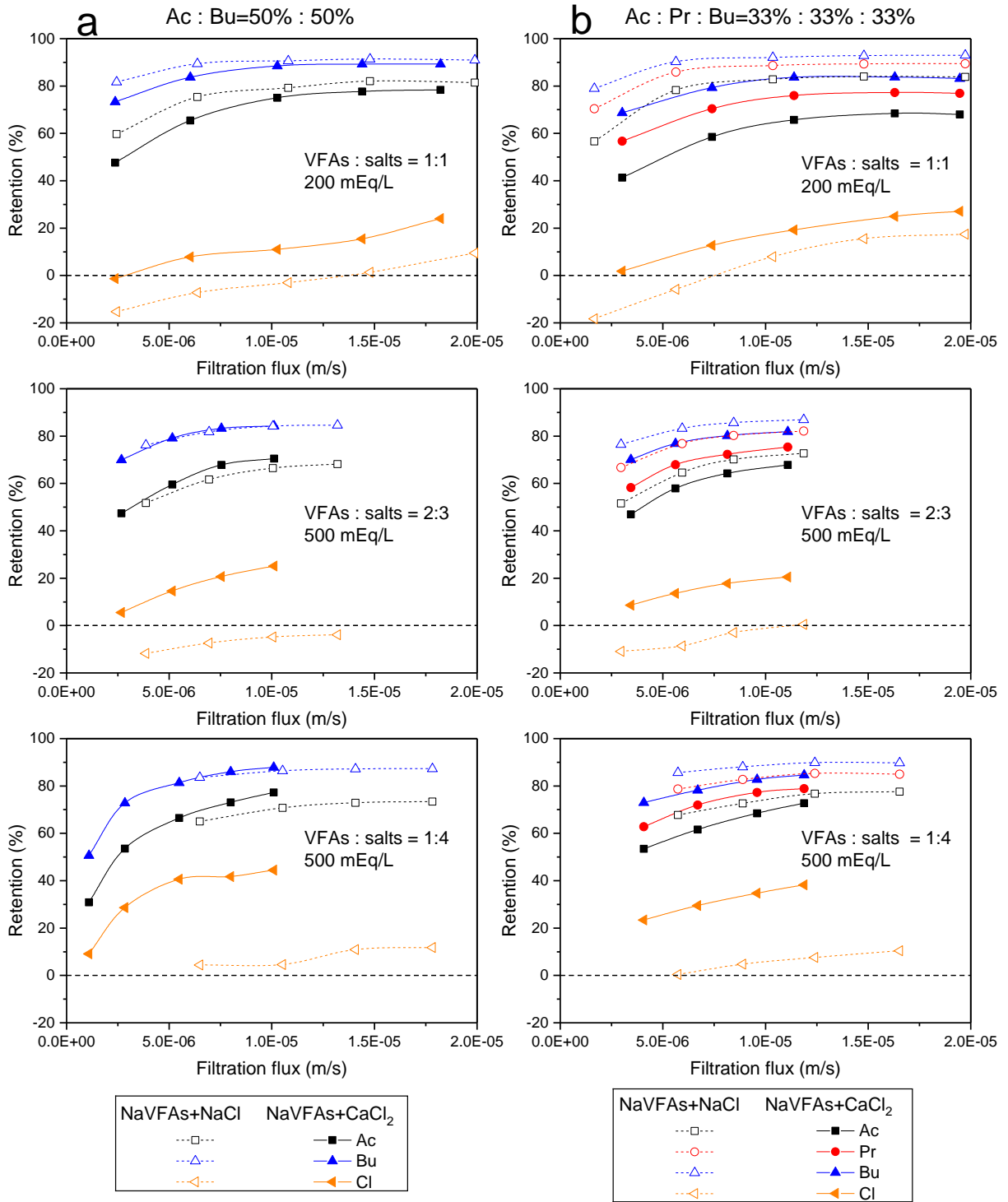


Figure IV-5 Retention of individual anions at different compositions: (a) Ac/Bu binary solution with CaCl_2 , (b) Ac/Pr/Bu ternary solution with CaCl_2 , using NF-45 membrane.

It was shown that the retention difference between SO_4^{2-} and Cl^- in a $\text{NaCl}/\text{Na}_2\text{SO}_4$ binary system decreases dramatically when the solution pH decreases from 8 to 3 [146]. A further interpretation by Luo et al. compared the retentions of SO_4^{2-} and Cl^- reported in ref. [146], shown that the retention of SO_4^{2-} maintain nearly equal to that in single solutions, while the retention of Cl^- in mixed solution decreases compared to that in single solution [142]. Furthermore, the authors suggested that the difference between retention of Cl^- in single and mixed solutions is due to co-ions competition, and the co-ions competition phenomenon is influenced by solution pH [142]. The maximum retention difference between Cl^- in single and mixed solutions are observed at neutral pH [142]. In ref. [142], Luo et al. also suggested that the influence of solution pH on the retention of strong electrolyte is mainly due to the variation of membrane charge [142]. Therefore, we suggested that the observation in ref. [146] probably indicate that the membrane charge can influence the co-ions competition.

As discussed previously, many scientists suggest that the membrane charge can be controlled by the competitive adsorption of co-ions and counter-ions. When the concentration of Ca^{2+} in the solution increases, the negative membrane charge decreases [132,196,200].

Based on those reports, we suggest that the reduction of the retention difference between VFAs and Cl^- in the presence of Ca^{2+} could be related to the reduction of membrane charge. Indeed, the NF membrane is an ion-exchange membrane. For the two cations investigated in this work, the cation exchange sequence is $\text{Ca}^{2+} > \text{Na}^+$. Therefore, when changing one part of Na^+ into Ca^{2+} , the cation equilibrating the membrane changed from only Na^+ to the combination of Na^+ and Ca^{2+} . Then, the thickness of electrical double layer (EDL) decreases and the negative membrane charge decreases.

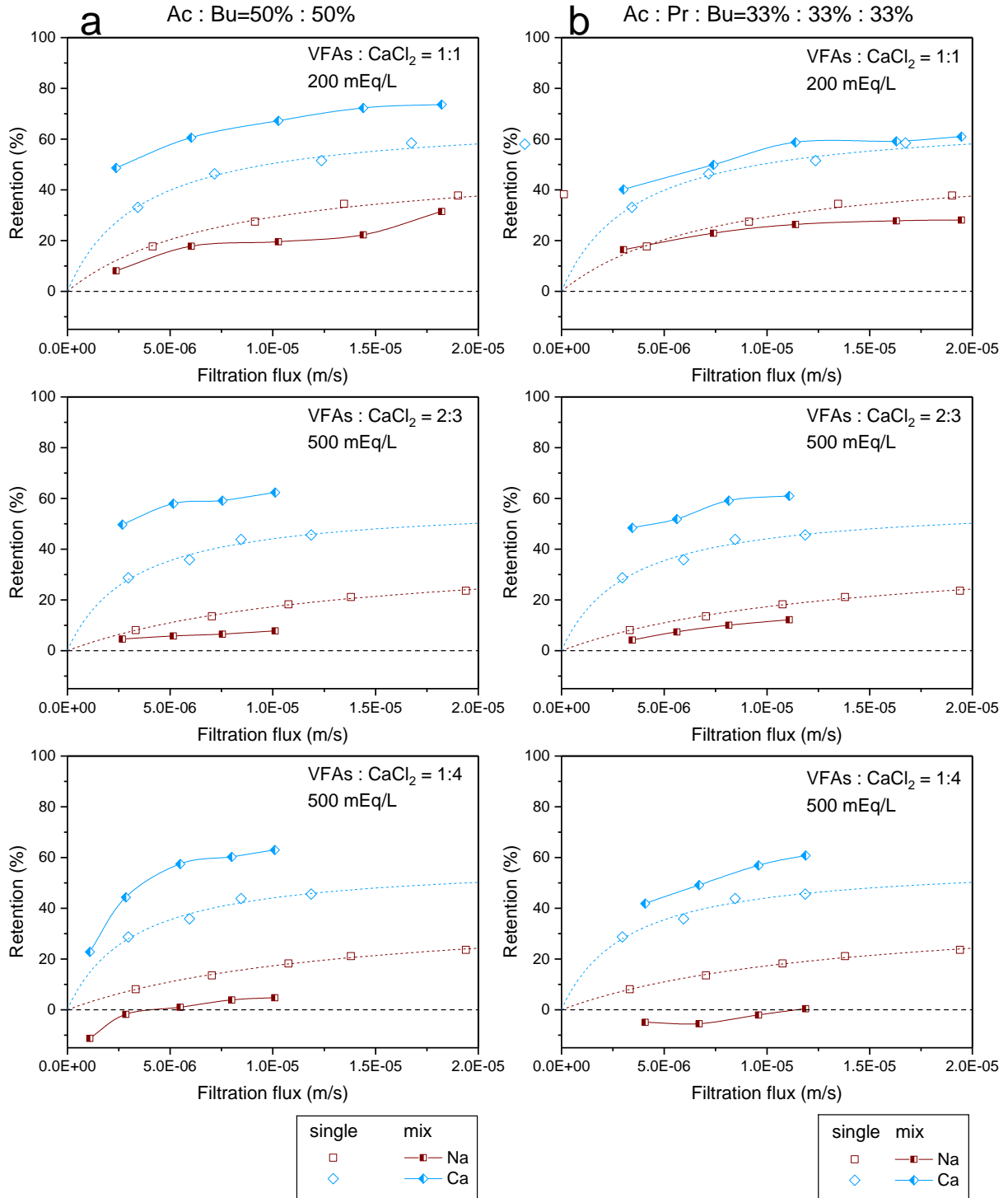


Figure IV-6 Retention of individual cations at different compositions: (a) Ac/Bu binary solution with CaCl₂, (b) Ac/Pr/Bu ternary solution with CaCl₂, using NF-45 membrane.

The retentions of cations in the NaVFAs+CaCl₂ system are given in Figure IV-6 for binary and ternary solutions with different compositions. The ratio of VFAs and CaCl₂ represents the concentration ratio of Na⁺: Ca²⁺ in the mixture since the VFAs used in this work are VFAs sodium salts. Retentions of Na⁺ and Ca²⁺ in single solutions (NaCl and CaCl₂, respectively) at corresponding concentrations are given as references.

One can observe that the retentions of Ca²⁺ are higher than the retentions of Na⁺, both in single and mixed solutions. The retentions of cations are similar in VFAs binary and ternary solutions, indicate that the presence of Pr does not significantly influence the retentions of cations, and the retentions of cations are determined by their concentration ratio. Then, retentions of Ca²⁺ in mixed solutions are always higher than those in CaCl₂ single solutions, and the retentions of Na⁺ in mixtures are always lower than those in NaCl single solutions. Thus the retention differences between Na⁺ and Ca²⁺ increases in the mixed solutions, and the differences are even higher at high concentration (500 mEq/L). For the concentration of 500 mEq/L, when the ratio of Na⁺: Ca²⁺ decreases from 2:3 to 1:4, the retention of Na⁺ decreases and negative values are even observed at low filtration flux for the ratio of 1:4, both in VFAs binary and ternary solutions.

In the NaVFAs+CaCl₂ system, Na⁺ is the less retained cation, and Ca²⁺ is the more retained one. The retention of Na⁺ decreases compared to that in NaCl single solutions, while the retention of Ca²⁺ increases compared to that in CaCl₂ single solutions. When the ratio of Na⁺: Ca²⁺ decreases, the retentions of both Na⁺ and Ca²⁺ decrease. A similar observation is reported for the filtration of Na⁺ and Ca²⁺ binary solution by a KP 90 CA reverse osmosis membrane, the retentions of Na⁺ in the mixed solutions are much lower than in the single solution, and negative values are reached at low filtration flux. In addition, when the concentration ratio of Ca²⁺ and Na⁺ decreases from 76.2mM : 20.8mM to 120mM : 20.5mM, the retention of Na⁺ slightly decreased [147]. Our results are in agreement with the previous reported ones, and one can conclude that the co-ions competition between the cations show the same behavior as that between anions.

IV.3 Solute transfer in mixed solutions

IV.3.1 Proportions of solutes in the permeate

IV.3.1.1 Proportions of anions in the permeate

The proportions of individual solutes versus filtration flux for VFAs+Na₂SO₄ binary and ternary solutions are given in Figure IV-7. One can observe that the proportion of SO₄²⁻ in the permeate decreases while the proportions of VFAs in the permeate increases when the filtration flux increases, reach a plateau (namely $P_i^{P^*}$) when the filtration flux is higher than a given value. Then, for the proportions of VFAs in the permeate, it is observed that the permeate proportion of the least retained VFA, Ac, increases the most, followed by Pr, the intermediately retained VFA, and the most retained VFA, Bu, increases the least.

The permeate proportions of all the anions in VFAs+ NaCl and VFAs+ CaCl₂ systems are given in Figure IV-8 and Figure IV-9 respectively. It is shown that the proportion of Cl⁻ in the permeate increases when the filtration flux increases, meanwhile, the proportions of VFAs decrease when the filtration flux increases, all those anions permeate proportions reach a plateau ($P_i^{P^*}$) when the filtration flux is higher than a given value. For VFAs, on the contrary of to what observed in VFAs+ Na₂SO₄ system, the permeate proportion of the least retained VFA, Ac, decreases the least, followed by Pr, the intermediately retained VFA, and the most retained VFA, Bu, decreases the most.

Current results are in agreement with the results observed in Chapter III. Indeed, for a given proportion in the feed, regardless of the concentration, one fixed solute proportion ($P_i^{P^*}$) is found in the permeate when the filtration flux is higher than a certain value.

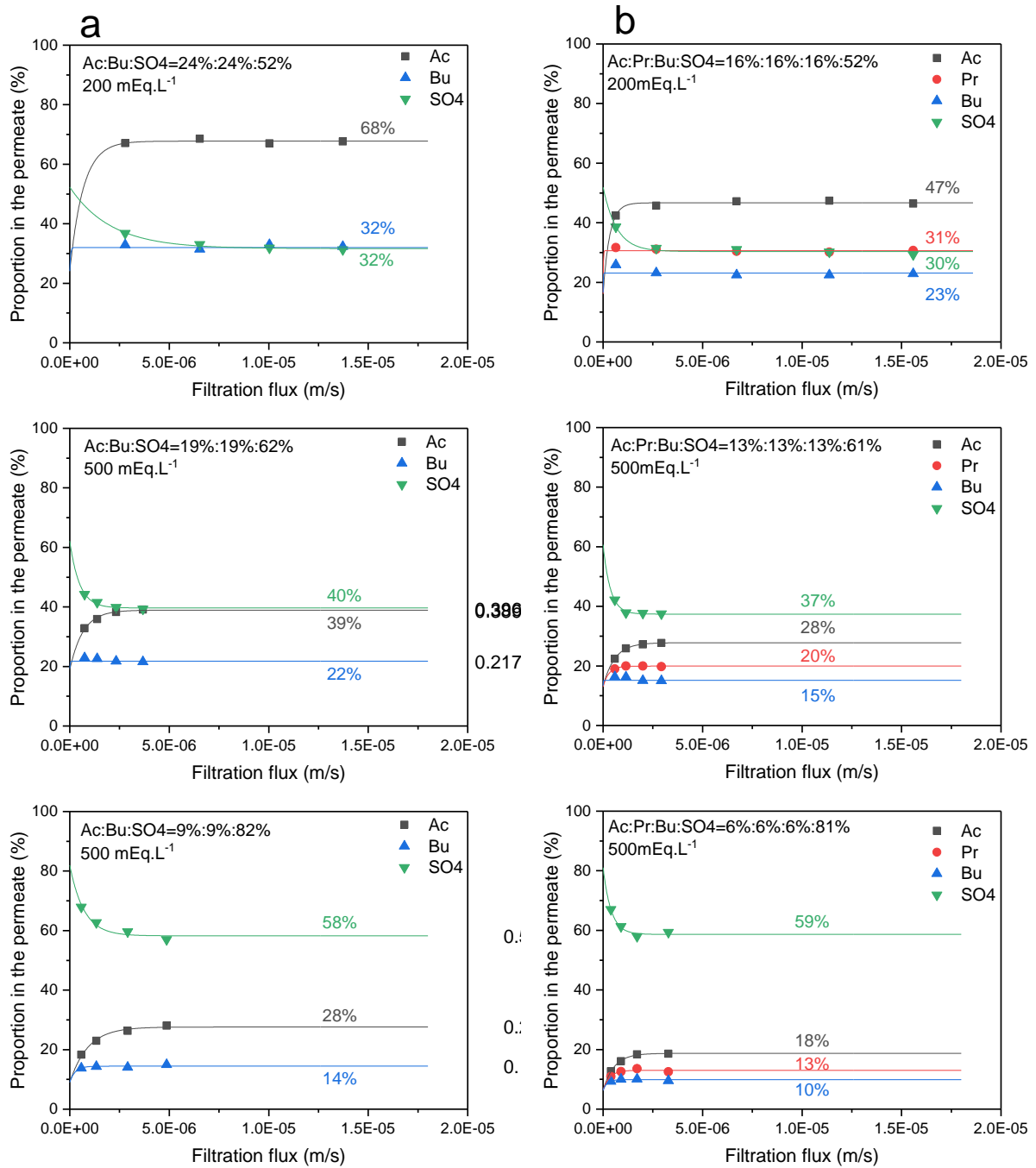


Figure IV-7 Proportions of all the solutes in the permeate versus filtration flux, for (a) Ac/Bu binary solution with Na₂SO₄, (b) Ac/Pr/Bu ternary solution with Na₂SO₄, using NF-45 membrane.

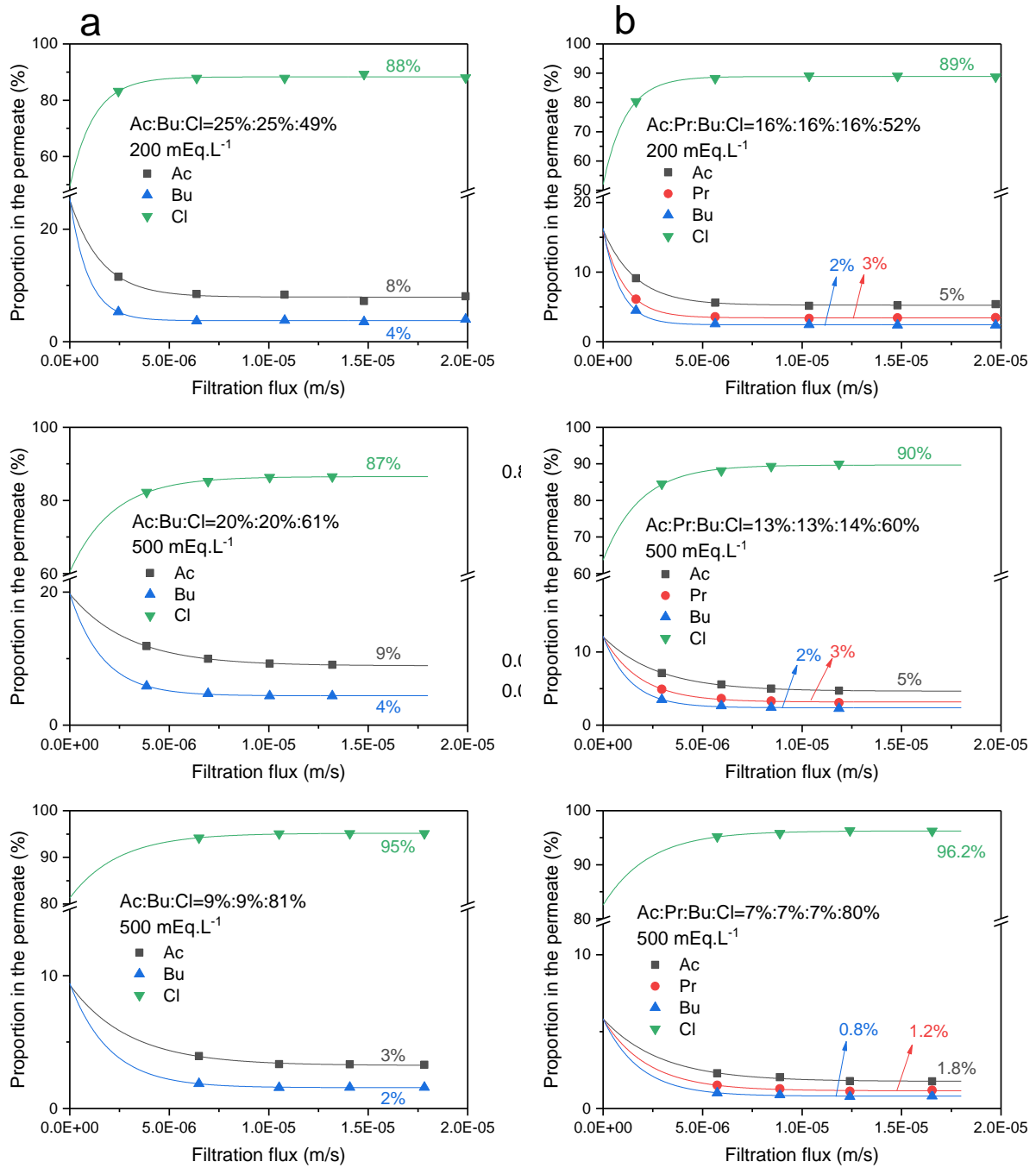


Figure IV-8 Proportions of all the solutes in the permeate versus filtration flux, for (a) Ac/Bu binary solution with NaCl, (b) Ac/Pr/Bu ternary solution with NaCl, using NF-45 membrane.

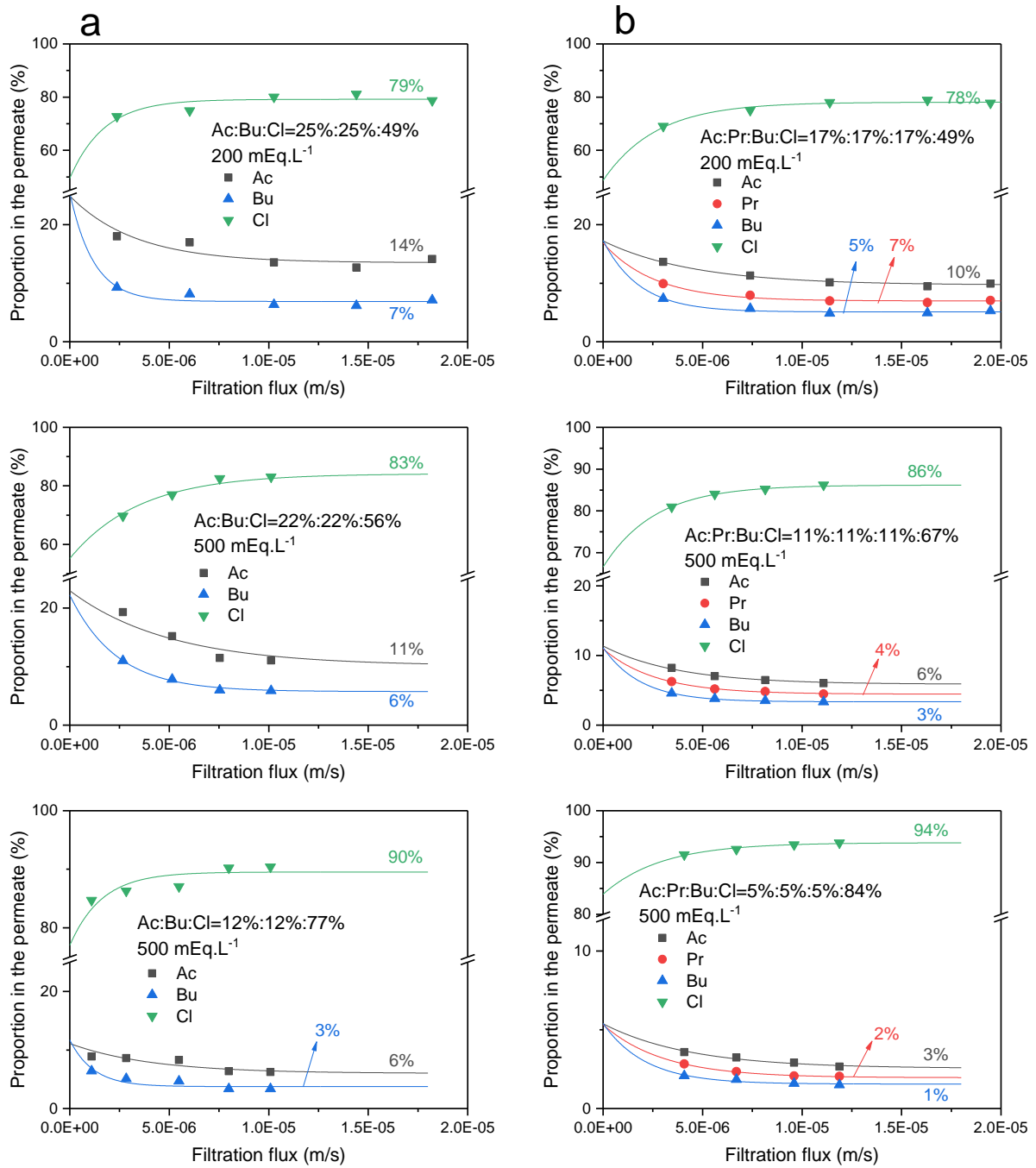


Figure IV-9 Proportions of all the solutes in the permeate versus filtration flux, for (a) Ac/Bu binary solution with CaCl₂, (b) Ac/Pr/Bu ternary solution with CaCl₂, using NF-45 membrane.

Table IV-1 summarizes the proportions of all the anions in the feed and permeate for all the conditions investigated. The proportions in the permeate are obtained from the individual solutes proportions at the plateau values.

Table IV-1 Comparison of the solute proportion in the feed and permeate, using NF-45 membrane, at pH 8

Proportion in the feed							Proportion in the permeate						
Ac	Pr	Bu	VFAs	SO ₄ ²⁻	Cl ⁻ (Na)	Cl ⁻ (Ca)	Ac	Pr	Bu	VFAs	SO ₄ ²⁻	Cl ⁻ (Na)	Cl ⁻ (Ca)
0.24		0.24	0.48	0.52			0.51		0.24	0.76	0.24		
0.16	0.16	0.16	0.48	0.52			0.36	0.23	0.18	0.77	0.23		
0.19		0.19	0.38	0.62			0.38		0.22	0.60	0.40		
0.13	0.13	0.13	0.39	0.61			0.27	0.20	0.15	0.62	0.38		
0.09		0.09	0.18	0.82			0.26		0.14	0.40	0.60		
0.06	0.06	0.06	0.19	0.81			0.18	0.13	0.10	0.40	0.60		
0.25		0.26	0.51		0.49		0.14		0.07	0.21		0.79	
0.16	0.16	0.16	0.48		0.52		0.10	0.06	0.04	0.20		0.80	
0.20		0.20	0.40		0.60		0.09		0.05	0.14		0.86	
0.12	0.12	0.12	0.36		0.64		0.06	0.04	0.03	0.12		0.88	
0.09		0.09	0.19		0.81		0.04		0.02	0.05		0.95	
0.06	0.06	0.06	0.19		0.81		0.02	0.01	0.01	0.05		0.95	
0.25		0.25	0.51			0.49	0.14		0.07	0.21			0.79
0.17	0.17	0.17	0.51			0.49	0.10	0.07	0.05	0.22			0.78
0.22		0.22	0.44			0.56	0.12		0.06	0.18			0.82
0.11	0.11	0.11	0.33			0.67	0.06	0.05	0.04	0.15			0.85
0.12		0.12	0.24			0.76	0.07		0.04	0.11			0.89
0.05	0.05	0.05	0.16			0.84	0.03	0.02	0.02	0.07			0.93

The data in Table IV-1 can be visualized in Figure IV-10, that gives the proportions of individual inorganic salts and VFAs in the permeate versus their proportions in the feed.

One can observe that, for all the conditions investigated, the proportion of solute in the permeate increases when its proportion in the feed increases. Then, the proportion of SO₄²⁻ in the permeate is always lower than its proportion in the feed, meanwhile, the proportion of Cl⁻ in the permeate is always higher than that in the feed, whatever the cation composition, Na⁺ only or mixed Na⁺ and Ca²⁺. However, with the same Cl⁻ proportion in the feed, when there are both Na⁺ and Ca²⁺ in the mixed solution, the proportion of Cl⁻ in the permeate is slightly lower than that with only Na⁺ as counter-ion (Figure IV-10a). This observation is the same as that reported for individual solutes retentions, i.e. the co-ions competition between VFAs and Cl⁻ seems to be reduced in the presence of Ca²⁺.

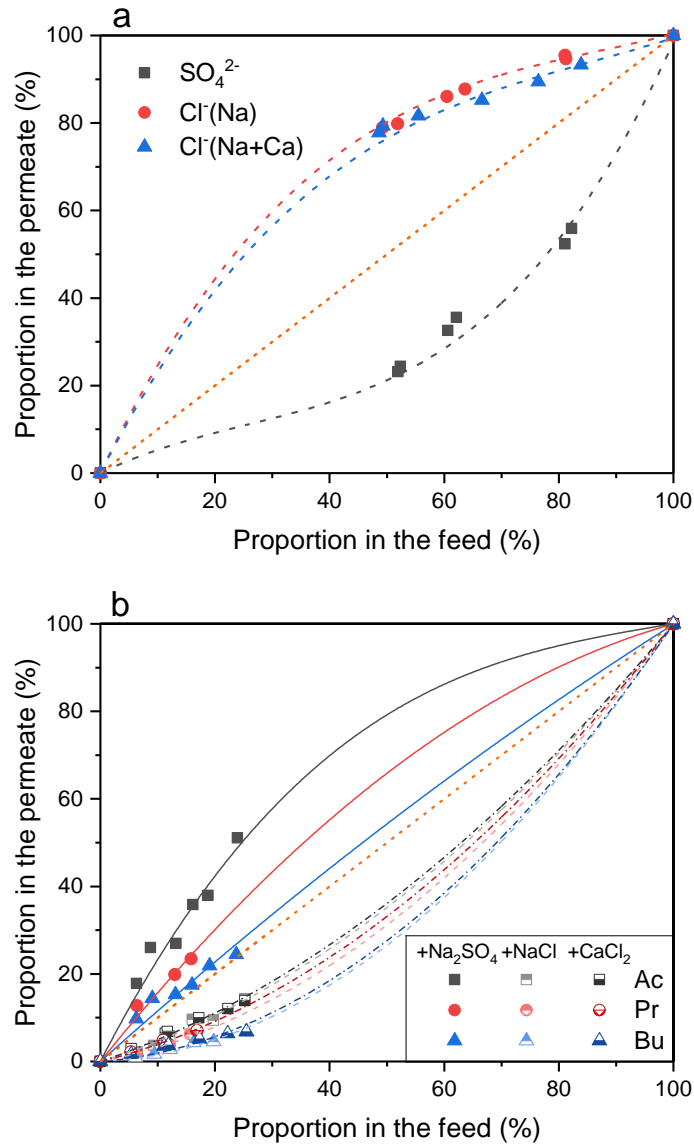


Figure IV-10 Variation of the permeate proportions versus the feed proportions for (a) inorganic salts (b) individual VFAs, using NF-45 membrane, at pH 8.

The proportion of individual VFAs in the permeate show different behaviors with the addition of SO_4^{2-} or Cl^- . With the presence of SO_4^{2-} , VFAs proportion in the permeate is higher than that in the feed. Ac proportion increases the most, followed by Pr, and Bu proportion increases the least. With the presence of Cl^- , VFAs proportion in the permeate is lower than that in the feed. Ac proportion decreases the least, followed by Pr, and Bu proportion decreases the most. It seems that, with the addition of a more retained co-ion (i.e., SO_4^{2-}), the proportion of VFAs in the permeate increases, the least retained VFA increases the most, while the most retained VFA increases the least. On the contrary, with the addition of a less retained co-ion (i.e., Cl^-), the

proportions of VFAs in the permeate decrease, the proportion of the least retained VFA decreases the least, while the proportion of the most retained one decreases the most.

IV.3.1.2 Proportions of cations in the permeate

The permeate proportions of all the cations in VFAs+CaCl₂ system are plotted in Figure IV-11 versus filtration flux. One can observe that the permeate proportion of Na⁺ increases while permeate proportion of Ca²⁺ decreases when the filtration flux increases, reach a plateau at a given filtration flux. This observation is the same as that for anions.

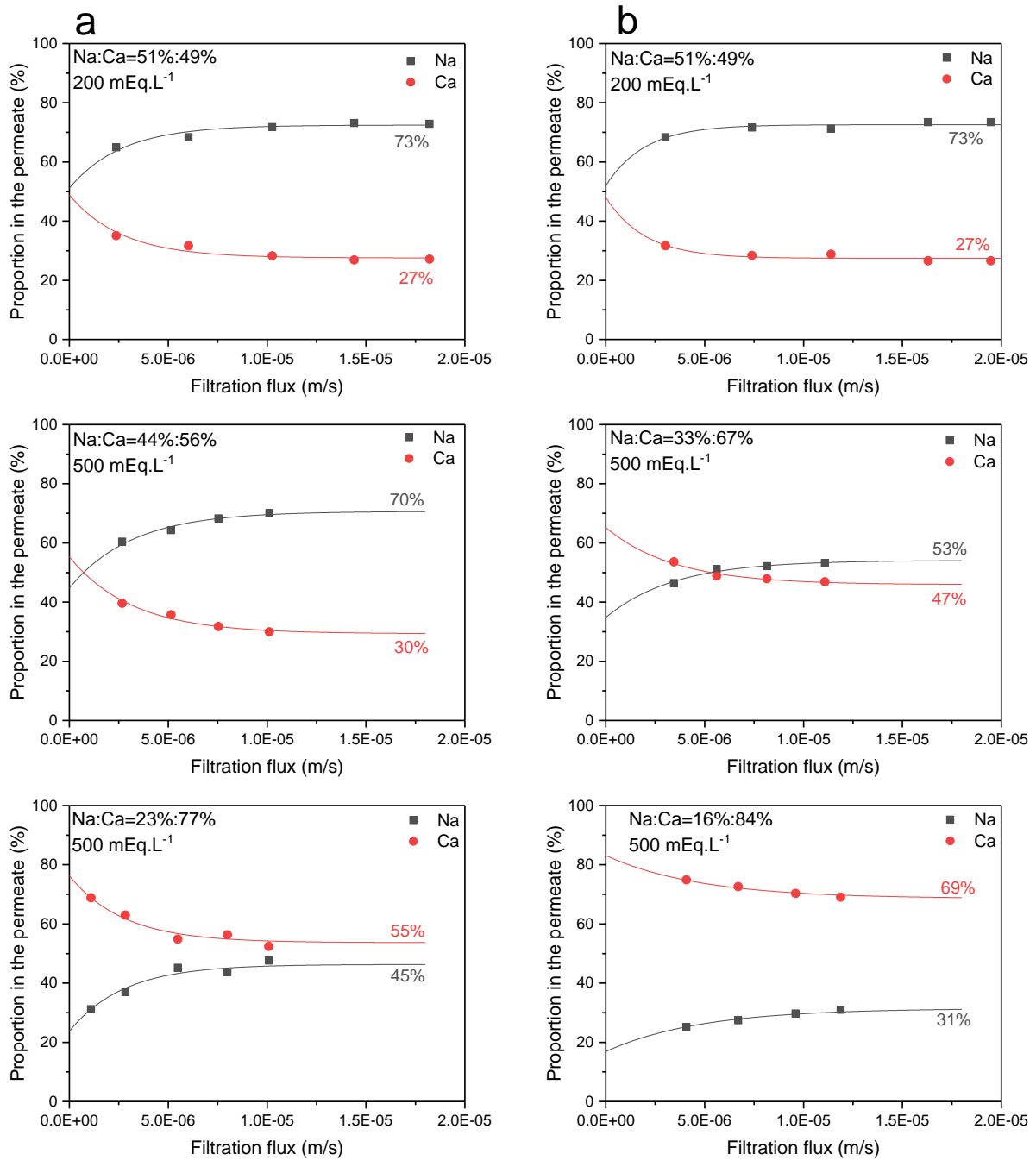


Figure IV-11 Proportions of all the cations in the permeate versus filtration flux, for (a) Ac/Bu binary solution with CaCl₂, (b) Ac/Pr/Bu ternary solution with CaCl₂, using NF-45 membrane, at pH 8.

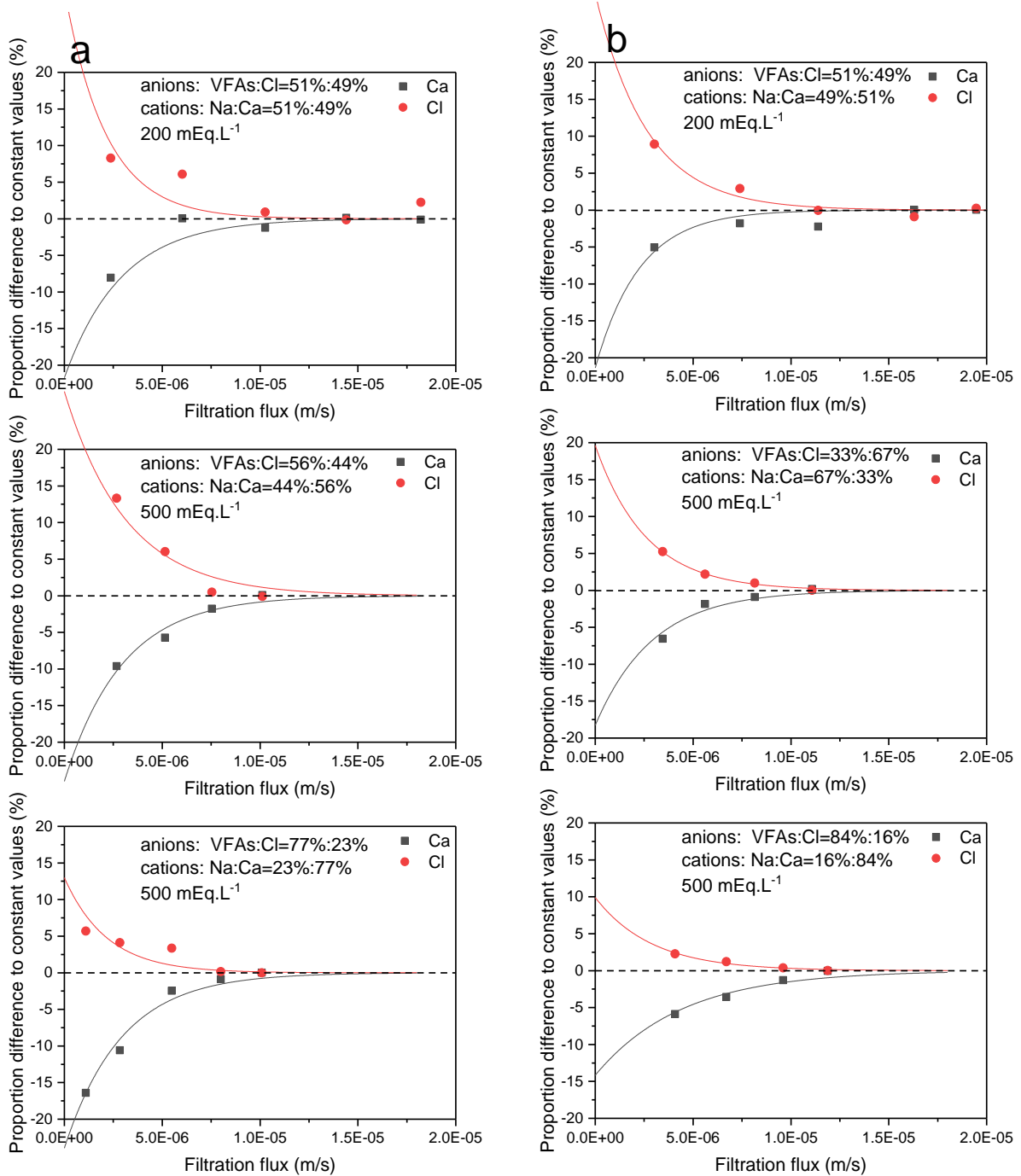


Figure IV-12 The difference of the permeate proportion to the constant values (proportion difference = $P_i^{P^*} - P_i^P$) for Ca²⁺ and Cl⁻ in (a) Ac/Bu binary solution with CaCl₂, (b) Ac/Pr/Bu ternary solution with CaCl₂, using NF-45 membrane, at pH 8.

The proportion difference to the constant values (proportion difference = $P_i^{P^*} - P_i^P$) for Ca^{2+} and Cl^- in VFAs+ CaCl_2 system is given in Figure IV-12. One can observe that as filtration flux increases, the proportion difference to the constant values decreases both for Ca^{2+} and Cl^- . Then, it is also shown that the filtration flux required for anions and cations to reach the plateau proportion in the permeate is almost the same, for all the conditions investigated. However, unlike the previously observed for mixed solutions without Ca^{2+} (shown in Figure IV-8), the filtration flux required to obtain the constant permeate proportion is nearly the same for the total concentrations of 200 mEq.L^{-1} and 500 mEq.L^{-1} .

The proportions of Na^+ and Ca^{2+} in the permeate versus their proportions in the feed are shown in Figure IV-13. As can be expected from the co-ions competition phenomenon previously discussed for anions, the proportions of both Na^+ and Ca^{2+} in the permeate increase as their proportion in the feed increase.

Furthermore, one can observe that for different ratios of VFAs : salts as well as VFAs compositions (100 mEq.L^{-1} , 200 mEq.L^{-1} , for binary and ternary solutions), one single continuous curve can fit all the conditions. This observation indicates that the influence of anions composition in the feed on the permeate proportion of cations is not significant.

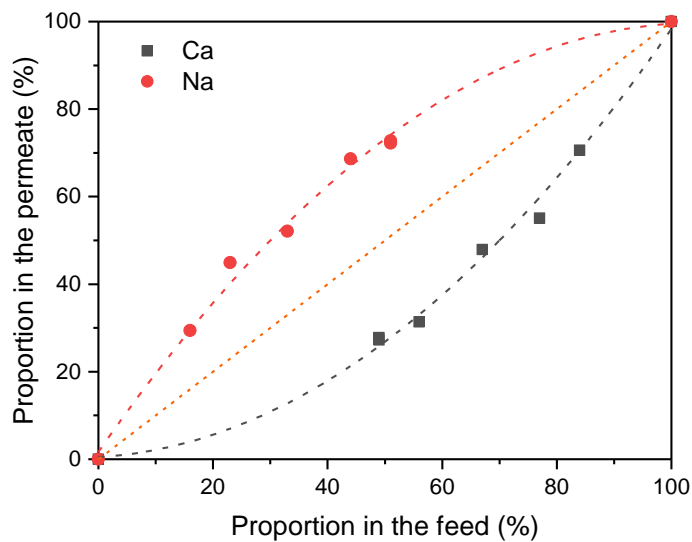


Figure IV-13 Variation of the permeate proportions versus the feed proportions for VFAs mixed solutions with the addition of CaCl_2 , using NF-45 membrane at pH 8.

IV.3.1.3 Relative proportions of VFAs in the permeate

In a more complex solution, the relative proportion of two solutes (defined in Chapter II, Eqs. 2.5, 2.6, 2.7, and 2.8) can give information for the separation of the two solutes. The relative proportions of Ac, Pr, and Bu in feed and permeate for the couples of Ac/Pr, Pr/Bu, and Ac/Bu at binary and ternary solutions without and with inorganic salts are listed in Table IV-2.

Table IV-2 can be visualized in Figure IV-14. The relative permeate proportions of Ac, Pr, and Bu in the couples of Ac/Pr, Pr/Bu, and Ac/Bu are plotted versus their relative feed proportions in the feed.

Table IV-2 Relative proportions of VFAs in the feed and permeate, for single and mixed solutions at different proportions without and with salts, using NF-45 membrane at pH 8.

Solution No.	Proportion in the feed							Relative proportion in the feed						Relative proportion in the permeate					
								Ac		Pr		Bu		Ac		Pr		Bu	
	Ac	Pr	Bu	VFAs	Na ₂ SO ₄	NaCl	CaCl ₂	Ac/Pr	Ac/Bu	Ac/Pr	Pr/Bu	Ac/Bu	Pr/Bu	Ac/Pr	Ac/Bu	Ac/Pr	Pr/Bu	Ac/Bu	Pr/Bu
s1	1							1.00	1.00					1.00	1.00				
s2		1								1.00	1.00					1.00	1.00		
s3			1									1.00	1.00					1.00	1.00
s4	0.5	0.5						0.50		0.50				0.59		0.41			
s5	0.2	0.8						0.20		0.80				0.25		0.75			
s6	0.5		0.5						0.50			0.50			0.66			0.34	
s7	0.2		0.8						0.20			0.80			0.32			0.68	
s8		0.5	0.5								0.50		0.50				0.58		0.42
s9	0.2	0.2	0.6					0.50	0.25	0.50	0.25	0.75	0.75	0.60	0.39	0.40	0.30	0.61	0.70
s10	0.2	0.6	0.2					0.25	0.50	0.75	0.75	0.50	0.25	0.31	0.66	0.69	0.81	0.34	0.19
s11	0.33	0.33	0.33					0.50	0.50	0.50	0.50	0.50	0.50	0.60	0.68	0.40	0.58	0.32	0.42
s12	0.6	0.2	0.2					0.75	0.75	0.25	0.50	0.25	0.50	0.82	0.87	0.18	0.59	0.13	0.41
s16	0.24		0.24	0.48	0.52			1.00	0.50			0.50	1.00	1.00	0.68			0.32	1.00
s17	0.16	0.16	0.16	0.48	0.52			0.50	0.50	0.50	0.50	0.50	0.50	0.60	0.67	0.40	0.57	0.33	0.43
s18	0.19		0.19	0.38	0.62			1.00	0.50			0.50	1.00	1.00	0.64			0.36	1.00
s19	0.13	0.13	0.13	0.39	0.61			0.50	0.50	0.50	0.50	0.50	0.50	0.57	0.64	0.43	0.57	0.36	0.43
s20	0.09		0.09	0.18	0.82			1.00	0.49			0.51	1.00	1.00	0.65			0.35	1.00
s21	0.05	0.05	0.06	0.17	0.83			0.49	0.50	0.51	0.50	0.50	0.50	0.60	0.70	0.40	0.61	0.30	0.39
s22	0.25		0.26	0.51		0.49		1.00	0.50			0.50	1.00	1.00	0.68			0.32	1.00
s23	0.16	0.16	0.16	0.48		0.52		0.50	0.50	0.50	0.49	0.50	0.51	0.61	0.69	0.39	0.59	0.31	0.41
s24	0.20		0.20	0.40		0.60		1.00	0.50			0.50	1.00	1.00	0.68			0.32	1.00
s25	0.12	0.12	0.12	0.36		0.64		0.50	0.50	0.50	0.50	0.50	0.50	0.60	0.68	0.40	0.58	0.32	0.42
s26	0.09		0.09	0.19		0.81		1.00	0.50			0.50	1.00	1.00	0.68			0.32	1.00
s27	0.06	0.06	0.06	0.17		0.83		0.50	0.50	0.50	0.50	0.50	0.50	0.61	0.69	0.39	0.59	0.31	0.41

Chapter IV

s28	0.25		0.25	0.51		0.49	1.00	0.50			0.50	1.00	1.00	0.67			0.33	1.00
s29	0.17	0.17	0.17	0.51		0.49	0.50	0.50	0.50	0.49	0.50	0.51	0.59	0.66	0.41	0.58	0.34	0.42
s30	0.22		0.22	0.44		0.56	1.00	0.50			0.50	1.00	1.00	0.65			0.35	1.00
s31	0.11	0.11	0.11	0.33		0.67	0.51	0.50	0.49	0.50	0.50	0.50	0.57	0.65	0.43	0.58	0.35	0.42
s32	0.12		0.12	0.24		0.76	1.00	0.50			0.50	1.00	1.00	0.64			0.36	1.00
s33	0.05	0.05	0.05	0.16		0.84	0.50	0.50	0.50	0.50	0.50	0.50	0.57	0.64	0.43	0.57	0.36	0.43

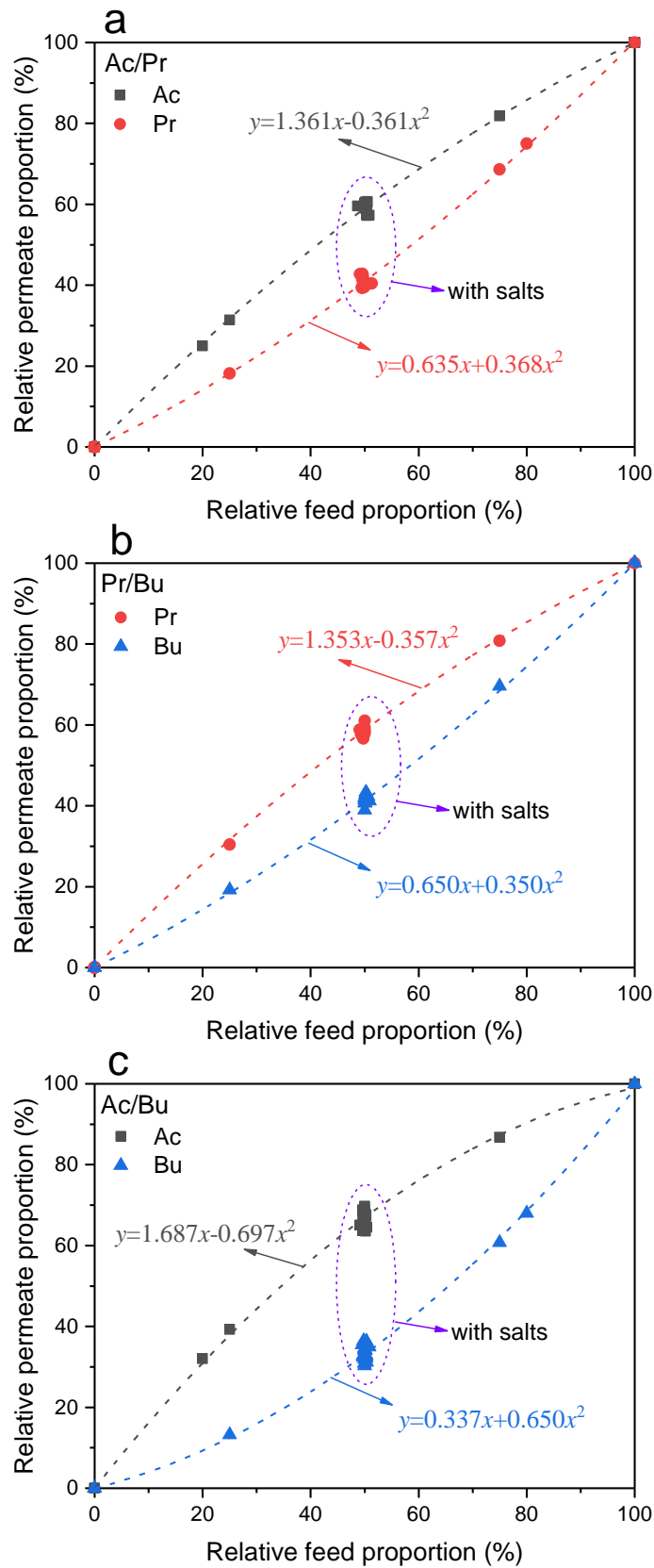


Figure IV-14 Relative proportions of VFAs in the couples of (a) Ac/Pr, (b) Pr/Bu, and (c) Ac/Bu, for all the compositions investigated, using NF-45 membrane at pH 8.

The relative proportions of VFAs in the feed solutions with the addition of inorganic salts are nearly the same for the three couples (i.e., about 50% for all the VFAs in the three couples). One can observe that the relative proportions of VFAs in the permeate for the conditions with the addition of inorganic salts are nearly the same too. The relative proportions of Ac in the couples of Ac/Pr and Ac/Bu are $59\% \pm 2\%$ and $67\% \pm 3\%$ respectively; the relative proportions of Pr in the couples of Ac/Pr and Pr/Bu are $41\% \pm 2\%$ and $59\% \pm 2\%$ respectively; the relative proportions of Bu in the couples of Pr/Bu and Ac/Bu are $41\% \pm 2\%$ and $33\% \pm 3\%$ respectively. This observation indicates that the addition of salts does not significantly influence the permeate proportion of VFAs. Furthermore, one can observe that for all the VFAs at all the conditions investigated (VFAs without and with the addition of inorganic salts at different compositions), one single polynomial curve can fit the relative proportions in the permeate versus relative proportions in the feed. The formulas of the polynomial curves are given for Ac, Pr and Bu in the couples of Ac/Pr, Pr/Bu, and Ac/Bu. y is the proportion in the permeate, x is the proportion in the feed.

The relative proportion of one solute in the permeate versus that in the feed (namely, enrichment factor) can be simulated by a binomial formulas. Amongst those formulas, the x is the feed proportion and the y represents the enrichment factor of a given solute in the permeate compared to that in the feed. Using the relative proportion of Ac in the feed and permeate for the couple of Ac/Pr as an example. The fitting formula is $y = 1.361x - 0.361x^2$, when $x = 0$, $y = 1.361$, indicate that when the relative proportion of Ac in the feed is near to 0%, the relative proportion of Ac in the permeate is 1.361 times higher than that in the feed. When $x = 1$, $y = 1$, shown that when the relative proportion of Ac in the feed is near to 100%, the relative proportion of Ac in the permeate is near to 1. Then, the enrichment factor of Ac for the couple of Ac/Pr decreases when the relative proportion of Ac in the feed increases. On the contrary, the enrichment factor for Pr for the couple of Ac/Pr increases when the feed proportion of Pr increases. It increases from 0.64 when the proportion of Pr in the feed is near to 0%, to about 1 when the proportion of Pr in the feed is near to 100%. The same findings are observed for the couples of Pr/Bu and Ac/Bu.

Present results show that for any couple of solutes, their relative proportions in the permeate are fixed by their relative proportion in the feed and do not depend on the presence of co-ions.

For cations, the same conclusion is also observed (shown in Figure IV-13).

IV.3.2 Solute transfer in mixed solutions

IV.3.2.1 Anions transfer

Figure IV-15 shows the individual solute flux versus the total solute flux in binary solutions of Ac/Bu (Ac : Bu = 50% : 50%), and ternary solutions of Ac/Pr/Bu (Ac : Pr : Bu = 33% : 33% : 33%) at different concentrations with addition of Na₂SO₄. The individual solutes flux versus total solute flux obtained with VFAs+NaCl (Figure IV-16) and VFAs+CaCl₂ (Figure IV-17) systems are also given.

For all the conditions investigated, one can observe that the individual solute flux linearly increases with the total solute flux, and the R square values for the linear approaches are higher than 0.96.

As explained in Chapter III, the slope of individual solute flux versus total solute flux represents the given solute proportion in the permeate. Current observation confirms that, for a given feed proportion, the total solute flux (i.e., the total amount of charge transfer through the membrane) fixes the individual solute flux.

Furthermore, since the individual solutes flux linearly increase with the total solutes flux, then, for any couple of solutes, the individual solutes flux should also linearly increase with the combined solutes flux of this couple.

Figure IV-18 gives the individual VFAs flux versus the combined solute flux for the couples of Ac/Pr, Pr/Bu, and Ac/Bu in mixed solutions without and with the addition of Na₂SO₄, NaCl, and CaCl₂ respectively. The relative proportion of Ac, Pr, and Bu in the feed for three couples are all equal to 50%.

One can observe that whatever the composition, without or with inorganic salts, the individual solute flux linearly increases with the combined solute flux nearly following the same slope. Current observation indicates that the mass transfer of a complex solution can be separated into various couples of solutes, and combined solute transfer controls the individual solute transfer.

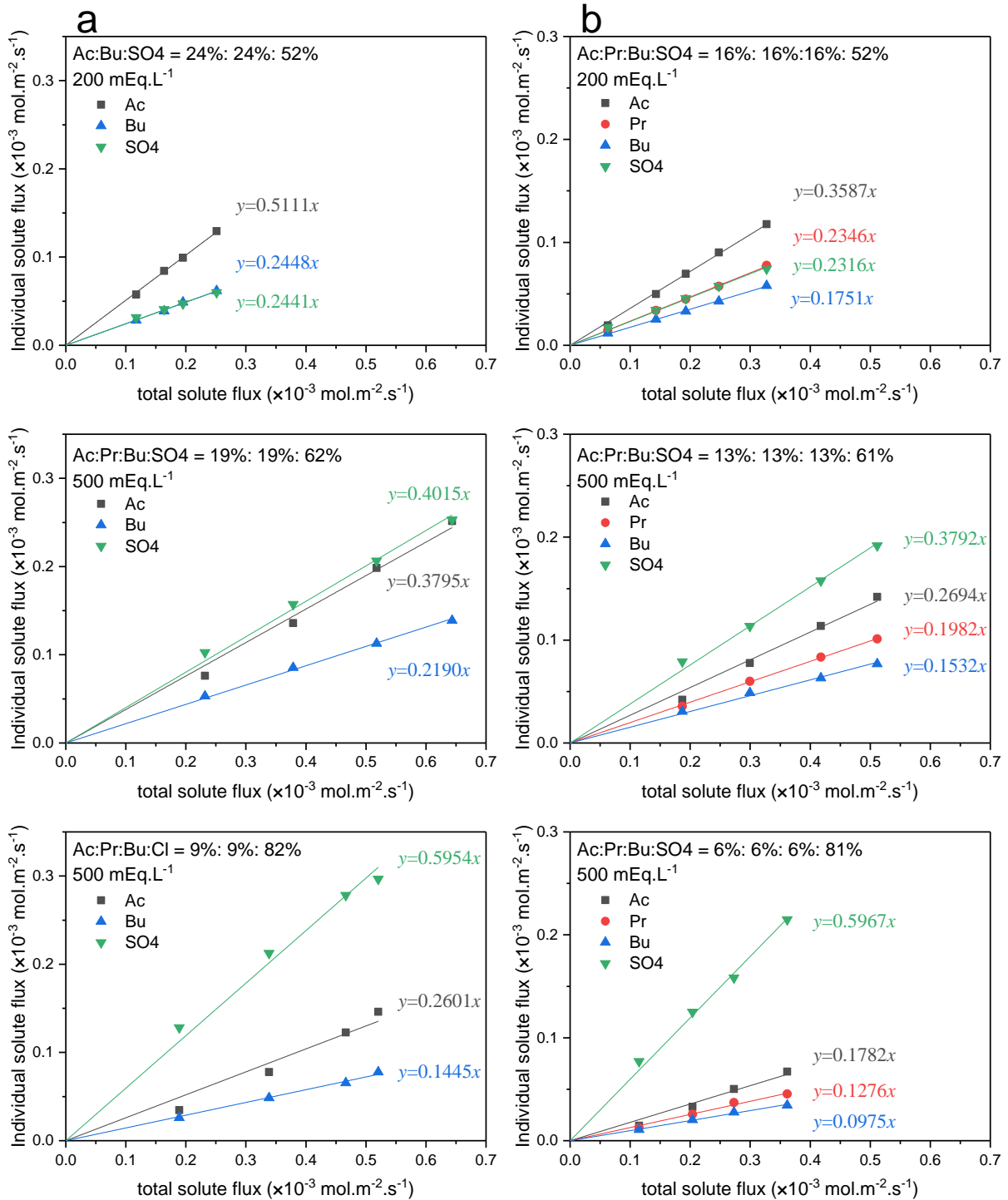


Figure IV-15 Individual solute flux versus total solute flux, for (a) Ac/Bu binary solution with Na₂SO₄, (b) Ac/Pr/Bu ternary solution with Na₂SO₄, using NF-45 membrane.

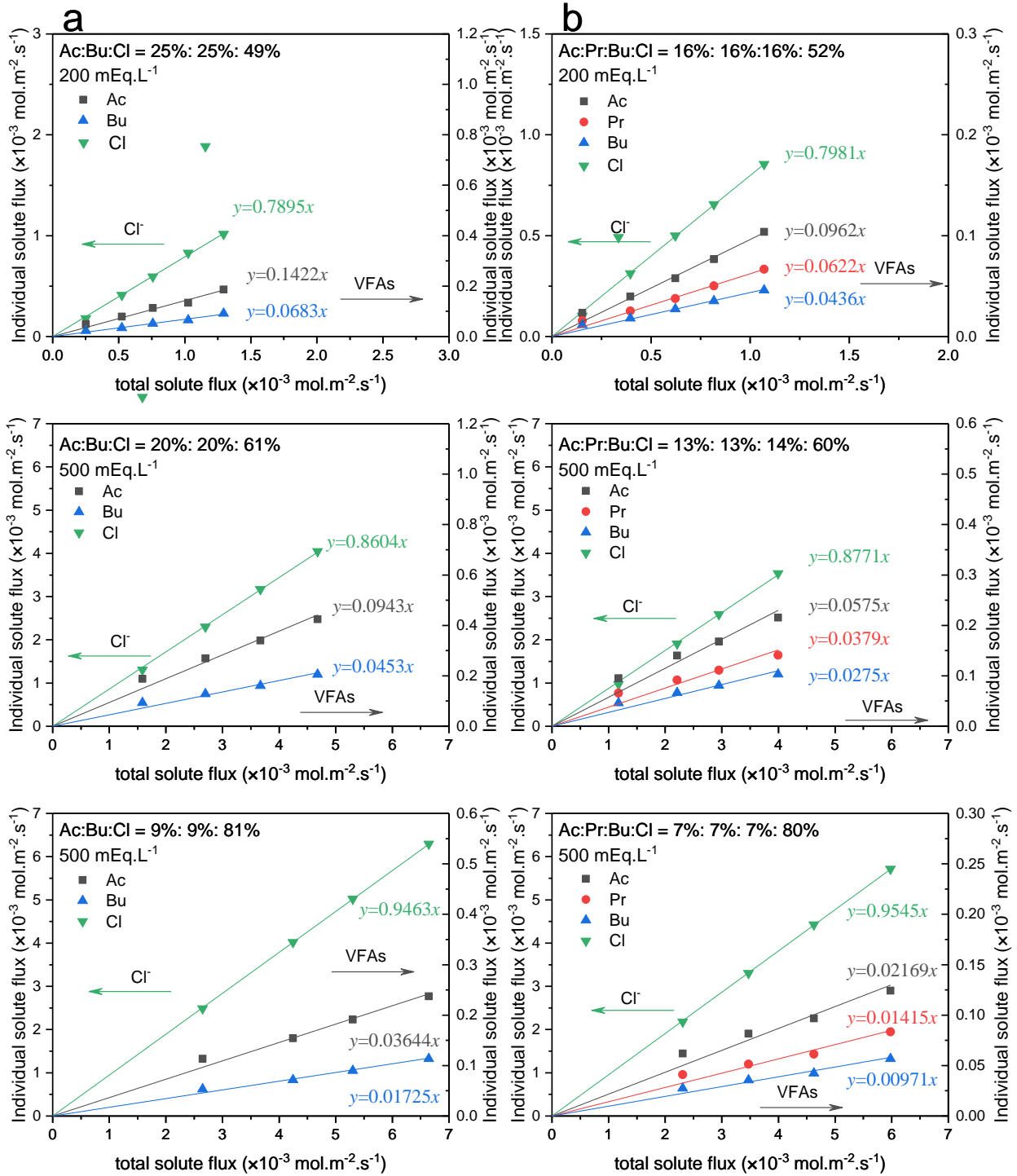


Figure IV-16 Individual solute flux versus total solute flux, for (a) Ac/Bu binary solution with NaCl, (b) Ac/Pr/Bu ternary solution with NaCl, using NF-45 membrane.

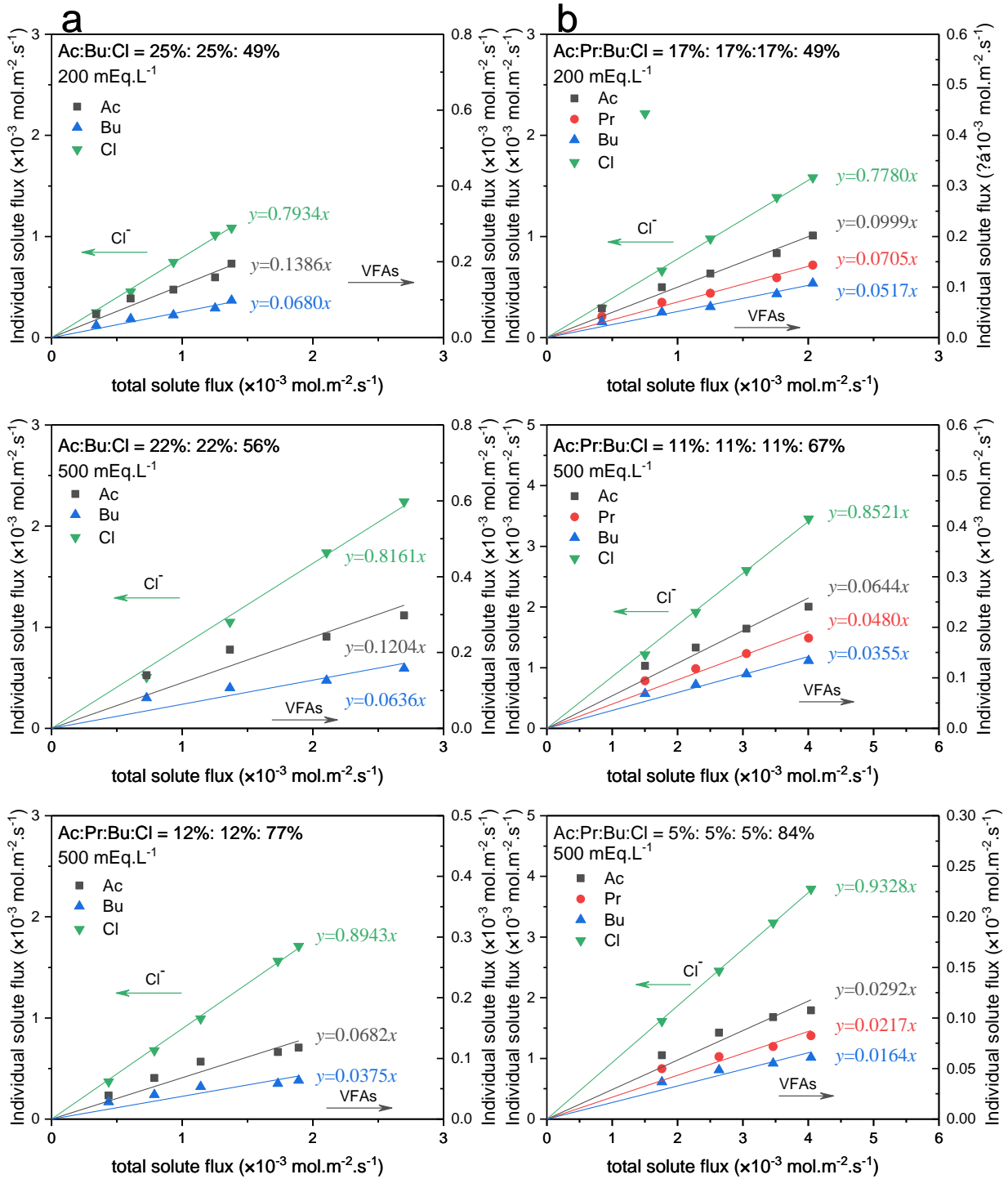


Figure IV-17 Individual solute flux versus total solute flux, for (a) Ac/Bu binary solution with CaCl₂, (b) Ac/Pr/Bu ternary solution with CaCl₂, using NF-45 membrane.

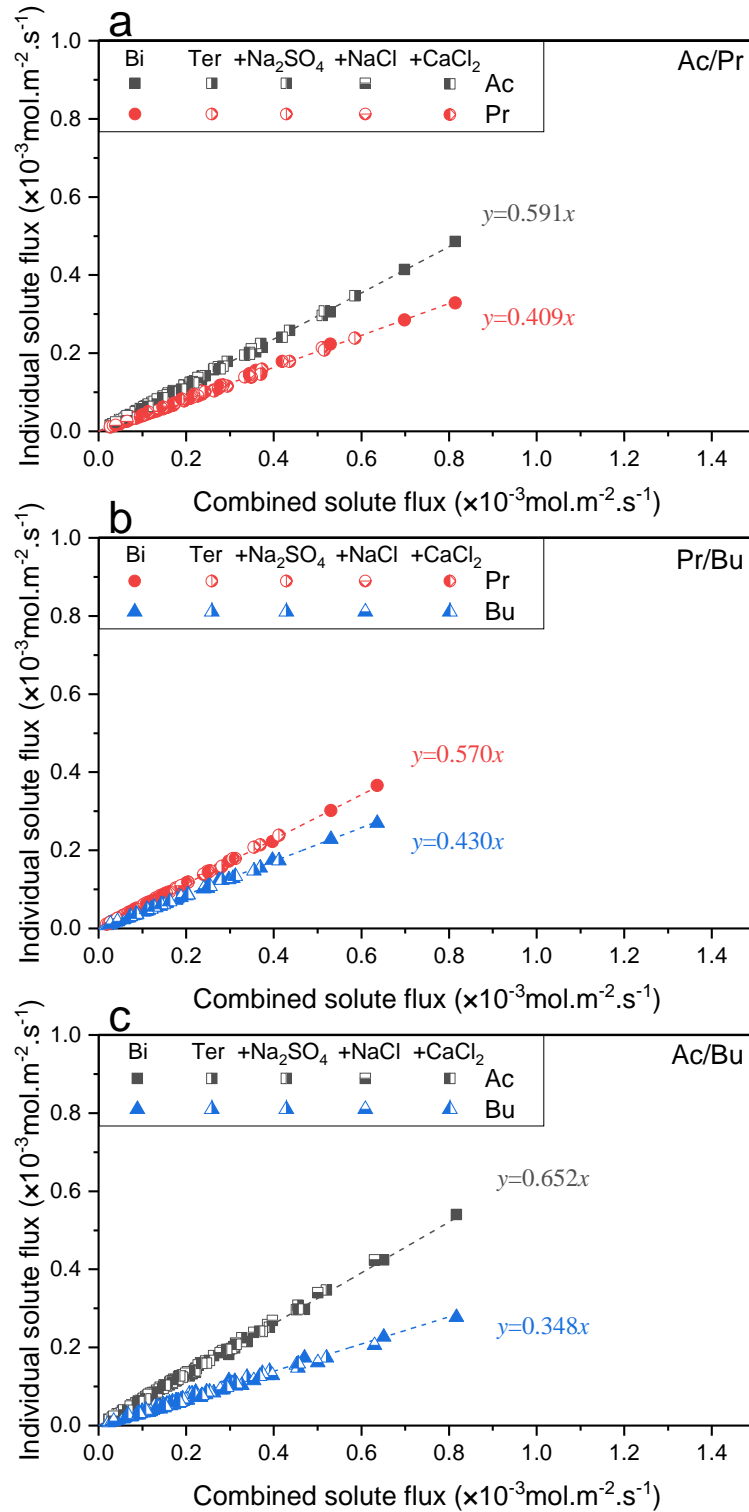


Figure IV-18 Individual solute flux versus the combined solute flux for the couples of (a) Ac/Pr, (b) Pr/Bu, and (c) Ac/Bu in binary, ternary solutions without inorganic salts and with the addition of Na₂SO₄, NaCl, and CaCl₂ respectively, using NF-45 membrane. The relative feed proportion of Ac, Pr, and Bu in the three couples are all equal to 50%.

IV.3.2.1 Cations transfer

The individual cations flux versus the total cations flux in the NaVFAs+ CaCl₂ system are given in Figure IV-19. One can notice that the linear relationship between individual cations flux and total cations flux is observed. Then, for cations, it is also observed that for a given feed proportion, the individual solute flux is fixed by the total solute flux (i.e., total charge transfer).

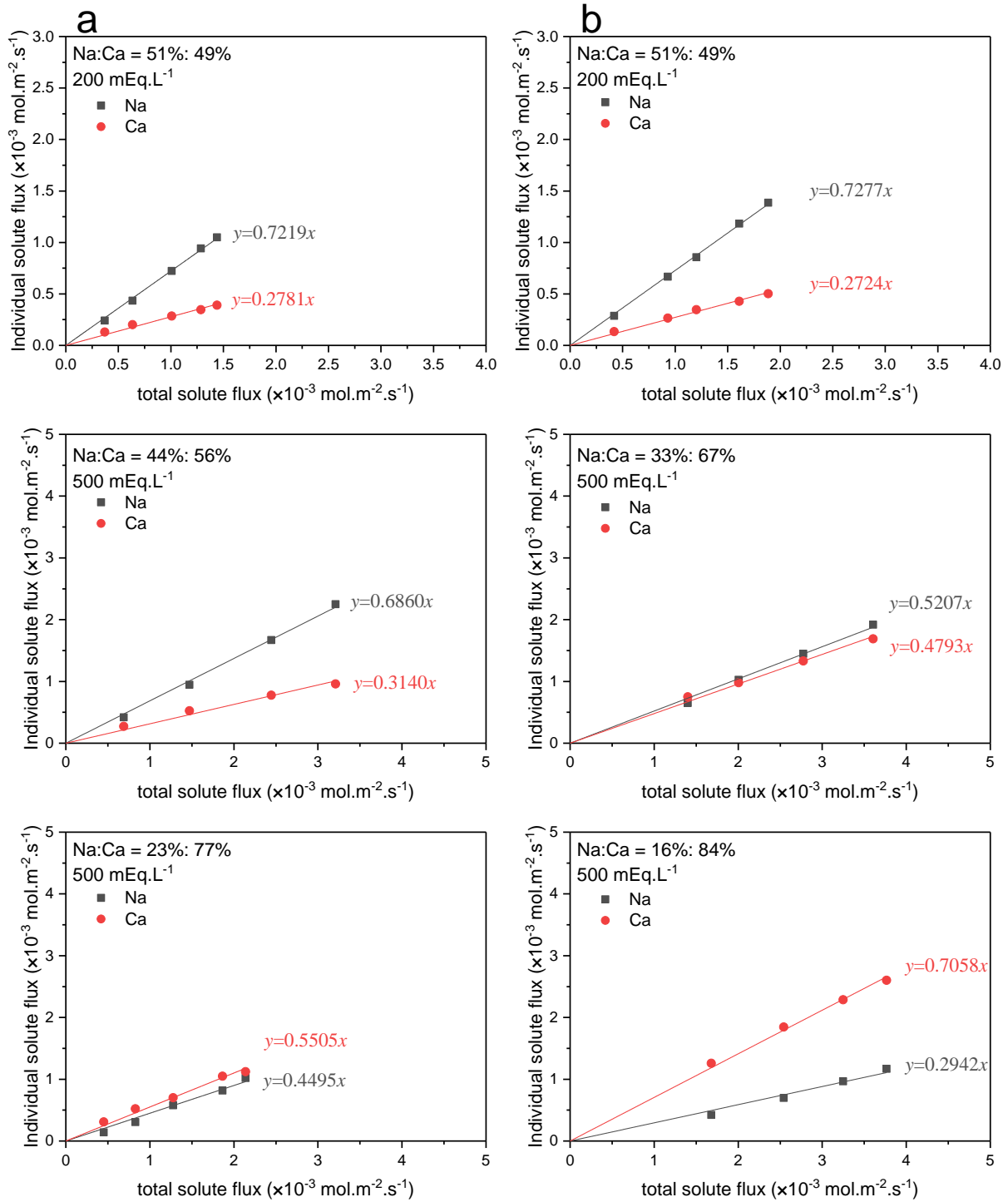


Figure IV-19 Individual solute flux versus total solute flux, for (a) Ac/Bu binary solution with CaCl₂, (b) Ac/Pr/Bu ternary solution with CaCl₂, using NF-45 membrane.

IV.3.3 Influence of the composition on the separation factors between VFAs

The aim of the investigation on solutes proportions in the feed and permeate is to investigate the separation performance of NF on VFAs at different compositions. In current Chapter, four types of mixed solution systems (VFAs without salt, VFAs+Na₂SO₄, VFAs+NaCl, and VFAs+CaCl₂) are investigated. It is concluded that the concentration of the solution does not influence the separation, therefore, the comparison of separation is applied for different feed proportions.

Table IV-3 Separation factor between Ac/Pr, Pr/Bu, and Ac/Bu at corresponding proportion in the feed for all the solutions investigated, using NF-45 membrane.

Solution number	Proportion in the feed						Separation factor		
	Ac	Pr	Bu	Na ₂ SO ₄	NaCl	CaCl ₂	Ac/Pr	Pr/Bu	Ac/Bu
s4	0.5	0.5					1.45		
s5	0.2	0.8					1.37		
s6	0.5		0.5						1.95
s7	0.2		0.8						1.89
s8		0.5	0.5					1.37	
s9	0.2	0.2	0.6				1.48	1.32	1.95
s10	0.2	0.6	0.2				1.39	1.42	1.98
s11	0.33	0.33	0.33				1.51	1.44	2.17
s12	0.6	0.2	0.2				1.49	1.43	2.13
s16	0.24		0.24	0.52					2.07
s17	0.16	0.16	0.16	0.52			1.50	1.35	2.03
s18	0.19		0.19	0.62					1.83
s19	0.13	0.13	0.13	0.61			1.38	1.33	1.83
s20	0.09		0.09	0.82					1.86
s21	0.06	0.06	0.06	0.81			1.41	1.29	1.82
s22	0.25		0.26		0.49				2.11
s23	0.16	0.16	0.16		0.52		1.52	1.48	2.24
s24	0.20		0.20		0.60				2.08
s25	0.12	0.12	0.12		0.64		1.52	1.39	2.10
s26	0.09		0.09		0.81				2.14
s27	0.06	0.06	0.06		0.81		1.52	1.42	2.15
s28	0.25		0.25			0.49			2.06
s29	0.17	0.17	0.17			0.49	1.39	1.40	1.95
s30	0.22		0.22			0.56			1.89
s31	0.11	0.11	0.11			0.67	1.30	1.38	1.79
s32	0.12		0.12			0.76			1.84
s33	0.05	0.05	0.05			0.84	1.33	1.34	1.78

Table IV-3 summarizes the separation factors (as defined in Chapter II) between Ac/Pr, Pr/Bu, and Ac/Bu at corresponding proportions in the feed for all the conditions investigated. The proportions of VFAs in the permeate used to calculate the separation factors are the plateau values previously observed.

Despite the variety of compositions, one can observe that the separation factors between Ac/Pr and Pr/Bu are within the range of 1.29 to 1.52, separation factors between Pr/Bu are systematically slightly lower than that of Ac/Pr, except for the conditions with addition of CaCl₂. Separation factors between Ac/Bu are in-between 1.78 to 2.24.

In order to compare the influence of the addition of salts, the conditions with identical proportions of VFAs (i.e., Ac:Bu=1:1 and Ac:Pr:Bu=1:1:1) are chosen and visualized in Figure IV-20. In Figure IV-20a, the separation factor between Ac/Bu obtained for binary VFAs solutions (Ac:Bu=1:1) without, with Na₂SO₄, with NaCl, and with CaCl₂ for VFAs:salts at 1:1, 2:3 and 1:4 are compared. In Figure IV-20b, the separation factors of Ac/Pr, Pr/Bu, and Ac/Bu for ternary VFAs solutions (Ac:Pr:Bu=1:1:1) at different VFAs:salts proportions are compared.

For binary solutions of VFAs (Ac:Bu=1:1), it seems that the addition of 100 mEq.L⁻¹ of salts (VFAs:salts=1:1), increases the separation factor between Ac and Bu for all the conditions. Then, when the proportions of VFAs:salts decrease to 2:3 and 1:4 (meanwhile, the ionic concentration of the mixed solutions increases to 500 mEq.L⁻¹), the separation factor decreases for the systems of VFAs+Na₂SO₄ and VFAs+CaCl₂, but, remains nearly constant for VFAs+NaCl system (Figure IV-20a).

For ternary solutions (Ac:Pr:Bu=1:1:1), with the addition of 100 mEq.L⁻¹ of salts (VFAs:salts=1:1), it seems that the separation factors of Ac/Pr, Pr/Bu, and Ac/Bu slightly increases with the addition of NaCl, and slightly decreases with the addition of Na₂SO₄ and CaCl₂ compared to the condition without the addition of salts. When the ratio of VFAs:salts=1:1 decreases to 2:3 and 1:4 (the ionic concentration increases to 500 mEq.L⁻¹), those separation factors all decrease compared to those without the addition of salts. With the addition of NaCl, the separation factors between VFAs decrease slightly, while decreases more with the addition of Na₂SO₄ and CaCl₂ (Figure IV-20b).

In Chapter III, it is concluded that the separation factor between Ac/Bu obtained in binary solutions at identical proportion (Ac:Bu=50%:50%) is higher than with other proportion (Ac : Bu=20%:80%). Then, the highest separation factors between VFAs are observed for ternary solution with identical proportion (Ac: Pr: Bu=33%:33%:33%).

Current observation is in agreement with the previous results. Indeed, for binary VFAs solutions, the addition of a third co-ion makes the VFAs+salts systems become ternary electrolyte solutions. As observed in Chapter III, the presence of an additional co-ion (Pr^-) increases the separation factor between Ac and Bu. In the current systems, the presence of the additional co-ions (SO_4^{2-} and Cl^-) also increases the separation factor between Ac and Bu.

As observed in Chapter III, decreasing the ratio of Ac:Bu and Ac:Pr:Bu from 50%:50% and 33%:33%:33% to 20%:80% and 20%:20%:60% respectively, the separation factor between Ac and Bu decreases. In current systems, when the ratio of VFAs : salts decreases from 1:1, 2:3 to 1:4, the proportions of these mixed electrolyte solutions are farther from identical proportion, the decrease of separation factor between Ac and Bu is also observed, except for VFAs+NaCl.

However, the influence of ionic composition on the separation of complex electrolyte solutions still needs further investigation.

For ternary VFAs solutions, the addition of a fourth co-ion (SO_4^{2-} or Cl^-) decreases the separation factors between VFAs except for VFAs+NaCl system at 1:1. It should be noticed that the proportions of co-ions in the quaternary electrolyte solutions are not at identical even when the ratio of VFAs : salts=1:1 (when VFAs : salts=1:1, the proportion of individual solute is Ac : Pr : Bu : salts=17%: 17%:17%: 49%). As reported in Chapter III, the best separation is observed for the condition with identical proportion, thus the separation factor in the quaternary electrolyte solutions could be lower than that in ternary VFAs solutions with identical proportion. Nevertheless, when the proportion is farther from the identical proportion (i.e., VFAs : salts decreases from 1:1, 2:3 to 1:4), the separation factors between VFAs all decrease. However, for the system of VFAs+NaCl, the separation factors between VFAs decrease less compared to that for the other two systems (VFAs+CaCl₂ and VFAs+Na₂SO₄).

In addition, both for binary and ternary VFAs solutions, the separation factors between VFAs are lower in VFAs+CaCl₂ system compared to those in VFAs+NaCl system. Then, when one part of counter-ions is changed from Na^+ to Ca^{2+} , the separation performance of NF on VFAs decreases.

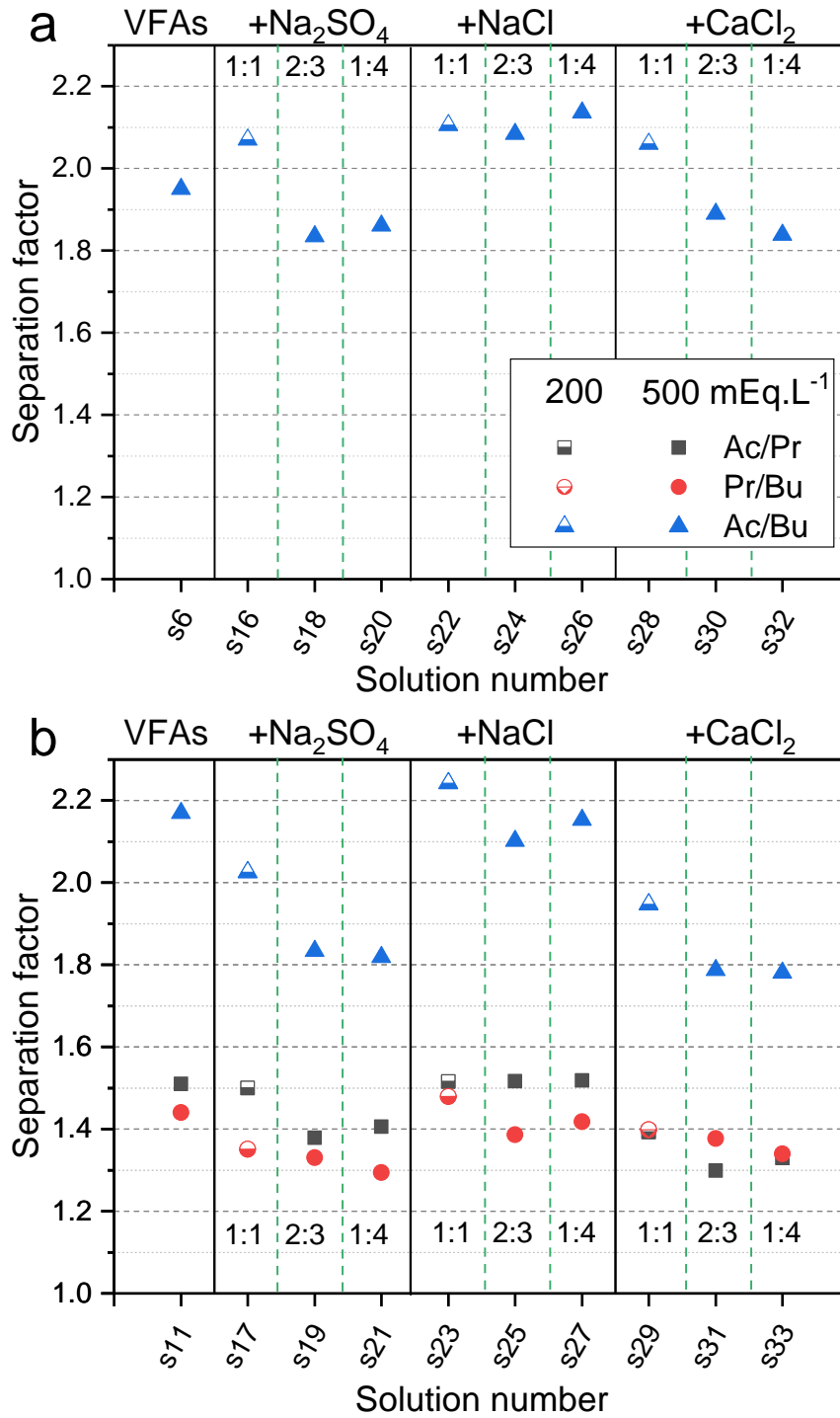


Figure IV-20 Separation factors between Ac/Pr, Pr/Bu, and Ac/Bu in (a) VFAs Binary solutions (Ac:Bu=1:1), and (b) VFAs Ternary solutions (Ac:Pr:Bu=1:1:1) without addition of salt, with Na₂SO₄, with NaCl, and with CaCl₂, respectively, using NF-45 membrane.

It was reported that the addition of inorganic salts can increase the selectivity between charged and uncharged solutes. The addition of NaCl can gradually increase the maximum separation factor between sodium lactate and glucose, from about 1.1 (without NaCl) to 1.5 (with 1000mEq.L⁻¹ of NaCl). Then, the addition of Na₂SO₄ can also increase the separation factor between the two solutes, maximum separation factor can reach 1.9 with 1000mEq.L⁻¹ of Na₂SO₄ [139].

Indeed, the mechanism for the influence of inorganic salts on the separation of sodium lactate and glucose is not the same as the mechanism for the influence of inorganic salts for the separation of VFAs. From the experimental data reported in ref. [139], it was observed that the addition of salts can decrease both the retention of lactate and glucose, due to the screening effect and dehydration respectively, the decrease of glucose retention (10% with 1000mEq.L⁻¹ of NaCl) is less than the decrease of lactate retention (30%, at $J=0.2 \times 10^{-5}$ m.s⁻¹, with 1000mEq.L⁻¹ of NaCl). Therefore, the retention difference between glucose and lactate increases, and then higher separation factor is observed. With the addition of Na₂SO₄, the same phenomenon was observed, the decrease of glucose retention due to the addition of Na₂SO₄ is less than 4% (with 1000mEq.L⁻¹ of Na₂SO₄), meanwhile, the retention of lactate decreases 50%, at $J=0.2 \times 10^{-5}$ m.s⁻¹, with 1000mEq.L⁻¹ of Na₂SO₄, then, an even better separation factor was achieved.

Beside the screening effect, the co-ions competition can also play a role. The decrease of lactate retention due to the influence of inorganic salts is a combination of screening effect (total ionic concentration increase) and co-ions competition (between Lac⁻/Cl⁻ and Lac⁻/SO₄²⁻).

Lac⁻ is the more retained co-ion while Cl⁻ is the less retained co-ion for the mixed solution of glucose/lactate/NaCl. Then, in the presence of Cl⁻, the retention of lactate should increase. However, the experiments were done at different ionic concentration (from 100mEq.L⁻¹ (only 100mM of glucose and 100mEq.L⁻¹ of lactate) to 1100mEq.L⁻¹ (100mM of glucose, 100mEq.L⁻¹ of lactate with 1000mEq.L⁻¹ of salts)), there is the influence of screening effect and the observed lactate retention decrease is the result of co-ions competition (tends to increase the retention of lactate) and screening effect (tends to decrease the lactate retention).

SO₄²⁻ is the more retained co-ions and Lac⁻ is the less retained co-ions for the mixed solution of glucose/lactate/Na₂SO₄. In the presence of SO₄²⁻, the co-ions competition between Lac⁻ and SO₄²⁻ tends to decrease the lactate retention, the same as the trend of screening effect. Therefore, retention of lactate decreases less (30%, at $J=0.2 \times 10^{-5}$ m.s⁻¹) in the presence of NaCl, while lactate

retention decreases more (50%, at $J=0.2 \cdot 10^{-5} \text{ m.s}^{-1}$) and even reached negative value at low filtration flux when lactate is coupled with Na_2SO_4 [139].

The current chapter shows the co-ions competition phenomenon between six co-ions in mixed solutions. It is shown that the ionic compositions do not significantly influence the co-ion competition between co-ions. This demonstrates that the behaviors of neutral and charged solutes in the mixed solution are different.

IV.4 Conclusions

It was pointed out in Chapter III that for a given VFAs proportion in the feed, a fixed proportion in the permeate is obtained. That is due to the transfer of individual VFAs are controlled by the total VFAs transfer. Then the individual VFAs transfer is the result of co-ions competition, and the contribution of each VFA for the total solute transfer depends on its proportion in the feed.

In the current Chapter, we investigated the influence of the addition of salts (Na_2SO_4 , NaCl , and CaCl_2) on the performance of nanofiltration on VFAs solutions. The co-ions competition phenomenon observed in Chapter III is investigated in the more complex systems (with five anions and two cations).

In the single solutions, the retention sequences of the five anions and two cations are $\text{Cl}^- < \text{Ac}^- < \text{Pr}^- < \text{Bu}^- < \text{SO}_4^{2-}$ and $\text{Na}^+ < \text{Ca}^{2+}$ respectively. Then, in the mixed solutions, it is observed that the permeate proportions of the more retained co-ions (anions or cations, i.e., SO_4^{2-} among $\text{VFAs}^- / \text{SO}_4^{2-}$, VFAs^- among $\text{Cl}^- / \text{VFAs}^-$, and Ca^{2+} among $\text{Na}^+ / \text{Ca}^{2+}$) decrease while the permeate proportions of less retained co-ions (anions or cations, i.e., VFAs^- among $\text{VFAs}^- / \text{SO}_4^{2-}$, Cl^- among $\text{Cl}^- / \text{VFAs}^-$, and Na^+ among $\text{Na}^+ / \text{Ca}^{2+}$) increase compared to their proportions in the feed. This observation extended the general trend of co-ions competition observed for VFAs mixed solutions.

For all the systems investigated ($\text{VFAs} + \text{Na}_2\text{SO}_4$, $\text{VFAs} + \text{NaCl}$, and $\text{NaVFAs} + \text{CaCl}_2$), for a given proportion in the feed, a fixed proportion in the permeate is observed, when the filtration flux is higher than a certain value. This observation applies to both anions and cations.

The proportion of each ion in the feed strongly influences its proportion in the permeate. The proportion of one given ion in the permeate increases when its proportion in the feed increases, for all the ions investigated.

With the presence of Ca^{2+} , the proportion of Cl^- in the permeate is slightly lower than the proportion of Cl^- in the permeate with Na^+ as only counter-ion, indicating that the presence of Ca^{2+} slightly reduced the co-ions competition between VFAs^- and Cl^- . This observation needs further investigation.

It is observed that the relative proportions of any couples of solutes in the permeate are nearly only depended on their relative proportions in the feed. The mass transfer investigation suggests that a complex mixed solution can be separated into various couples of solutes, the individual solute transfer is controlled by the combined solutes transfer, and does not influenced by the transfer of other co-ions.

The separation factors between Ac/Pr, Pr/Bu, and Ac/Bu for VFAs, VFAs+ Na_2SO_4 , VFAs+ NaCl , and $\text{NaVFAs}+\text{CaCl}_2$ are given. On the contrary to what observed with mixed solution with uncharged and charged solutes, the addition of both co-ions (anions) and counter-ions (cations) does not have a significant influence on the separation factors between VFAs.

V.

Chapter V
Influence of the pH on the retention of
VFAs

This chapter investigated the retention of VFAs with different compositions at different pH, aim to figure out the variation of charge interaction between VFA and membrane.

Chapters III and IV give the influence of solution composition on the retentions of VFAs at pH 8, when the solutes and membrane are both negatively charged. From the knowledge in Chapter I, it is known that the pH of the solution can significantly influence the retention of VFAs, due to the change in the membrane charge and solutes dissociation.

On the one hand, the fraction of dissociated VFAs in the solution is depending on the pK_a values of each solute and the solution pH. The retention of undissociated VFAs is mainly due to size effect, and the retention of dissociated VFAs could be due to both size and charge effect when the membrane is also charged. The influence of solution pH changes the fraction of dissociated VFAs and then changes the VFAs retention.

On the other hand, the membrane charge is mainly fixed by the dissociation of functional groups on the membrane surface, and the fraction of dissociated functional groups on the membrane determines the membrane charge density. Solution pH can also change the fraction of dissociated functional groups on the membrane.

Therefore, the retention of VFAs versus solution pH is related to the dissociation of both solutes and membrane functional groups.

In this chapter, the influence of solution pH on the retention of individual and global retention (i.e. the weighted average of all the individual solutes retentions in the mixture) of VFAs in single and mixed solutions is investigated. Retentions and global retentions of VFAs in single and mixed solutions respectively with different total concentrations are measured and calculated respectively. The influence of solution pH on solutes dissociation and membrane charge is discussed based on the assumption that the dissociated and undissociated VFAs transfer through the membrane separately. The impact of ionic concentration is taken into account, and the influence of solution pH on solute charge as well as membrane charge is explored.

All the results discussed in this chapter are obtained using NF-45 membrane.

Equations used in the investigation:

The total concentration of VFAs in the feed and permeate are given in Eq. (V.1) and Eq. (V.2).

$$C_f^{VFAs} = \sum_{i=1}^n C_i^f \quad (V.1)$$

$$C_p^{VFAs} = \sum_{i=1}^n C_i^p \quad (V.2)$$

C_i^f and C_i^p represent the concentration of individual VFA i in the feed and permeate solution respectively.

Then the global retention of VFAs, is defined in Eq. (V.3).

$$R_{glo}^{VFAs} = 1 - \frac{C_{VFAs}^p}{C_{VFAs}^f} = 1 - \frac{\sum_{i=1}^n C_i^p}{\sum_{i=1}^n C_i^f} \quad (V.3)$$

Eq. (V.3) can be rewritten as the weighted average of individual VFAs retentions, considering the proportion of individual solute in the mixed solution,

$$R_{glo}^{VFAs} = \sum_{i=1}^n P_i^f R_i^{mix} \quad (V.4)$$

In Eq. (V.4), R_i^{mix} is the retention of individual VFA i in the mixed solution, P_i^f is the proportion of individual VFA i in the feed solution, and the sum of the proportions of individual VFA i in the feed is 1.

$$\sum_{i=1}^n P_i^f = 1 \quad (V.5)$$

The fraction of dissociated VFAs in the single solution is given in Eq. (V.6).

$$P_{VFAs^-}^{sgl} = \frac{10^{pH-pK_{ai}}}{1+10^{pH-pK_{ai}}} \quad (V.6)$$

With pK_{ai} represent the pK_a value of individual VFA i . i represent Ac, Pr, or Bu.

For a mixed solution, the total proportion of dissociated VFAs, $P_{VFAs^-}^{mix}$, is the weighted average of individual proportions of dissociated VFAs, shown in Eq. (V.7).

$$P_{VFAs^-}^{mix} = \sum_{i=1}^n (P_i^f \times \frac{10^{pH-pK_{ai}}}{1+10^{pH-pK_{ai}}}) \quad (V.7)$$

P_i^f represent the proportion of individual VFA i with pK_{ai} in the feed solution. i represent Ac, Pr, or Bu.

For mixed solutions, one average pK_a value, $pK_{a_{av}}$, can be determined using the following equation, Eq. (V.8).

$$P_{VFAs^-}^{mix} \approx \frac{10^{pH-pK_{a_{av}}}}{1+10^{pH-pK_{a_{av}}}} \quad (V.8)$$

V.1 Solutes retentions in single and mixed solutions

V.1.1 VFAs retentions in single solutions

Retentions of acetate/acetic acid (Ac), propionate/propionic acid (Pr), and butyrate/butyric acid (Bu) at different solution pH and three concentrations are plotted versus filtration flux in Figure V-1 and Figure V-2. The curves are fitted according to the model proposed by J. M. K. Timmer et al. [143], and the solute retention at a given filtration flux is calculated from the fitted equation as explained in Chapter II. Retentions at $J_1=0.2\times 10^{-5} \text{ m}\cdot\text{s}^{-1}$, $J_2=0.5\times 10^{-5} \text{ m}\cdot\text{s}^{-1}$, $J_3=1\times 10^{-5} \text{ m}\cdot\text{s}^{-1}$, and $J_4=1.5\times 10^{-5} \text{ m}\cdot\text{s}^{-1}$ are obtained from the fitting curves for different concentrations. For 500mM, only J_1 is shown since the other filtration flux are not in the experimental range.

For any condition, one can observe that the retentions of VFAs increase with the filtration flux. Then, at given filtration flux, the retentions of the three VFAs increase when the solution pH increases. The lowest retentions of Ac and Pr are observed at pH 3. The experimental results of the retention of Bu at pH 3 are obtained. Meanwhile, the VFAs retention at pH 3 seems not influenced by concentration, retentions of Ac at 100mM and 500mM are similar, which is 2% at the filtration flux of J_3 . The same observation is found for the retention of Pr. The retentions of Pr at the two concentrations (100mM and 500mM) and filtration flux of J_3 is 4%. The highest retentions of the three VFAs are observed at pH 8. Moreover, the retention at high pH are more concentration-dependent. It is observed that the retentions of VFAs decrease when the concentration increases. For instance, the retentions of Ac at three concentrations (100mM, 200mM, and 500mM) are 65%, 59%, and 38% respectively for a filtration flux of J_1 ($0.2\times 10^{-5} \text{ m}\cdot\text{s}^{-1}$).

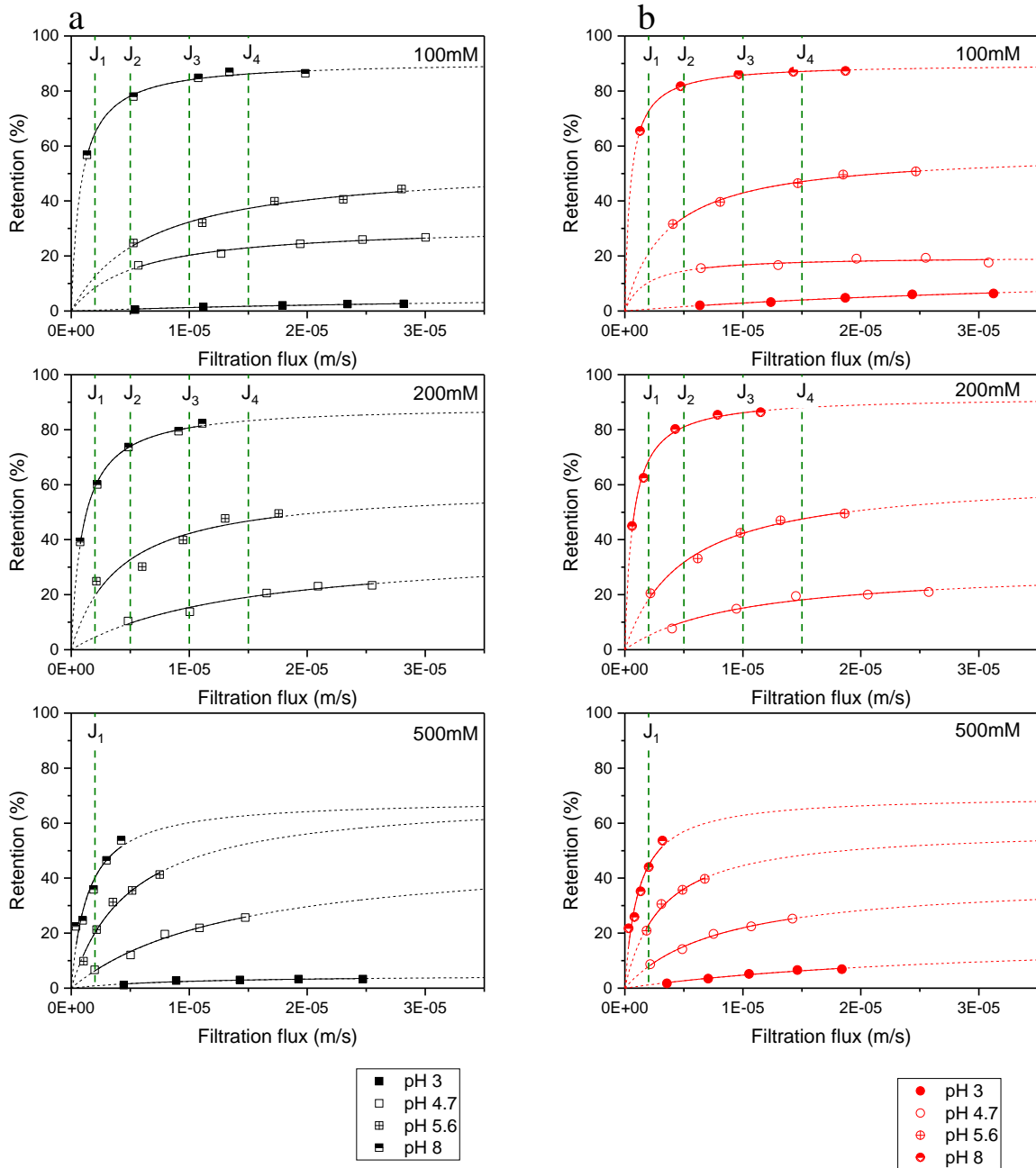


Figure V-1 Retentions of (a) Ac, and (b) Pr in single solutions, versus filtration flux at different solution pH and varying total concentration, using NF-45 membrane. Retentions at $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, and $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$ are compared, for 500mM, only J_1 is in the experimental range.

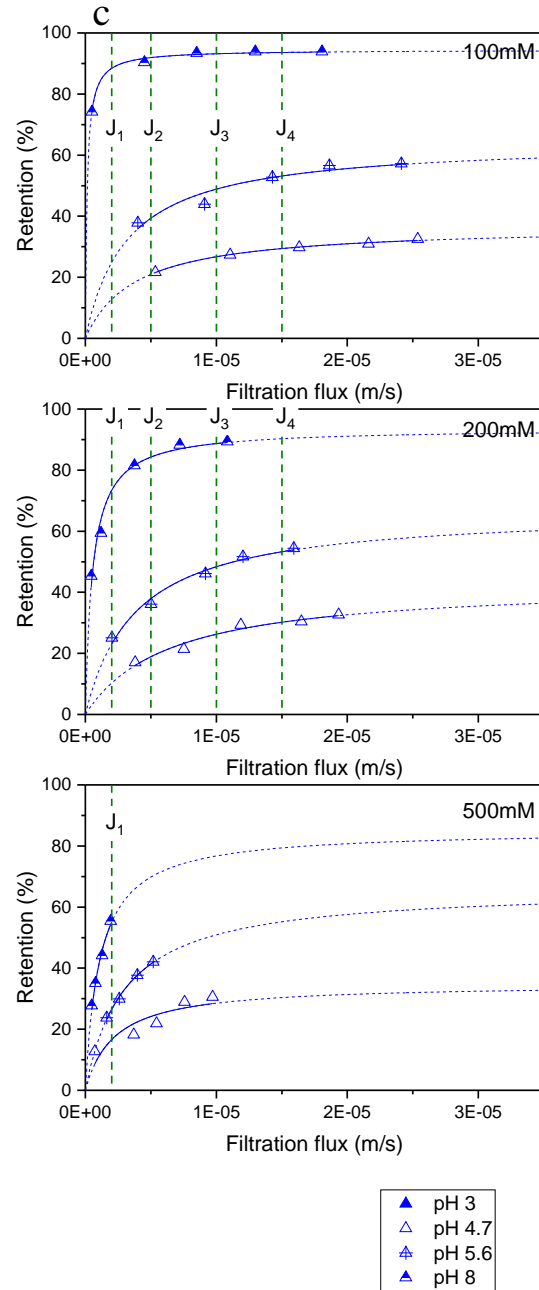


Figure V-2 Retentions of Bu in single solutions, versus filtration flux at different solution pH and varying total concentration, using NF-45 membrane. Retentions at $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, and $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$ are compared, for 500mM, only J_1 is in the experimental range.

The retention mechanism of VFAs by NF membrane is a combination of size and charge effect. At pH 3, VFAs are uncharged, and the retention is mainly due to size effect. Since VFAs have much lower MWs than the MWCO of the membrane, low retention is expected. In addition, it is known that the influence of concentration on the retention of a neutral solute is negligible, as reported for glucose solutions for instance both in single [104,139] and mixed (glucose/xylose) solutions [153]. Then the concentration is expected to have a negligible influence on the retention of VFAs at pH 3, as observed. On the contrary, at pH 8, both the VFAs and the membrane are charged, and the charge effect plays an important role in VFAs retention. Indeed, much higher retentions than those obtained at pH 3 are observed, and the retentions increase with solution pH from 3 to 8. Similar results were also reported in previous works investigating the retention of weak acids [128,146,164,169]. Furthermore, when the concentration of VFAs increases, the ionic strength of the solution increases, and then the charge interactions between membrane and VFAs are weakened. This is reported as a screening effect [128,139], according to which the retention is expected to decrease with the concentration, as observed.

The retentions of Ac, Pr, and Bu at given filtration flux (J_1 , J_2 , J_3 , and J_4) versus solution pH for the three concentrations are plotted in Figure V-3 and Figure V-4. The fitting curves of solutes retentions versus pH are obtained from sigmoid curve fitting by Origin software. The dissociation curves of Ac, Pr, and Bu (obtained from Eq. 5.6) are also plotted as references. For the concentration of 500mM, the filtration flux is much lower than that at lower concentrations, then only the retentions at J_1 are shown.

One can observe that the increase of the individual VFA retentions versus the solution pH follows a sigmoid curve, for the four filtration flux investigated. The different curves are obtained according to the filtration flux, for a given pH, the retention increases for increasing filtration flux. Moreover, the retention follows the dissociation curve.

These results are in agreement with previous ones obtained with other weak acid, e.g. succinic acid, for which it was reported that, for different filtration flux, the retention increases with the solution pH following the fraction of the divalent form (Suc^{2-}) [128].

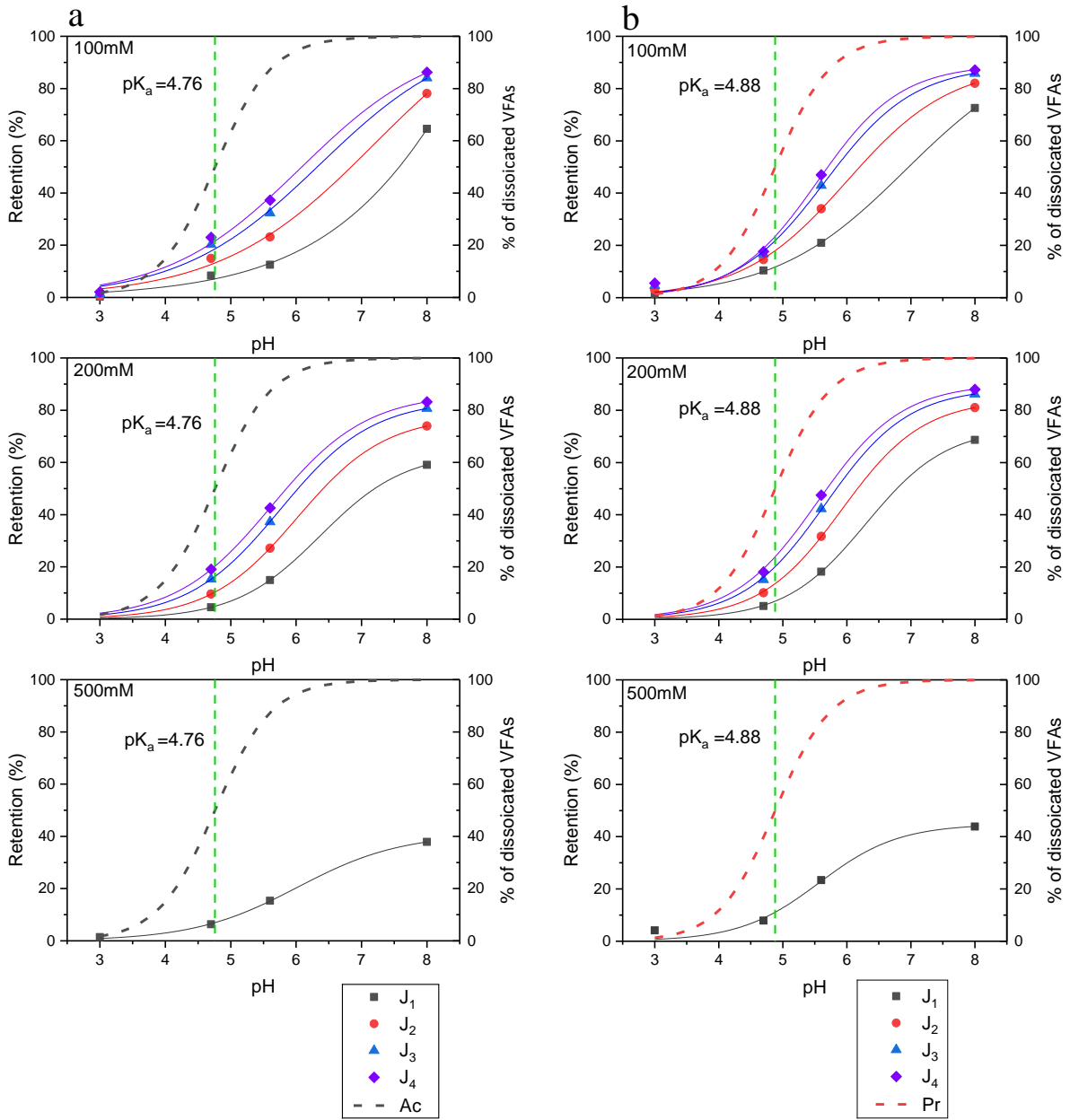


Figure V-3 Retentions of (a) Ac and (b) Pr in single solutions, at given filtration flux versus solution pH for three concentrations, using NF-45 membrane. $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$, for 500mM, only J_1 is in the experimental range. The dissociation curves of Ac and Pr are given as references and the pK_a of each VFA is marked in the figure.

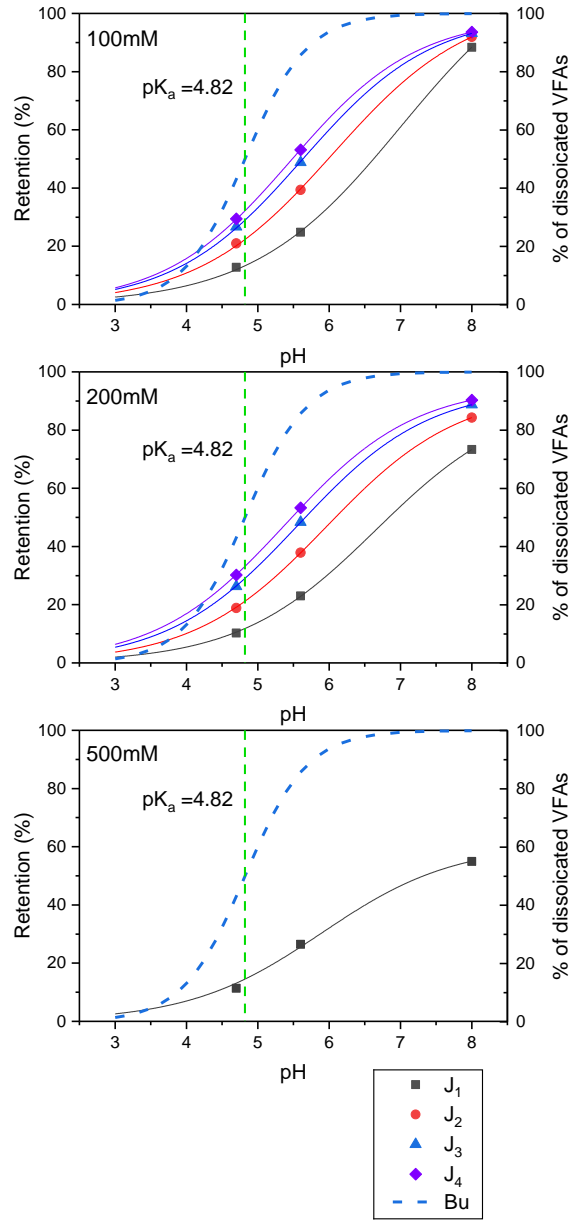


Figure V-4 Retentions of Bu in single solutions, at given filtration flux versus solution pH for three concentrations, using NF-45 membrane. $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$, for 500mM, only J_1 is in the experimental range. The dissociation curve of Bu is given as reference and the pK_a of Bu is marked in the figure.

V.1.2 Individual VFAs retentions in mixed solutions

The retentions of individual Ac, Pr, and Bu in ternary solutions (s6, Ac: Pr: Bu = 33%: 33%: 33%) at given filtration flux (J_1 , $0.2 \times 10^{-5} \text{ m.s}^{-1}$) and three total concentrations are plotted versus solution pH in Figure V-5. The retentions of VFAs in single solutions at the same concentration and filtration flux are also given as references. The individual VFAs retentions obtained at different pH values versus filtration flux, and individual VFAs retentions versus pH obtained for the other three filtration flux values (J_2 , J_3 , and J_4) show similar behavior at that observed at J_1 , those results are not shown.

As observed for single solutions, the individual VFAs retentions in mixed solutions increase with pH following an S-shape curve. An exception is observed for the retention of Ac at the highest concentration (500 mM), that firstly increases with the pH, reaches a maximum at pH 6.6, and decreases when the pH increases to 8. At low pH values, the individual VFAs retentions in the mixed solutions are similar to those in single solutions at the same concentration. But, at high pH value (pH 8), the individual VFAs retentions in single and mixed solutions are different. In the mixed solution, the retention of the most retained VFA, Bu, is similar to that in the single solution while the retention of the least retained VFA, Ac, is lower than in the single solution and that of the intermediately retained VFA, Pr, nearly unchanged between single and mixed solutions. Then the retention differences between VFAs in the mixed solutions are larger compared to those in single solutions, especially at high concentration. Furthermore, one can observe that the retentions of individual VFAs follow the same sequence (Ac<Pr<Bu) for the three total concentrations and whatever the solution pH between 3 and 8.

Retention of VFAs at low pH are mainly fixed by size effect, then the co-existence of other VFAs does not influence the individual VFAs retentions in the mixed solutions. Then, similar retentions are expected for single and mixed solutions, as observed. When the pH increases, the contribution of charge effect gradually increases due to both the increase of the percentage of dissociated VFAs in the solution and the increase of membrane charge. At high pH values, VFAs are dissociated, and the retention of VFAs are dominated by charge effect. Then, higher retention at high pH values compared to low pH values is observed.

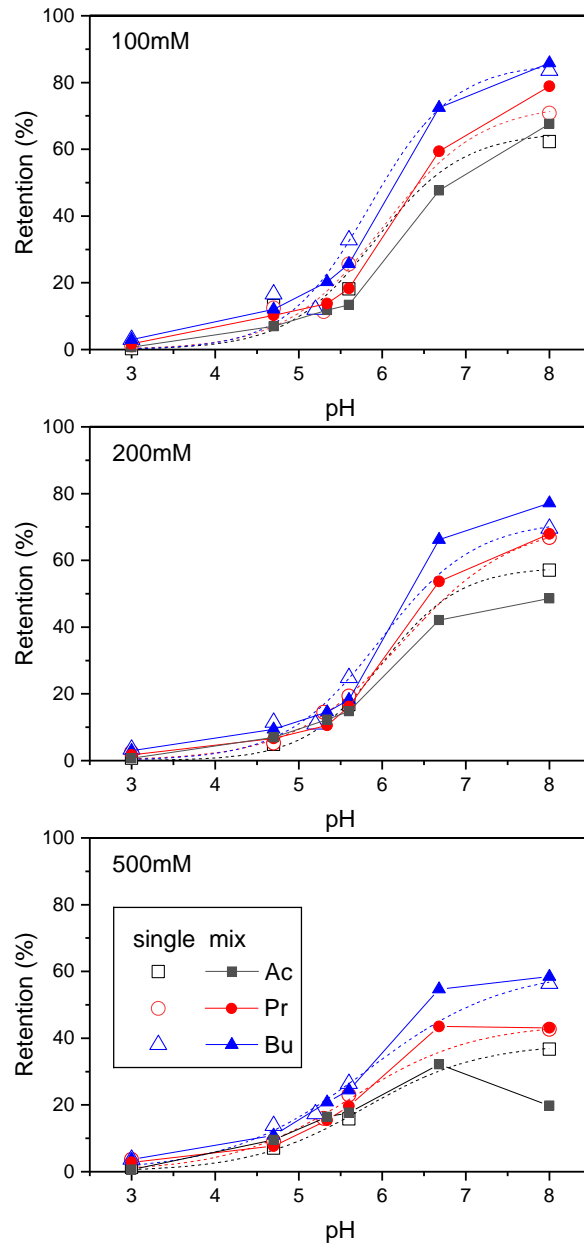


Figure V-5 Individual VFAs retentions in Ac/Pr/Bu ternary mixture with three concentrations versus solution pH at a filtration flux of $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, using NF-45 membrane.

The proportions of individual VFAs in the permeate versus filtration flux for ternary solutions (Ac:Pr:Bu=33%:33%:33%) at three concentrations (100, 200, 500mM) and various solution pH values are given in Figure V-6.

For all the pH investigated, it seems that the proportion of Ac in the permeate increases when the filtration flux increases, reaches a plateau when the filtration flux is higher than a certain value. On the contrary, the proportion of Bu in the permeate decreases and reaches a plateau value when the filtration flux is higher than a certain value. Furthermore, the filtration flux required to reach the plateau value for different pH is not the same, the lower the solution pH, the higher the filtration flux required to reach the plateau value. As observed in Chapter III, the permeate proportion of given solute at given solution pH does not change with the total concentration.

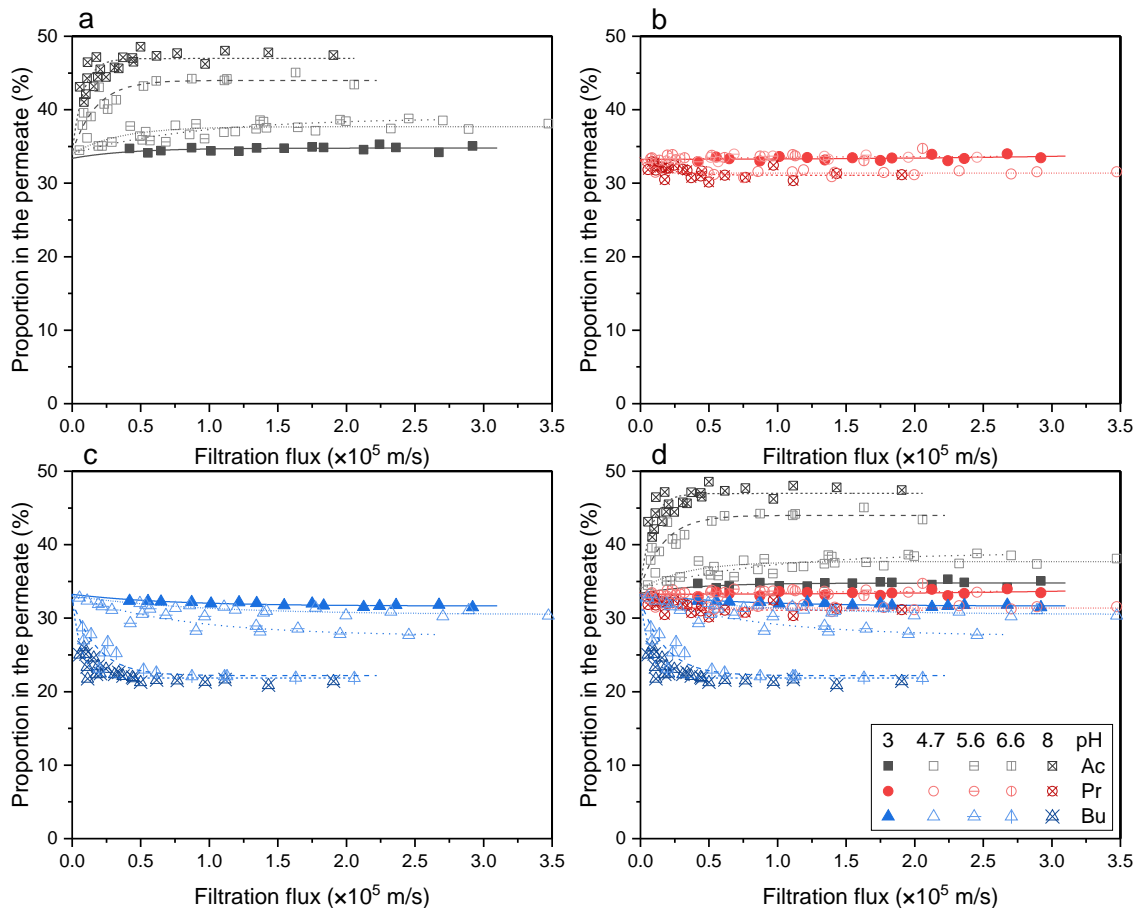


Figure V-6 Individual solutes proportions in the permeate versus filtration flux for ternary solutions (Ac:Pr:Bu=33%:33%:33%) at all the concentrations and various solution pH, using NF-45 membrane. (a) Proportion of Ac, (b) Proportion of Pr, (c) Proportion of Bu, (d) Proportions of the three VFAs.

One can observe that, when the solution pH increases from 3 to 8, the proportion of Ac in the permeate gradually increases from 35% at pH 3, to 47% at pH 8 (Figure V-6a). On the contrary, the proportion of Bu in the permeate continuously decreases from 32% at pH 3 to 22% at pH 8 (Figure V-6c). The proportion of Pr in the permeate is not significantly influenced by solution pH, it decreases slightly from 34% at pH 3 to 31% at pH 8 (Figure V-6b).

The proportions in binary and ternary solutions are not the same and difficult to compare. However, as observed in Chapter IV, the relative proportions of one couple of VFAs in the permeate are dependent to their relative proportion in the feed and not influenced by the presence of other solutes. Considering the relative proportion, the relative proportions in ternary solution with identical proportions are the same as that in binary solutions. Then it could be interesting to compare the relative proportions as three couples of VFAs in ternary solutions with the proportions in binary solutions.

The relative proportions of VFAs for the couples of Ac/Pr, Pr/Bu, and Ac/Bu at different solution pH can be obtained using Eqs. (II.5), (II.6), (II.7), and (II.8) (see Chapter II), and the results versus filtration flux are given in Figure V-7, Figure V-8, and Figure V-9.

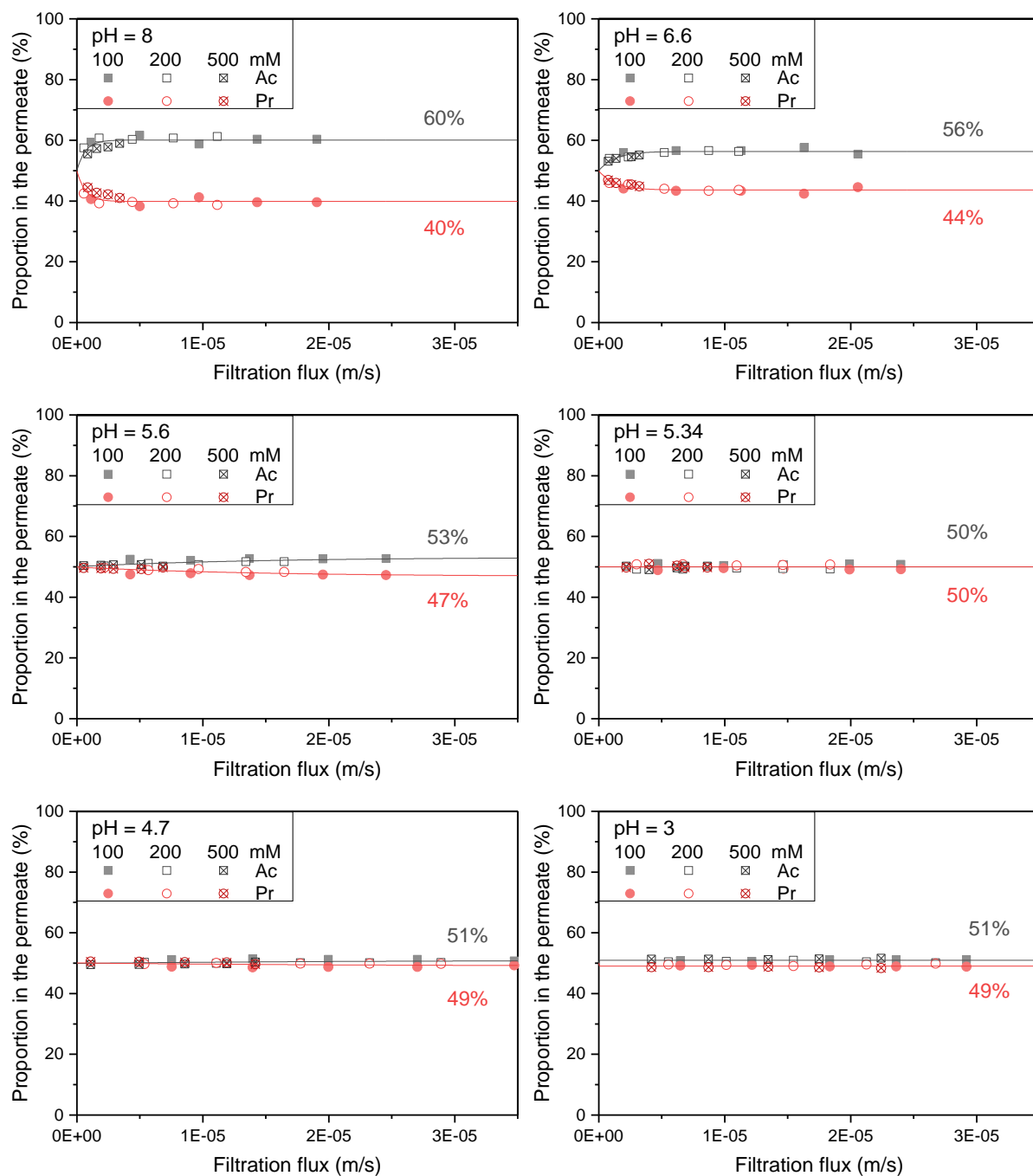


Figure V-7 Relative proportions of Ac and Pr for the couple of Ac/Pr in ternary solutions (Ac:Pr:Bu=33%:33%:33%) at all the concentrations and various solution pH from 3 to 8, using NF-45 membrane.

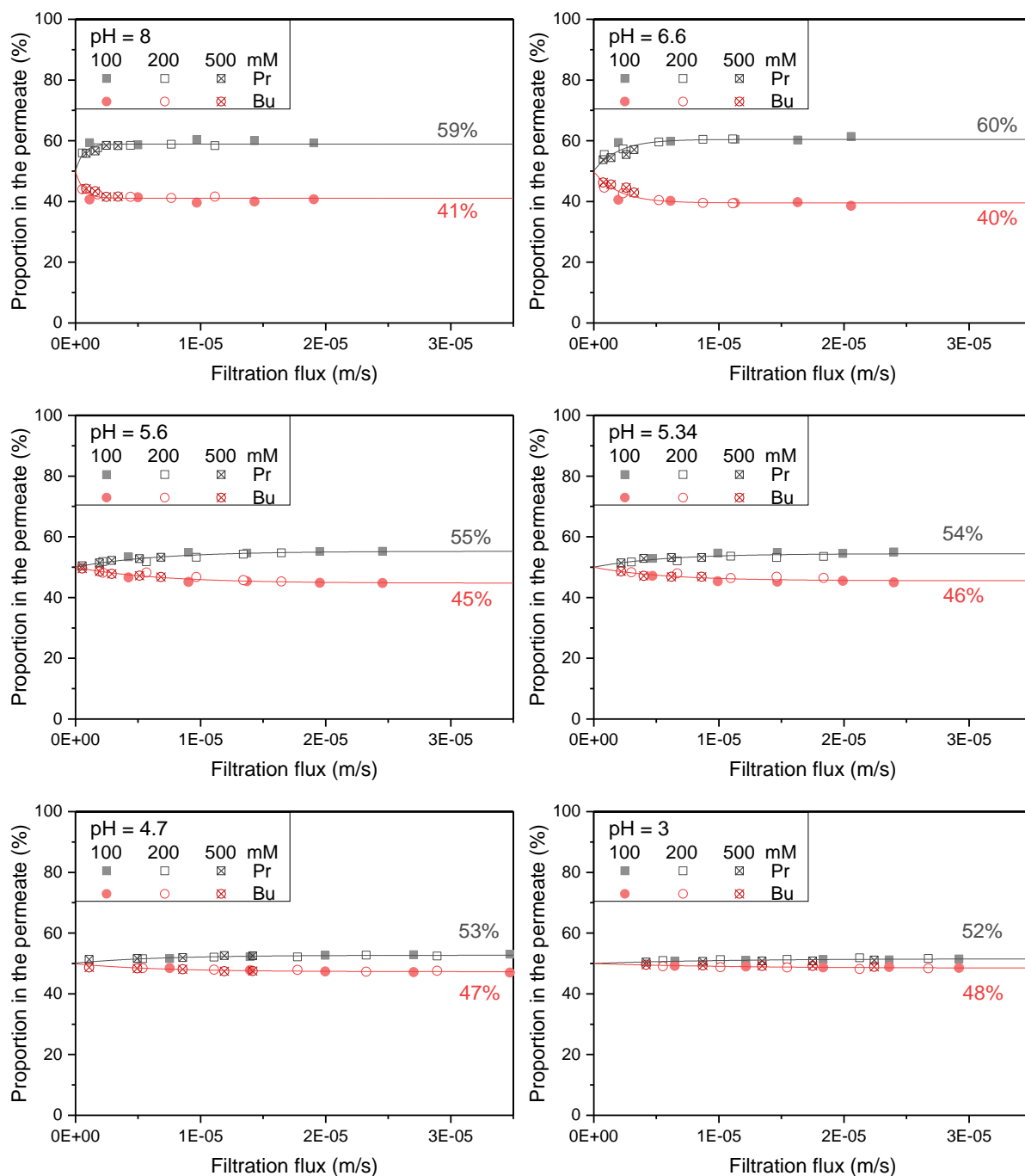


Figure V-8 Relative proportions of Pr and Bu for the couple of Pr/Bu in ternary solutions (Ac:Pr:Bu=33%:33%:33%) at all the concentrations and various solution pH from 3 to 8, using NF-45 membrane.

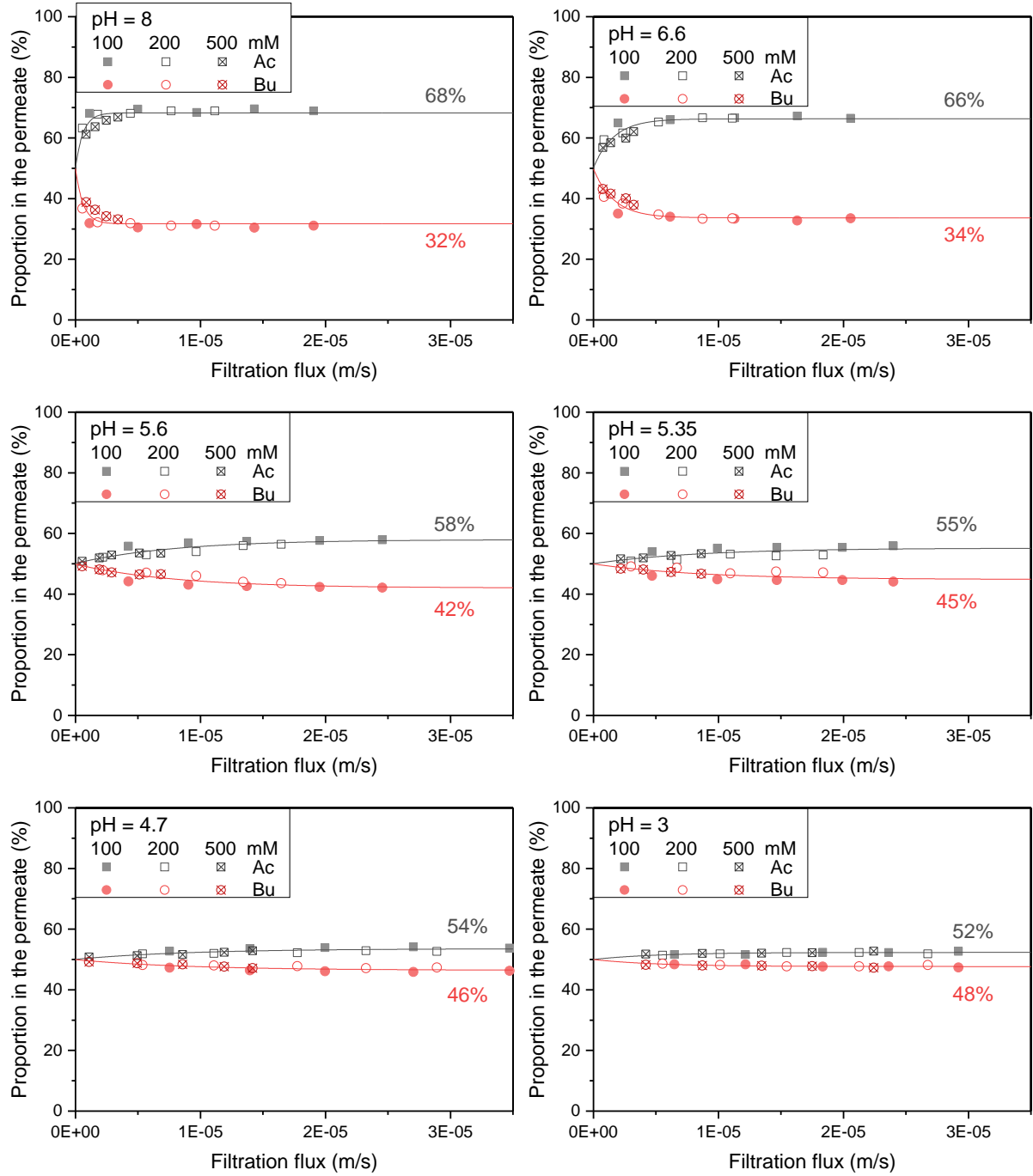


Figure V-9 Relative proportions of Ac and Bu for the couple of Ac/Bu in ternary solutions (Ac:Pr:Bu=33%:33%:33%) at all the concentrations and various solution pH from 3 to 8, using NF-45 membrane.

One can observe that, as the solution pH increases from 3 to 8, the proportion of Ac for the couples of Ac/Pr and Ac/Bu increases gradually, while the proportion of Bu for the couples of Pr/Bu and Ac/Bu decreases continuously. For Pr, its permeate proportion decreases with the pH for the couple of Ac/Pr, while increases with the pH for the couple of Pr/Bu.

Similar observation is found for binary solutions of Ac/Pr (Figure V-10), Pr/Bu (Figure V-11), and Ac/Bu (Figure V-12).

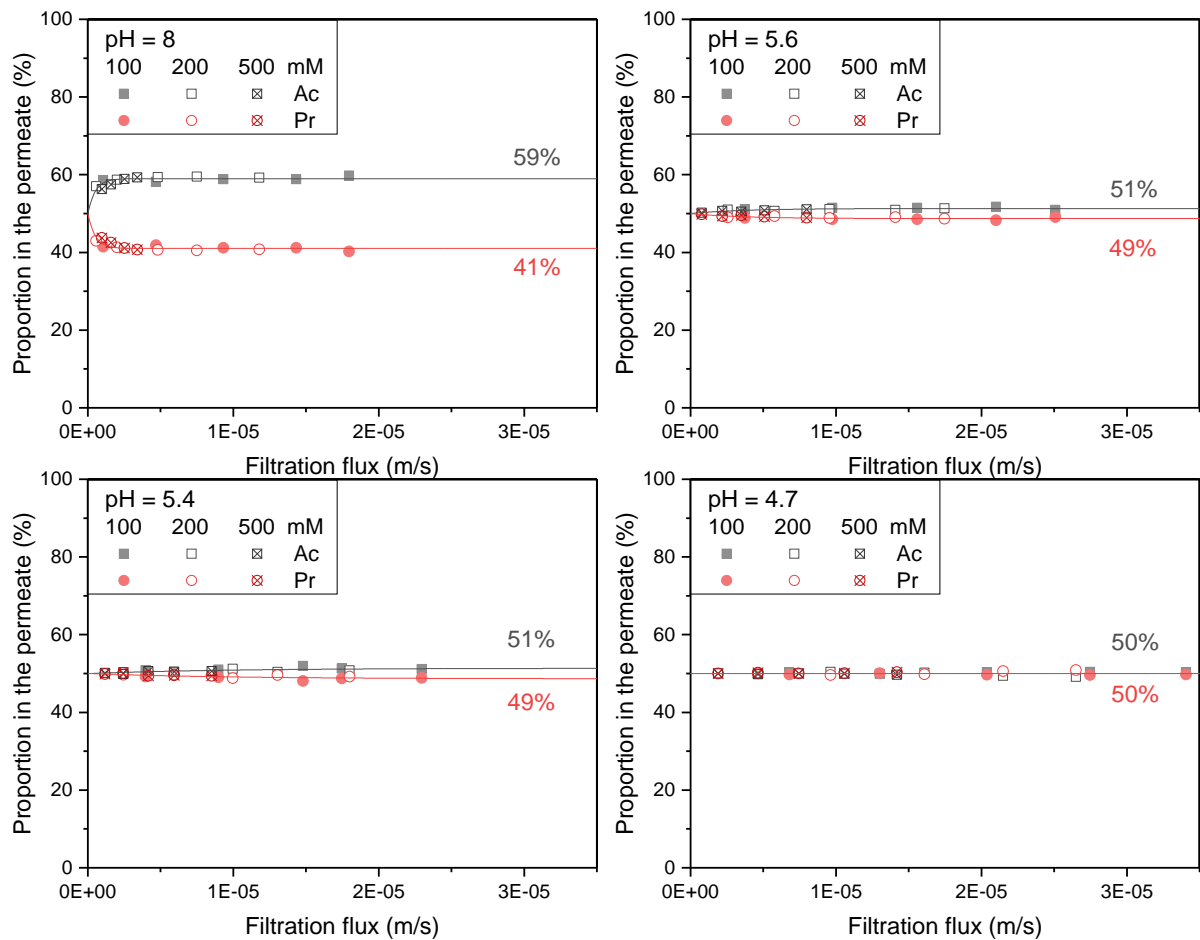


Figure V-10 Individual solutes proportions in the permeate versus filtration flux for Ac/Pr binary solutions (Ac:Pr =33%:33%:33%) at all the concentrations and various solution pH, using NF-45 membrane.

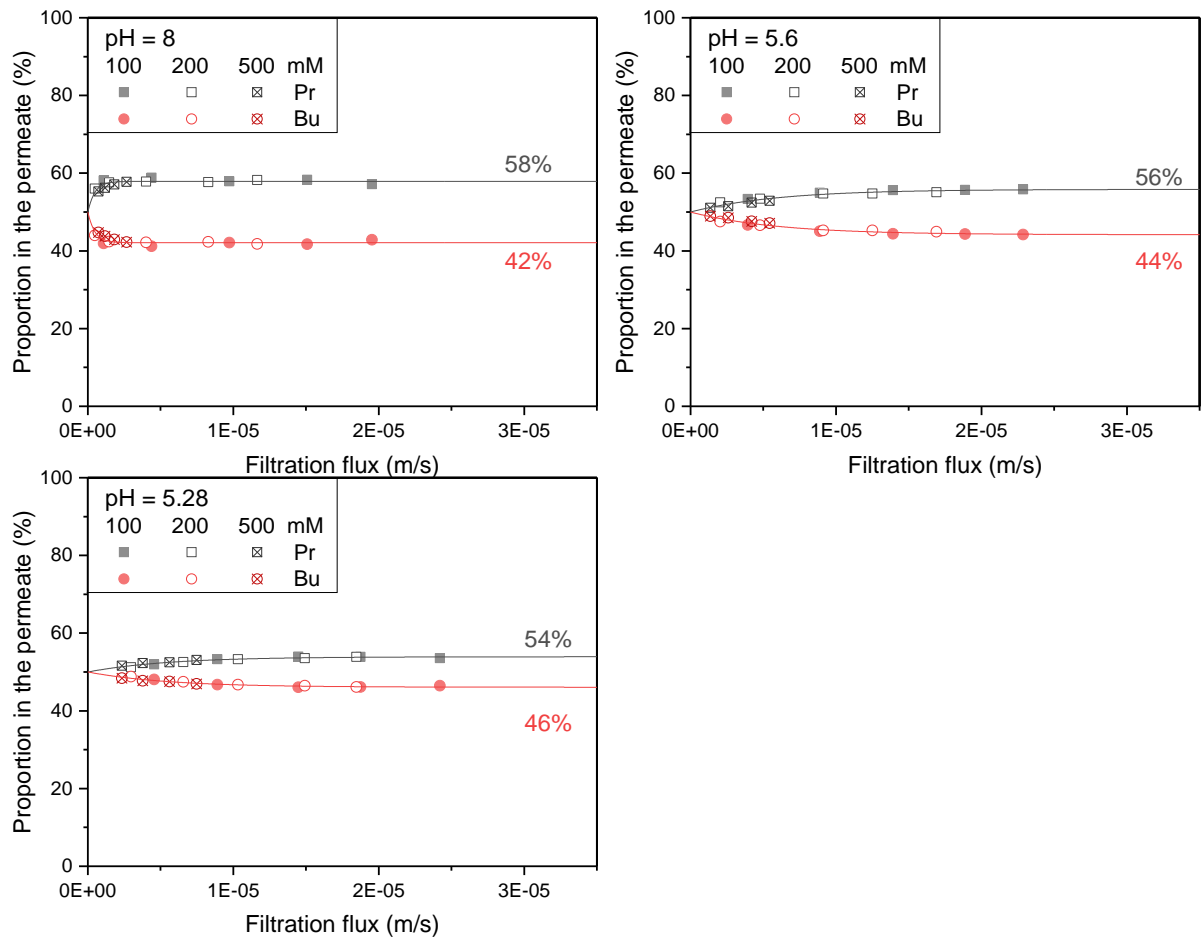


Figure V-11 Individual solutes proportions in the permeate versus filtration flux for Pr/Bu binary solutions (Pr:Bu =33%:33%:33%) at all the concentrations and various solution pH, using NF-45 membrane.

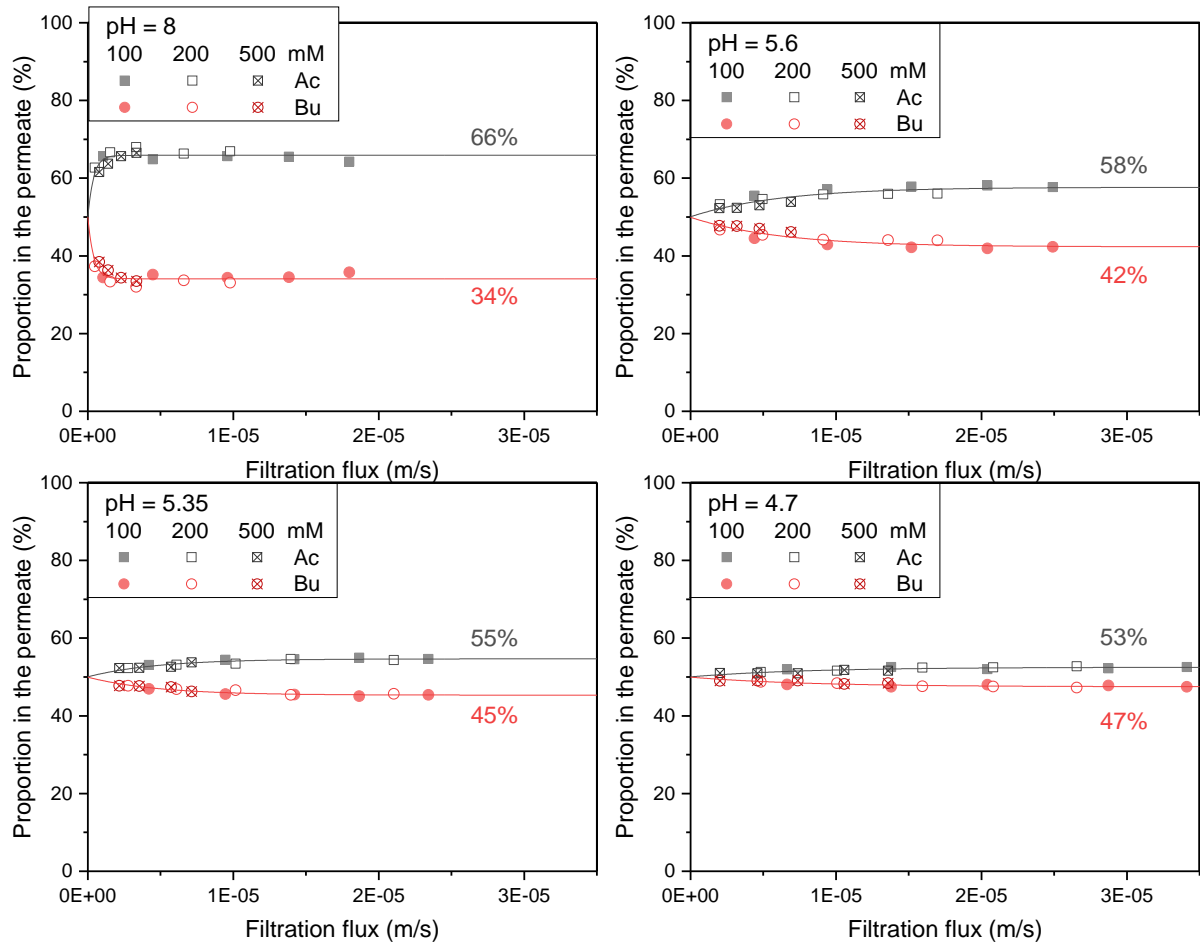


Figure V-12 Individual solutes proportions in the permeate versus filtration flux for Ac/Bu binary solutions (Ac:Bu =33%:33%:33%) at all the concentrations and various solution pH, using NF-45 membrane.

Figure V-13 compares the relative proportions (at the plateau value) of Ac, Pr, and Bu in the permeate for binary and ternary solutions at different solution pH. It is shown that the relative proportions of VFAs in binary and ternary solutions are nearly the same. Then, as the solution pH increase, the relative proportions of Ac for the couples of Ac/Pr and Ac/Bu increase from 51% and 52% to 60% and 68%, respectively. Meanwhile, the proportions of Bu for the couples of Pr/Bu and Ac/Bu decrease from about 48% at pH 3 to 40% and 32% respectively at pH 8. For Pr, its proportion decreases in the presence of Ac while increases in the presence of Bu. Besides, one can observe that the variation of the relative proportions of all VFAs in the permeate with solution pH follows a sigmoid curve, the higher the solution pH, the more significant the difference between the relative proportions of VFAs.

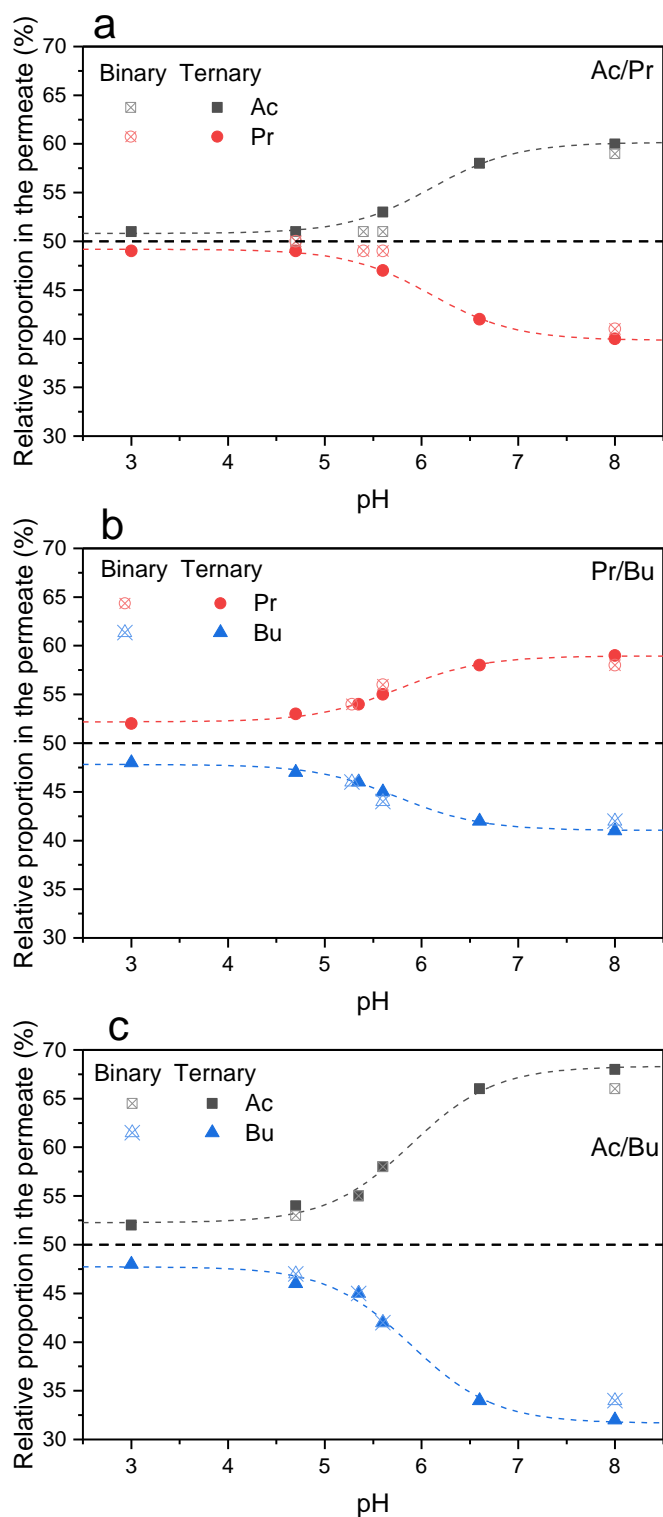


Figure V-13 Relative proportions of Ac, Pr, and Bu for the couples of (a) Ac/Pr, (b) Pr/Bu and (c) Ac/Bu, in the permeate versus solution pH in the binary (Ac:Pr=50%:50%, Pr:Bu=50%:50%, Ac:Bu=50%:50%) and ternary (Ac:Pr:Bu =33%:33%:33%) solutions, using NF-45 membrane.

It is clearly shown that the solution pH can significantly change the proportion of individual VFAs in the permeate. When the pH increases, the charge of membrane and VFAs both increases, leading to stronger co-ions competition, and then the differences between relative proportions of VFAs in the permeate increases.

The individual VFAs retentions in the mixed solutions are influenced by the presence of other VFAs, especially at high pH values. Thus, the variation of individual VFAs retentions versus solution pH in the mixed solutions are influenced by both solution pH and co-ions competition between VFAs. Therefore, the variation of individual solutes retentions in single and mixed solutions with solution pH are not the same.

V.1.3 Global retentions in mixed solutions

The previous discussion has shown that, due to the co-ions competition phenomenon, the variation of individual VFAs retentions in single and mixed solutions with solution pH are different. Global retention, which is defined as the weighted average of individual VFAs retentions in the mixed solution, is introduced into the discussion. Global retention of the mixed solution instead of individual ones at different solution pH is investigated.

The global retentions of VFAs in binary (s4, Ac: Pr = 50%:50%; s5, Ac: Bu = 50%:50%) and ternary (s6, Ac: Pr: Bu = 33%:33%:33%) solutions at different solution pH and total concentrations versus filtration flux are given in Figure V-4 and Figure V-15. The curves are fitted and the global retention at given filtration flux is calculated as that for single solutions (explained in Chapter II). Global retention of VFAs at $J_1=0.2\times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5\times 10^{-5} \text{ m.s}^{-1}$, $J_3=1\times 10^{-5} \text{ m.s}^{-1}$, and $J_4=1.5\times 10^{-5} \text{ m.s}^{-1}$ are obtained from the fitting curves for different total concentrations. As for single solutions, for 500mM, only the results at J_1 , are shown.

For all the mixed solutions, one can observe that the global retentions of VFAs increase with filtration flux. At a given filtration flux, the global retentions of VFAs in all the mixed solutions increases gradually when the solution pH increases.

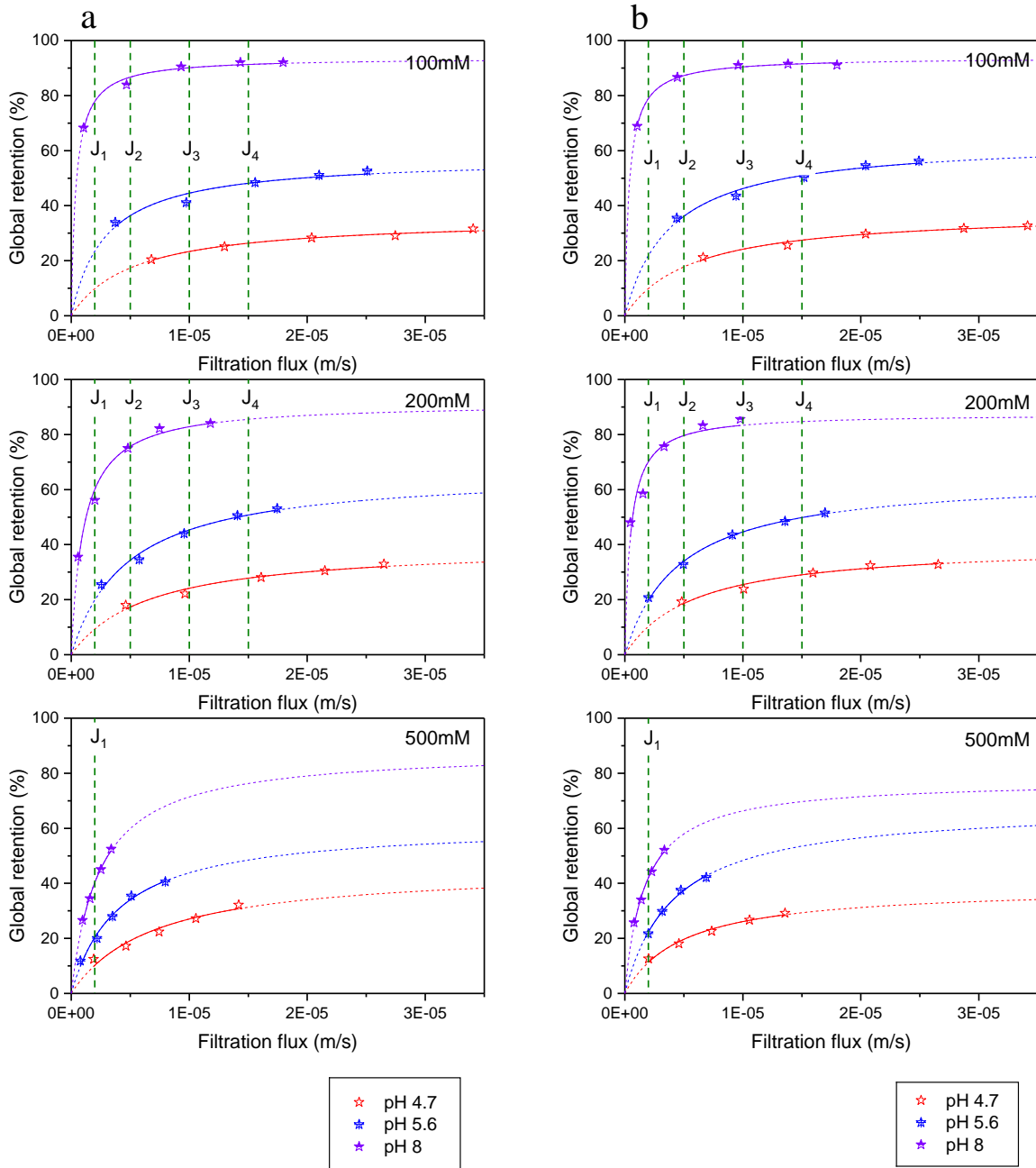


Figure V-14 Global retentions of VFAs in binary solutions (a) Ac/Pr and (b) Ac/Bu of varying total concentration versus filtration flux, using NF-45 membrane. Global retentions at $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, and $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$ are compared, for 500mM, only J_1 is in the experimental range.

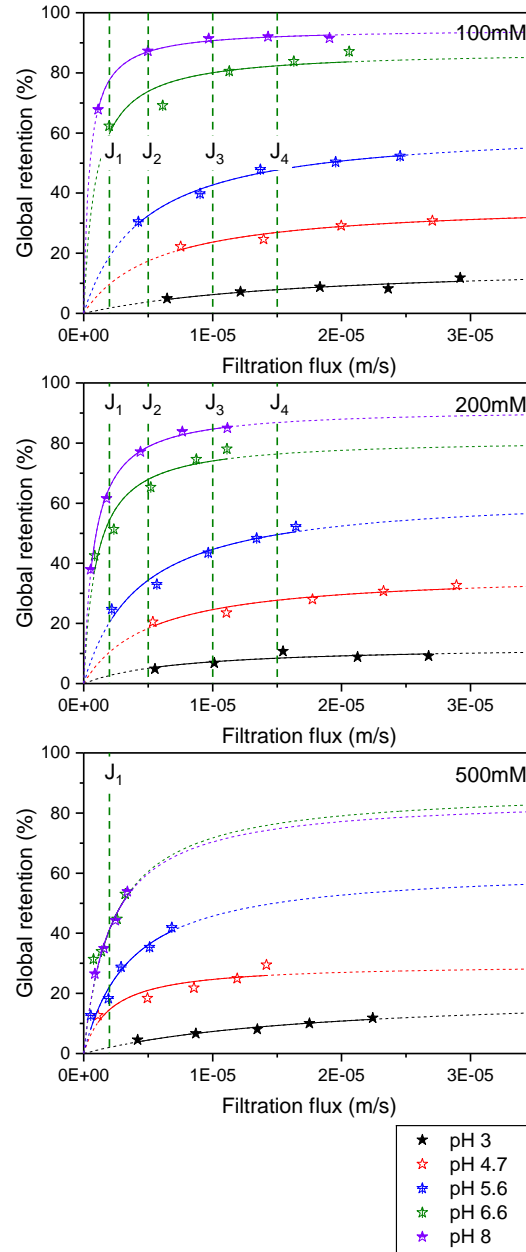


Figure V-15 Global retentions of VFAs in ternary solutions (Ac/Pr/Bu) of varying total concentration versus filtration flux, using NF-45 membrane. Global retentions at $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, and $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$ are compared, for 500mM, only J_1 is in the experimental range.

The global retentions of VFAs at given filtration flux (J_1 , J_2 , J_3 , and J_4) versus solution pH for the three total concentrations are plotted in Figure V-16 and Figure V-17. The percentage of the dissociated VFAs versus solution pH, obtained from Eq. (V.7), are also given accordingly for each figure as references.

For all the solutions and operating conditions investigated, the global retention of VFAs increases with solution pH following a sigmoid curve, from the lowest values obtained at pH 3 to the highest values at pH 8.

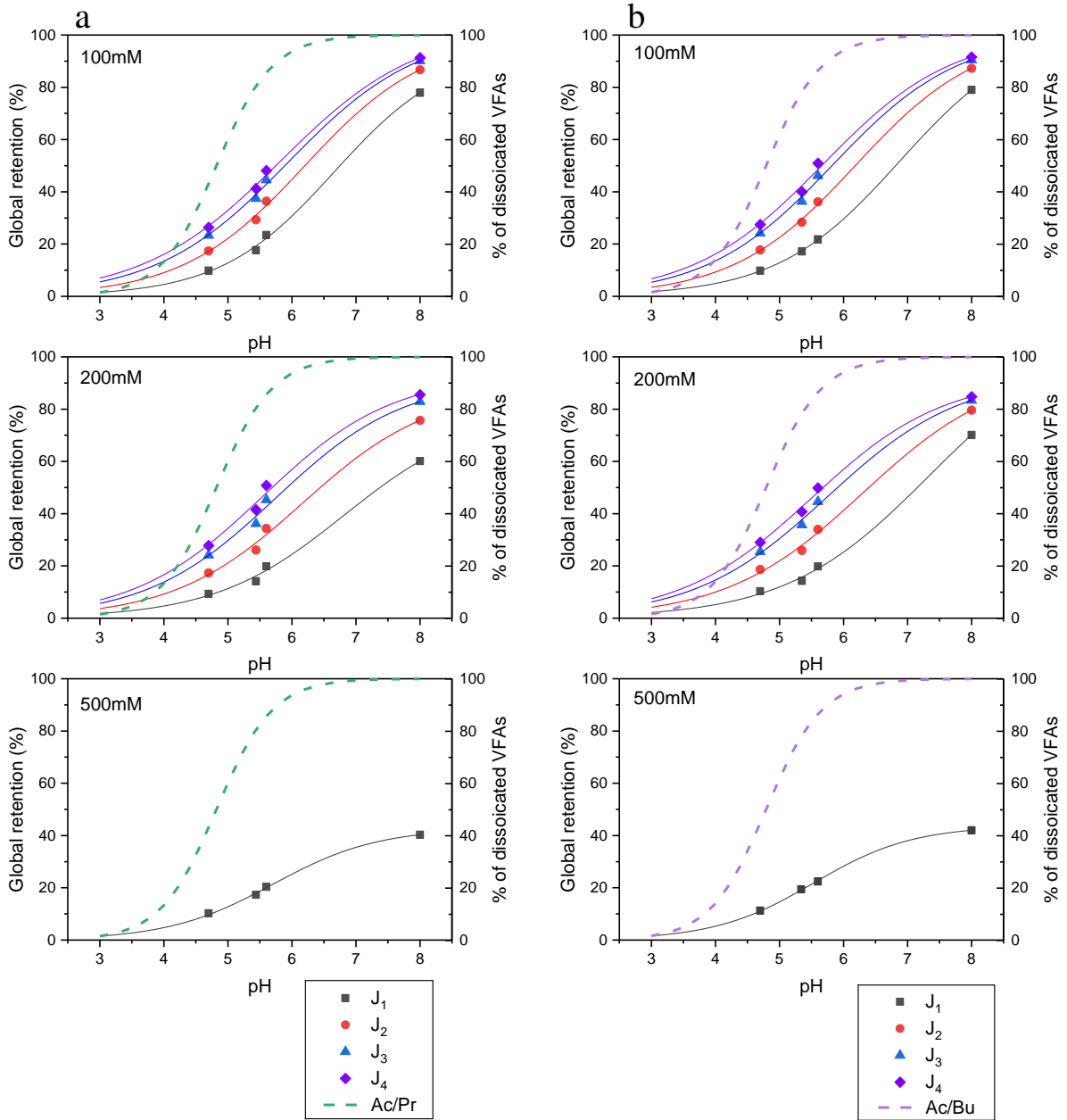


Figure V-16 Total VFAs retentions of VFAs in binary solutions (a) Ac/Pr (Ac: Pr =50%:50%) and (b) Ac/Bu (Ac: Bu =50%:50%) at given filtration flux versus solution pH for three total concentrations, using NF-45 membrane. The filtration flux $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$, for 500mM, only J_1 is in the experimental range. The fitting curves are obtained from sigmoid curve fitting. The percentage of the dissociation VFAs at each pH values are given as references.

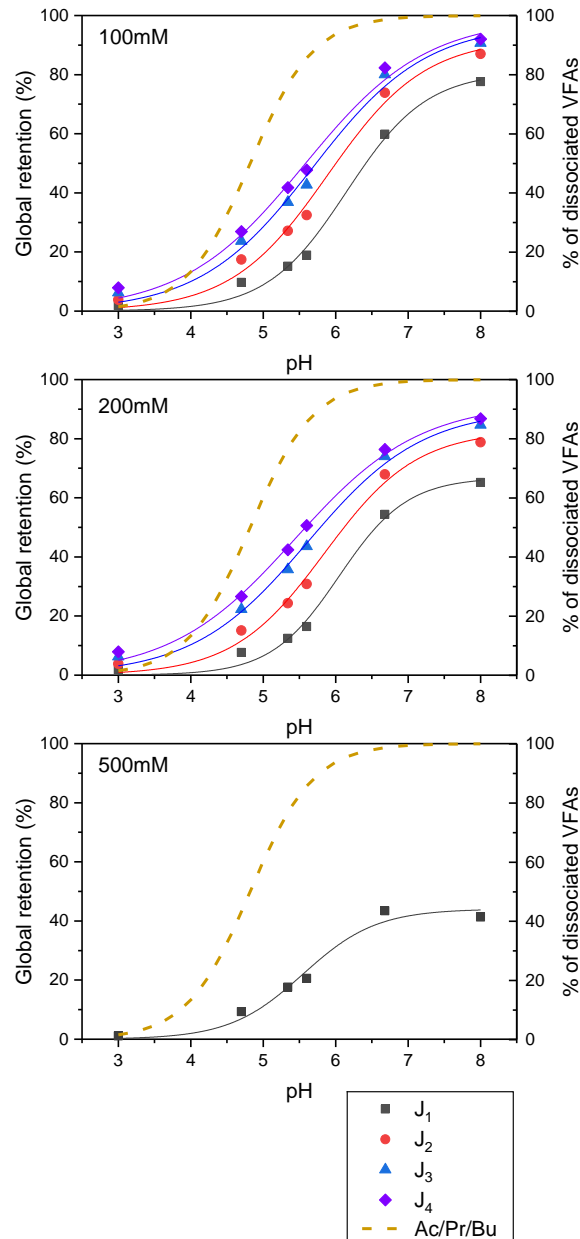


Figure V-17 Total VFAs retentions of VFAs in ternary solutions Ac/Pr/Bu (Ac: Pr: Bu=33%:33%:33%) at given filtration flux versus solution pH for three total concentrations, using NF-45 membrane. The filtration flux $J_1=0.2 \times 10^{-5} \text{ m.s}^{-1}$, $J_2=0.5 \times 10^{-5} \text{ m.s}^{-1}$, $J_3=1 \times 10^{-5} \text{ m.s}^{-1}$, $J_4=1.5 \times 10^{-5} \text{ m.s}^{-1}$, for 500mM, only J_1 is in the experimental range. The fitting curves are obtained from sigmoid curve fitting. The percentage of the dissociation VFAs at each pH values are given as references.

V.1.4 Influence of concentration on the retentions of VFAs in single and mixed solutions

Figure V-18 shows the retentions of VFAs in single solutions (Ac, Pr, and Bu) and the global retentions of VFAs in mixed solutions (Ac/Pr, Ac/Bu, and Ac/Pr/Bu) at a filtration flux of $0.2 \times 10^{-5} \text{ m.s}^{-1}$ and different solution pH as the function of VFAs concentration/total concentration. Same trends are obtained for individual retentions in single solutions and global retentions in mixed ones. One can observe that for the lowest pH values, the retention remains almost constant when the concentration increases. On the contrary, for the highest pH values, the retention decreases with the concentration.

It is known that the retentions of charged solutes decrease when the ionic concentration increases at neutral or alkaline conditions. This phenomenon is reported by many authors, and it is due to the screening effect [128,139]. When the solution pH decreases, the influence of concentration is less significant at low pH than at high pH. This phenomenon could be due to two factors.

On the one hand, for a lower pH value, only part of those weak acids are dissociated, then the ionic concentration is lower than the ionic concentration at high pH, and the influence is weaker. The concentration of dissociated VFAs in the solution, c_{VFAs^-} , which represent the ionic concentration of the solution, is given by Eq. (V.9).

$$c_{VFAs^-} = c_{VFAs} \times P_{VFAs^-} \quad (\text{V.9})$$

c_{VFAs} is the concentration of dissociated and undissociated VFAs in the solution, P_{VFAs^-} is the proportion of dissociated VFAs in the solution, which is obtained from Eqs. (V.6). It is shown that c_{VFAs^-} is pH-dependent, approximately equal to 0 at pH 3 while equivalent to c_{VFAs} at pH 8. Therefore, the influence of ionic concentration is nearly negligible at pH 3, increase when pH increase, and reaches the maximum at pH 8.

On the other hand, the membrane charge is also pH-dependent. It is generally believed that the negative membrane charge is lowest at IEP of the membrane (4.0 for NF-45 membrane). When the pH increases, the membrane is more negatively charged and the zeta potential which represent membrane charge reaches a plateau when pH higher than about 7 [201]. The weakened membrane charge could reduce the screening effect, and then the screening effect is more pronounced at high pH values. This phenomenon is proved by the nanofiltration of strong electrolyte solution, for which the dissociation of solute is negligible. In a report investigating the retention of KCl at different concentrations and solution pH, it was observed that the retention of KCl decreases with

the increasing KCl concentration at pH 9 and 7, then the influence of KCl concentration become nearly negligible when solution pH dropped to 5 [150].

For simplification, the latter discussions use VFAs retention to represent retention/global retention of VFAs in single and mixed solutions.

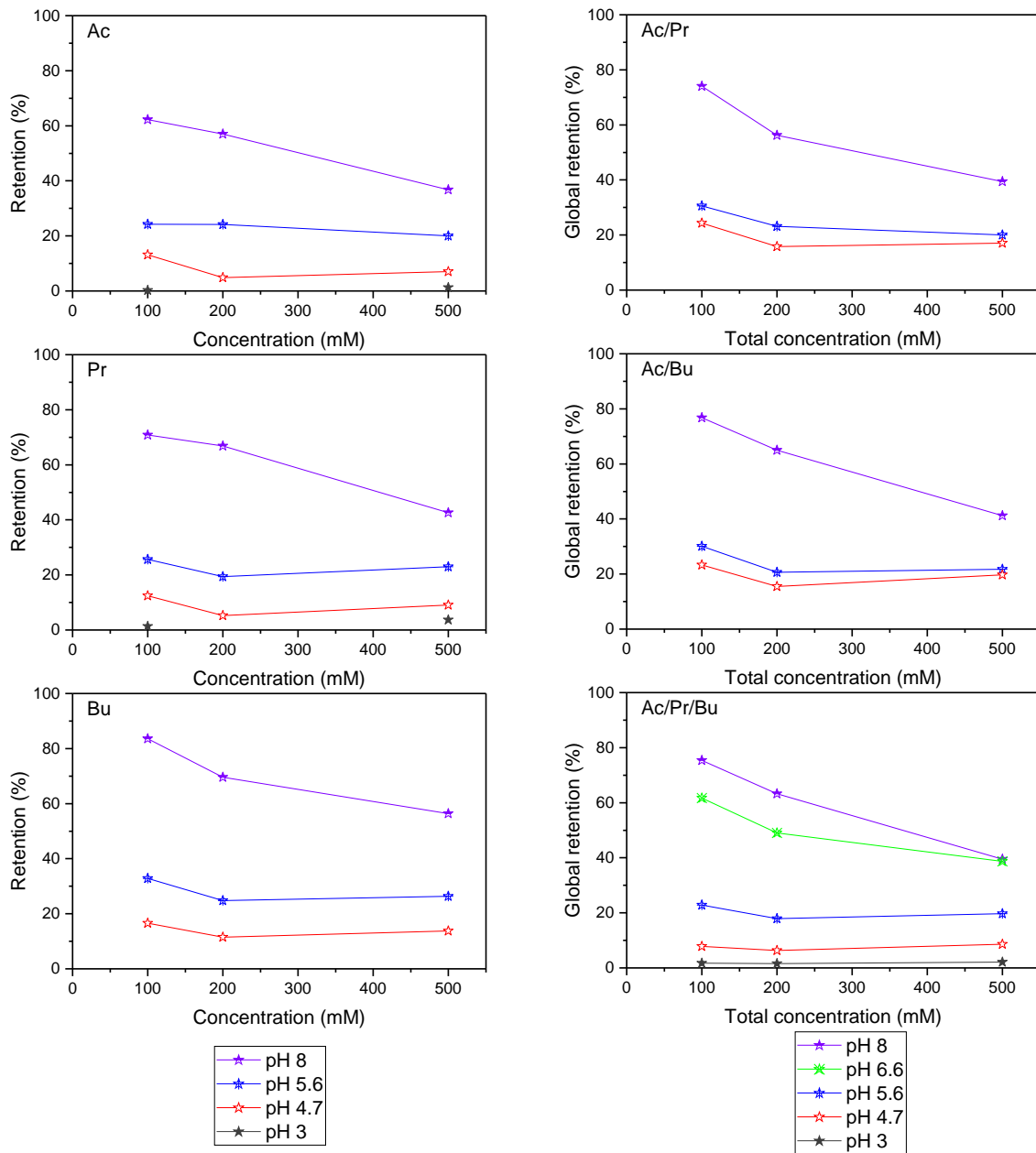


Figure V-18 Retentions/global retentions of VFAs at a filtration flux of $0.2 \times 10^{-5} \text{ m.s}^{-1}$ in single (Ac, Pr, Bu) binary (Ac/Pr, Ac/Bu) and ternary (Ac/Pr/Bu) solutions as a function of total concentration for various solution pH, using NF-45 membrane.

V.2 Description of the VFAs retention versus pH

The observed retention of a weak acid, like VFA, is a combination of the retentions of the dissociated and undissociated forms of the acid, the proportions of which are provided by Eq. (V.6), according to the pK_a of the acid and the pH of the solution .

From previous work, it is suggested that the interactions between undissociated and dissociated forms of weak acids are not significant [143]. The mass transfer parameters of dissociated and undissociated lactic acid were determined from an experimental investigation concluding that the two forms transfer through the membrane separately [143]. Therefore, this is what will be assumed in the following.

Then, the retention of VFAs can be calculated as the weighted average of undissociated and dissociated VFAs retentions using the following equation.

$$R_{VFAs}^{cal} = R_{HVFAs} \times (1 - P_{VFAs^-}) + R_{VFAs^-(C_{VFAs^-})} \times P_{VFAs^-} \quad (V.10)$$

P_{VFAs^-} is the proportion of dissociated VFAs in the solution obtained from Eq. (V.6). R_{HVFAs} is the retention of undissociated VFAs, $R_{VFAs^-(C_{VFAs^-})}$ is the retention of dissociated VFAs.

Eq. (V.10) is used with the following assumptions:

- (1) Dissociated and undissociated VFAs transfer through the membrane independently;
- (2) Retention of HVFAs, R_{HVFAs} , is that obtained at pH 3 and does not depend on the concentration;
- (3) Retention of $VFAs^-$, $R_{VFAs^-(C_{VFAs^-})}$, is that obtained at pH 8 at the corresponding ionic concentration.

The calculation of the second term in Eq. (V.10) requires to know the values of $R_{VFAs^-(C_{VFAs^-})}$ for different ionic concentrations.

Figure V-19 gives the retentions of VFAs in single solutions and the global retentions of VFAs in binary and ternary mixtures at a filtration flux of $0.2 \times 10^{-5} \text{ m.s}^{-1}$ and pH 8 versus the concentration. These variations are fitted using Origin software with an exponential function. The functions, as well as the parameters obtained from the fitting for the different solutions, are listed in Table V-1.

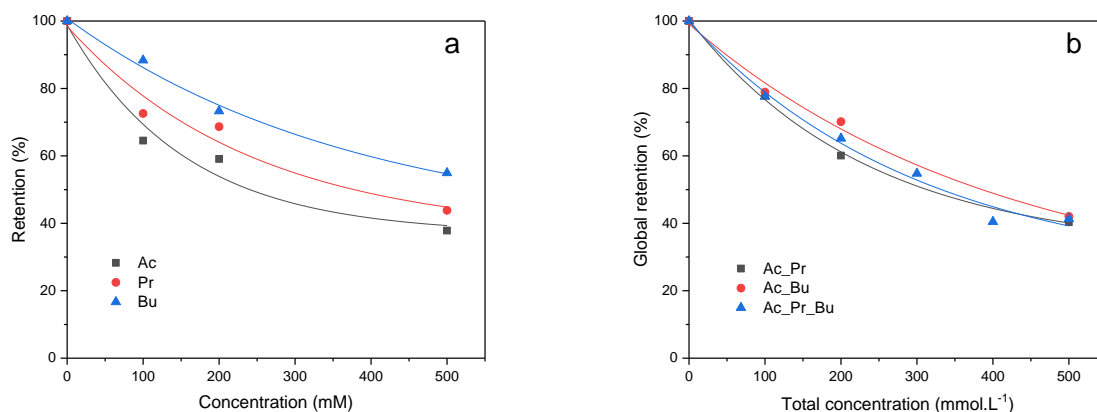


Figure V-19 Retentions of acetate, propionate, butyrate (a) and the global retentions of Ac/Pr, Ac/Bu binary and Ac/Pr/Bu ternary mixed solutions (b) versus concentration at a filtration flux of $0.2 \times 10^{-5} \text{ m.s}^{-1}$ and pH 8, using NF-45 membrane. Points are experimental values and the curves are those from equations in table 4.

Table V-1 VFAs retention as a function of ionic concentration at a filtration flux of $0.2 \times 10^{-5} \text{ m.s}^{-1}$ and pH 8, using NF-45 membrane.

Equation	$R_{VFAS^-}(c_{VFAS^-}) = a + b \times c^{c_{VFAS^-}}$					
Parameters	Ac	Pr	Bu	Ac/Pr	Ac/Bu	Ac/Pr/Bu
<i>a</i>	0.369	0.368	0.375	0.319	0.188	0.243
<i>b</i>	-0.619	-0.616	-0.631	-0.684	-0.803	-0.754
<i>c</i>	0.00157	0.0168	0.0734	0.0143	0.0863	0.0390
<i>R</i> ²	0.973	0.967	0.993	0.998	0.992	0.988

Figure V-20 gives the variations of the calculated (using Eq. (V.10)) and experimental VFAs retentions in single and mixed solutions versus the pH at a given filtration flux J_1 ($0.2 \times 10^{-5} \text{ m.s}^{-1}$) for the 3 total concentrations investigated. As previously mentioned, the variation of individual VFAs retentions in single and mixed solutions with solution pH are not the same, the global retention is considered for mixed solutions. One can observe that both experimental and calculated VFAs retentions increase with solution pH following a sigmoid curve. However, the calculated retentions are always higher than the experimental ones, for single, binary, and ternary solutions. The highest differences between calculated and experimental VFAs retentions are observed at the concentration of 100mM, for all the solutions investigated.

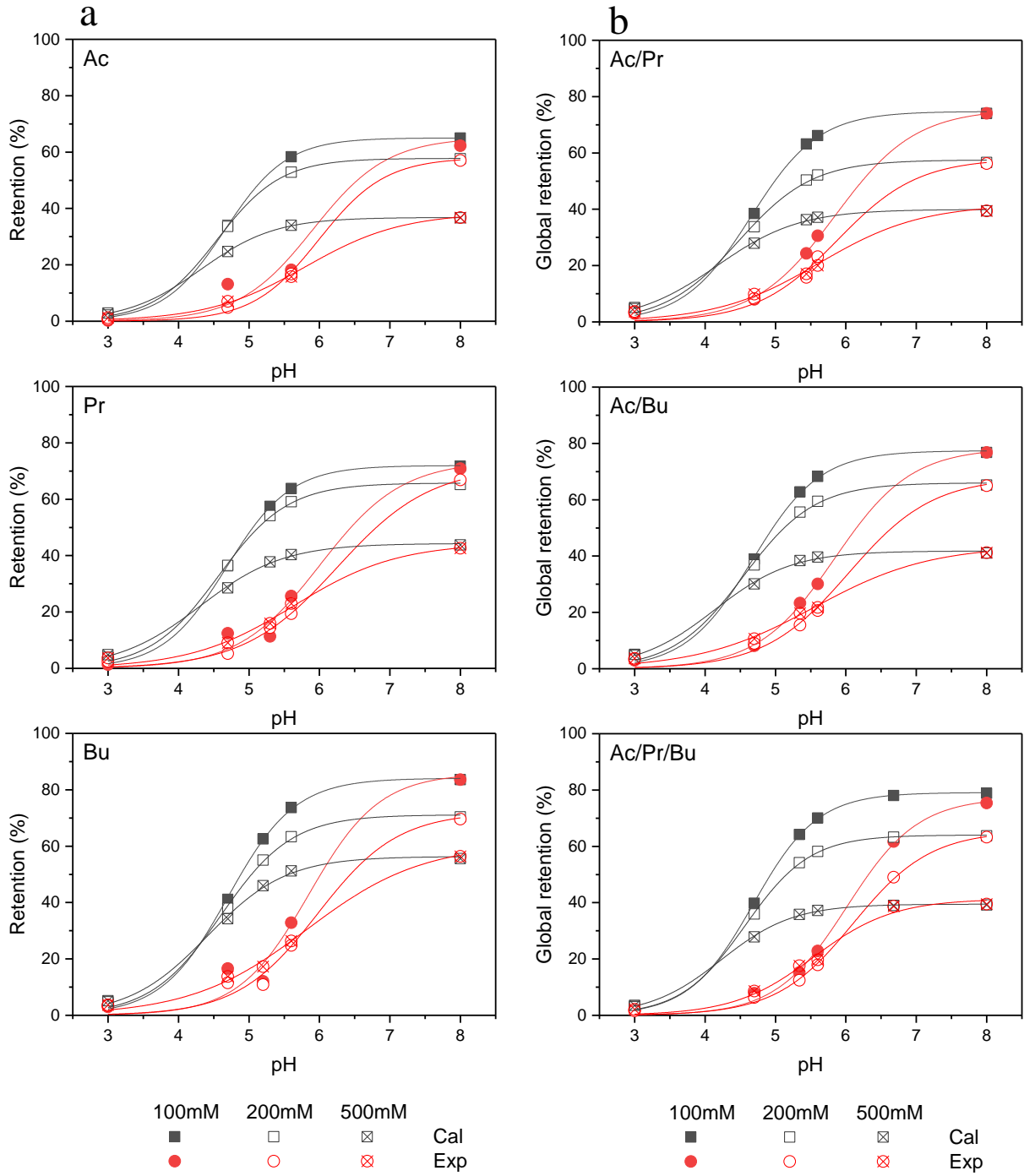


Figure V-20 Calculated and experimental VFAs retention in single (left side), binary, and ternary (right side) solutions versus the solution pH for various total concentrations, using NF-45 membrane. The experimental and calculated VFAs retentions are obtained at filtration flux= $0.2 \times 10^{-5} \text{ m.s}^{-1}$.

Since size effect is almost not influenced by the pH, this overestimation of retention can be attributed to an overestimation of the charge effect on the VFA retention. This is confirmed by the greater overestimation observed at low concentration.

As previously explained, charge effect is due to both the solute and membrane charge, which vary with the solution pH according to their respective pK_a values.

Previous calculation was made considering the theoretical pK_a values of the VFAs. Then, Equation (V.10) was further used to determine the pK_a values to fit experimental and calculated variations of the VFAs retention versus pH (namely fitted pK_a , pK_{a-f}). The values of P_{VFAs^-} were obtained from Eqs. (V.6) and (V.8), for single and mixed solutions respectively. The fitted pK_{a-f} values are obtained from Eq. (V.10) using the Origin software.

The results are reported in Table V-2, that gives the fitted pK_{a-f} values and the fitting coefficient of determination (R^2). For comparison, the theoretical pK_a values for single solutions and global pK_a values (from Eq. (V.8)) for mixed solutions are also reported as well as the differences between pK_{a-f} and pK_a ($pK_{a-f}-pK_a$), for all the compositions investigated.

One can observe that for each condition, the fitting is in excellent agreement with the experimental values ($R^2 > 0.982$). Then the fitted pK_{a-f} values obtained at different concentrations and proportions are similar, no clear trend is observed. The average pK_{a-f} value for all the compositions is about 1.24 ± 0.09 units higher than the theoretical pK_a values of the solutions.

Table V-2 Theoretical pK_a , fitted pK_a , pK_{a-f} , and the differences between pK_a and pK_{a-f} obtained from the fitting of the retention curves for single, binary, and ternary solutions at three concentrations for the filtration flux of J_1 ($0.2 \times 10^{-5} \text{ m.s}^{-1}$), using NF-45 membrane.

Solutions	100mM				200mM				500mM			
	pK_{a-f}	R^2	pK_a	$pK_{a-f}-pK_a$	pK_{a-f}	R^2	pK_a	$pK_{a-f}-pK_a$	pK_{a-f}	R^2	pK_a	$pK_{a-f}-pK_a$
Ac	6.12	0.983	4.76	1.36	6.11	0.996	4.76	1.35	6.05	0.997	4.76	1.29
Pr	6.07	0.989	4.88	1.19	6.19	0.999	4.88	1.31	6.04	0.999	4.88	1.16
Bu	5.94	0.982	4.82	1.12	6.09	0.995	4.82	1.27	5.92	0.995	4.82	1.10
Ac/Pr	5.95	0.999	4.82	1.13	6.14	0.998	4.82	1.32	6.09	0.998	4.82	1.27
Ac/Bu	5.92	0.999	4.79	1.13	6.13	0.998	4.79	1.34	5.93	0.997	4.79	1.14
Ac/Pr/Bu	6.13	0.998	4.82	1.31	6.22	0.998	4.82	1.40	5.95	0.999	4.82	1.13

Figure V-21 gives the variations of calculated and experimental VFAs retentions versus pH at different concentrations for filtration flux J_1 ($0.2 \times 10^{-5} \text{ m.s}^{-1}$). Calculated values are those obtained from Eq. (V.10) considering the individual pK_{a-f} values for each solutions ($\text{pK}_{a-f} = \text{pK}_a + 1.24$). It is shown that it is possible to describe the influence of the pH on the VFAs retention using the previous model on the condition to consider a modified value of the solutes pK_a that is 1.24 pH units higher than the theoretical values.

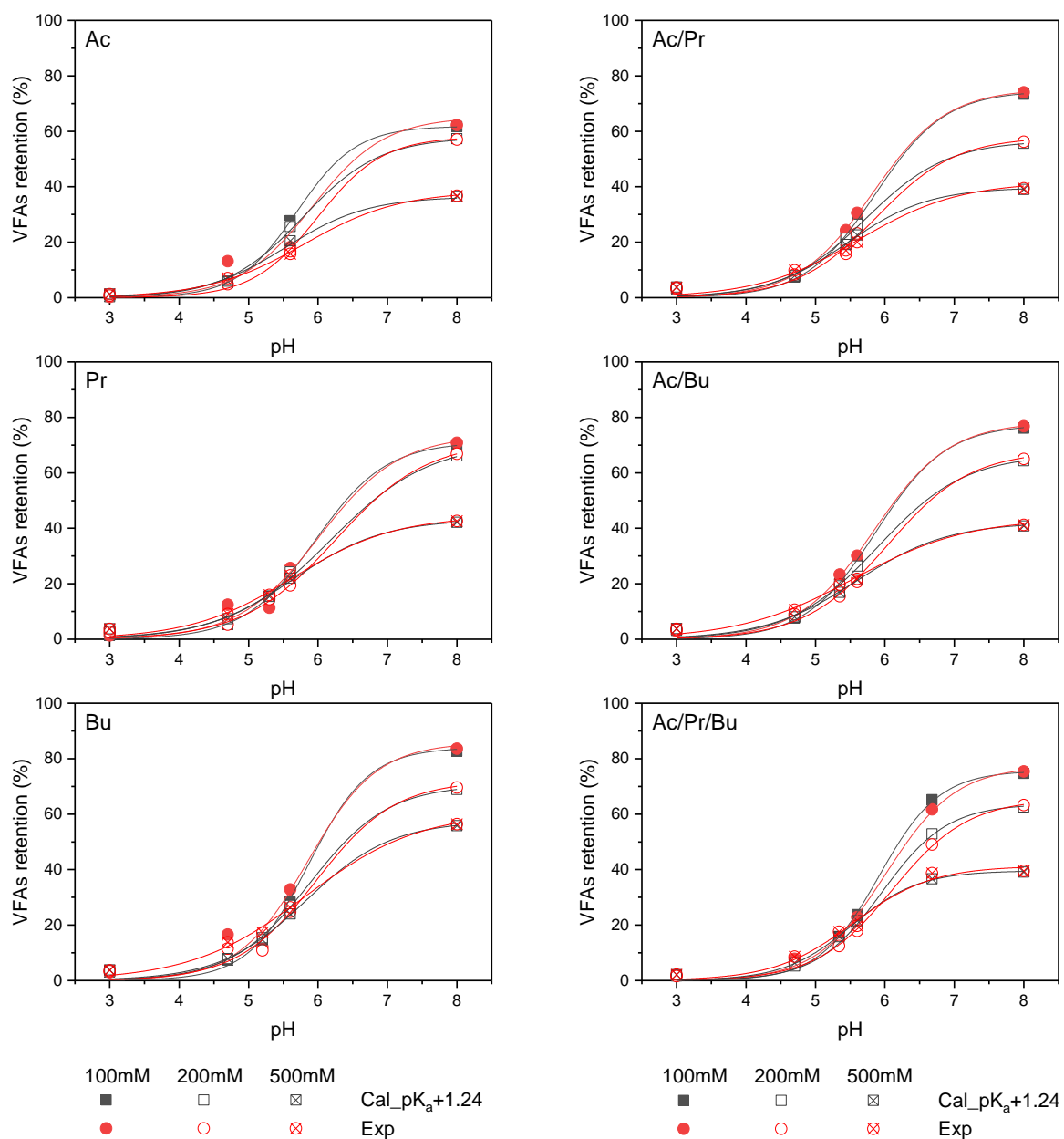


Figure V-21 Calculated VFAs retentions with $pK_{a-f}=pK_a+1.24$ compared with experimental VFAs retentions in single, binary, and ternary solutions at different solution pH and varying total concentrations, using NF-45 membrane. The experimental and calculated VFAs retentions are obtained at filtration flux= $0.2 \times 10^{-5} \text{ m.s}^{-1}$.

Further calculations on higher filtration flux (i.e., J_2 , J_3 , and J_4) are carried out, and the results are given in Table V-4. It is shown that when the filtration flux increase, the fitted pK_{a-f} values decrease. The detailed calculation is not shown.

Table V-3 Theoretical pK_a , fitted pK_a , pK_{a-f} , and the differences between pK_a and pK_{a-f} obtained from the fitting of the retention curves for single, binary, and ternary solutions at two concentrations and filtration flux of J_2 ($0.5 \times 10^{-5} \text{ m.s}^{-1}$), J_3 ($1 \times 10^{-5} \text{ m.s}^{-1}$), and J_4 ($1.5 \times 10^{-5} \text{ m.s}^{-1}$), using NF-45 membrane.

Solutions	100mM							200mM						
	pK_{a-f}			pK_a	$pK_{a-f}-pK_a$			pK_{a-f}			pK_a	$pK_{a-f}-pK_a$		
	J_2	J_3	J_4		J_2	J_3	J_4	J_2	J_3	J_4		J_2	J_3	J_4
Ac	6.06	5.87	5.77	4.76	1.30	1.11	1.01	5.88	5.71	5.61	4.76	1.12	0.95	0.85
Pr	5.81	5.65	5.58	4.88	0.93	0.77	0.70	5.88	5.71	5.63	4.88	1.00	0.83	0.75
Bu	5.82	5.60	5.49	4.82	1.00	0.78	0.67	5.83	5.61	5.49	4.82	1.01	0.79	0.67
Ac/Pr	5.82	5.69	5.62	4.82	1.00	0.86	0.80	5.82	5.65	5.56	4.82	1.00	0.83	0.74
Ac/Bu	5.80	5.63	5.55	4.79	1.01	0.84	0.76	5.84	5.63	5.53	4.79	1.05	0.84	0.74
Ac/Pr/Bu	5.90	5.70	5.60	4.82	1.08	0.88	0.78	5.87	5.62	5.47	4.82	1.05	0.80	0.65

The difference between the fitted pK_{a-f} and solution pK_a ($pK_{a-f}-pK_a$) for various compositions (single, binary, and ternary solutions at a total concentration of 100mM, 200mM, and 500mM) versus filtration flux is given in Figure V-22. One can observe that the difference between pK_{a-f} and pK_a ($pK_{a-f}-pK_a$) decreased from about 1.24 ± 0.09 at J_1 , 1.04 ± 0.09 at J_2 , 0.86 ± 0.09 at J_3 , to 0.76 ± 0.10 at J_4 following an exponential curve. This observation indicates that when the filtration flux increases, the fitted pK_a (pK_{a-f}) approaches the theoretical value. Nevertheless, an increase of about 1 unit (1.00 ± 0.24) of the solutes pK_a values is needed to describe the variation of VFAs retention versus pH.

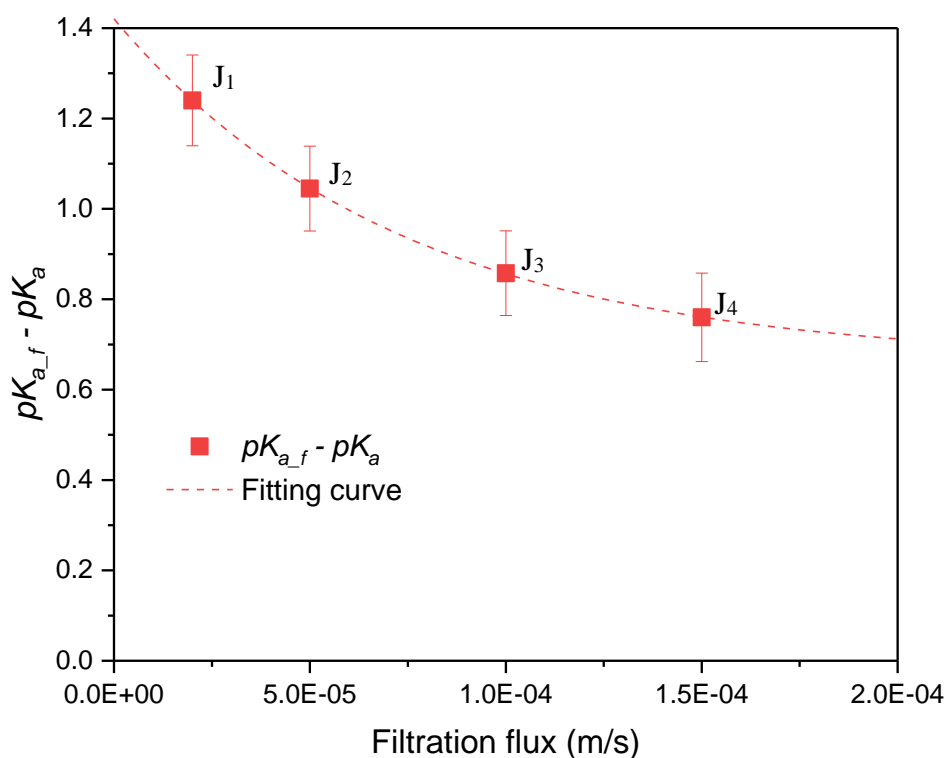


Figure V-22 Average difference between the fitted pK_{a_f} and solution pK_a ($pK_{a_f} - pK_a$) for various compositions (single, binary, and ternary solutions at concentration of 100mM, 200mM, and 500mM) versus filtration flux. Results obtained using NF-45 membrane.

The retention of sulfuric acid is reported to increase with solution pH, from nearly 0% at pH 1, to close to 100% when the pH higher than 5, for various NF membranes investigated [170,199]. Then, in the two publications, it was observed that the retention of sulfuric acid begins to increase with solution pH once the pH reaches a value that is about 1 pH unit higher than its pK_{a2} (1.99) [170,199]. This observation indicate if the pK_a value of sulfuric acid increases by 1 unit (i.e., $pK_a + 1$), then the retention could be in accordance with the dissociation curve of sulfuric acid.

The theoretical pK_a values considered are the ones in water, at 25 °C and infinite dilution. However, it is known that the properties of the bulk solution can significantly influence the pK_a values of weak acids. For instance, it was reported that the pK_a of acetic acid increases from 4.76 to 9.72 when the dielectric constant of the solvent decreases from $\epsilon=78.3$ (water, 25 °C) to $\epsilon = 32.64$ (methanol, 25 °C) and that pK_a values of propionic and butyric acids also follow the same trend [202]. Moreover, it is known that in a confined space, the dielectric constant can be lower than in the bulk [203]. Then one can expect a higher solute pK_a for confined solution due to the

decrease of dielectric constant. This could be an explanation the higher pK_a values necessary to fit the results.

On the other hand, previous calculations were made considering that the membrane charge remains constant. Indeed, it was assumed that the retention of the charged VFA was identical to that obtained at pH 8 at the corresponding ionic concentration. However, not only the proportion of charged solute but also the membrane charge can vary with the pH.

In order to consider the change of the membrane charge with the pH, and its impact on the retention of dissociated VFAs, a correction parameter, α , is introduced in the model. The modified model is shown in Eq. (V.11).

$$R_{VFAs}^{cal} = R_{HVFAs} \times (1 - P_{VFAs^-, pK_a}) + \alpha \times R_{VFAs^-}(c_{VFAs^-, pK_a}) \times P_{VFAs^-, pK_a} \quad (V.11)$$

P_{VFAs^-, pK_a} is the proportion of dissociated VFAs with the theoretical pK_a value of the solution, c_{VFAs^-, pK_a} is the concentration of dissociated VFAs calculated with the theoretical pK_a value of the solution.

The correction parameters for different compositions obtained from Eq. (V.11) are plotted versus the solution pH in Figure V-23a. Following the definition, the correction parameter is equal to 0 at pH 3, while equal to 1 at pH 8.

One can observe that the values of α obtained for each condition increase with solution pH from 0 to 1 following a sigmoid curve. Furthermore, the values obtained for a given total concentration and different composition are comparable. The values of α obtained at 100mM and 200mM are nearly equal while those obtained at the highest concentration (500mM) are higher.

One constant value (namely pK_{eff}) is used to simulate the variation of α values versus pH obtained for each solution at given concentration using Eq. (V.12).

$$\alpha = \frac{10^{pH-pK_{eff}}}{1+10^{pH-pK_{eff}}} \quad (V.12)$$

Figure V-23b gives the fitting curves for the ternary solutions at three concentrations as an example. One can notice that the experimental curves are slightly broaden compared to the fitted curves. At pH lower than 5.6, α is higher than the simulation curve.

The pK_{eff} values obtained for all the compositions are listed in Table V-4.

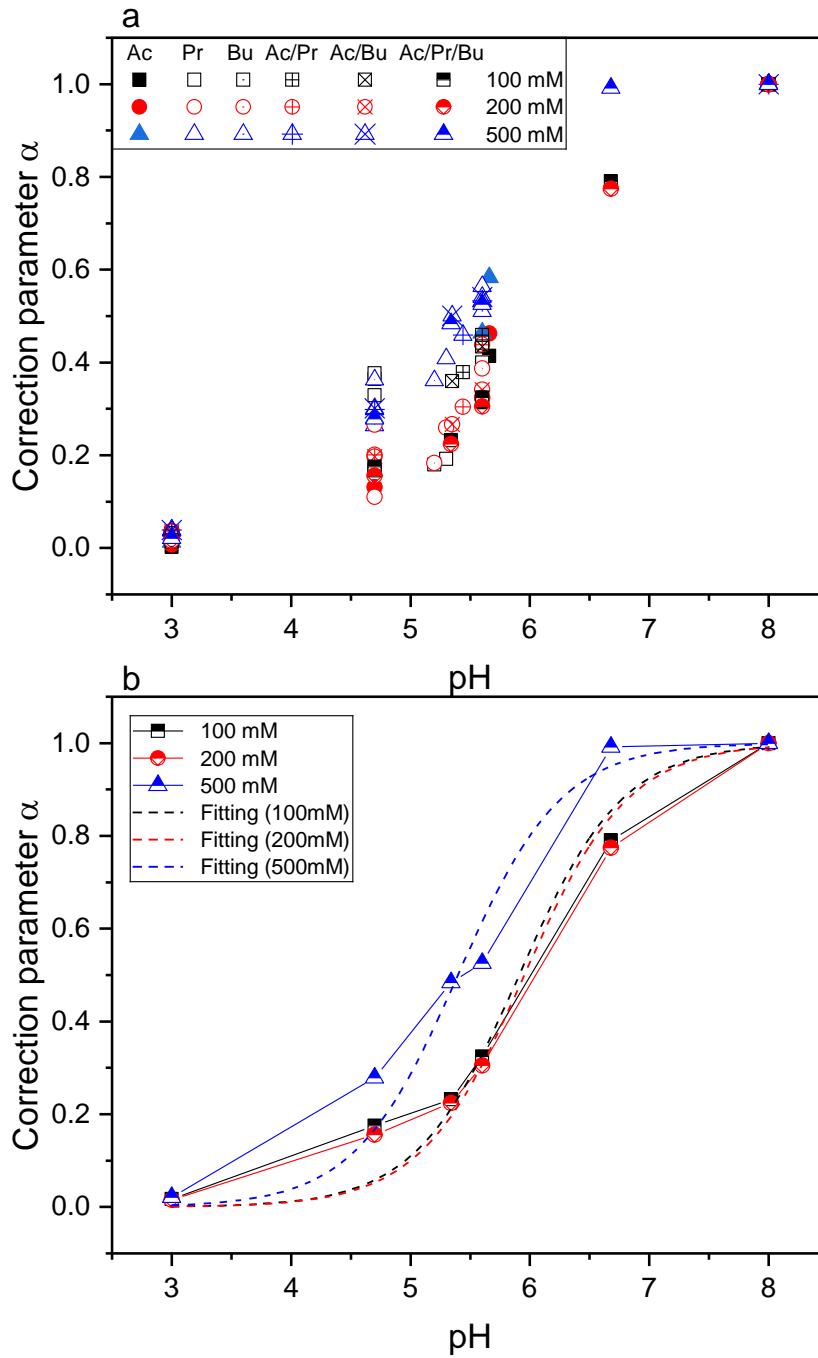


Figure V-23 Correction parameter α (obtained from Eq. (V.11)) as a function of solution pH, (a) for all the compositions investigated, (b) for the ternary solutions (Ac/Pr/Bu) and fitting using Eq. (V.12) with pK_{eff} values in Table V-4. Results obtained using NF-45 membrane. The values are obtained at filtration flux = $0.2 \times 10^{-5} \text{ m.s}^{-1}$.

Table V-4 pK_{eff} values (obtained from Eq. (V.12)) and the coefficient of determination for the fitting at different compositions, filtration flux= $0.2 \times 10^{-5} \text{ m.s}^{-1}$. Results obtained using NF-45 membrane.

Solution	100mM		200mM		500mM	
	pK_{eff}	R^2	pK_{eff}	R^2	pK_{eff}	R^2
Ac	5.79	0.822	5.80	0.984	5.52	0.944
Pr	5.74	0.877	5.84	0.990	5.42	0.970
Bu	5.78	0.924	5.69	0.829	5.46	0.892
Ac/Pr	5.64	0.987	5.80	0.966	5.36	0.951
Ac/Bu	5.64	0.989	5.71	0.970	5.46	0.946
Ac/Pr/Bu	5.91	0.971	5.95	0.978	5.39	0.970

It is shown that the pK_{eff} values obtained for different solutions at low concentrations (100mM and 200mM) are comparable (5.75 ± 0.09 , and 5.80 ± 0.08 respectively), while the pK_{eff} values obtained at the highest concentration (500mM) is about 0.33 unit lower (5.44 ± 0.05).

Figure V-24 shows the comparison of calculated VFAs retentions at given filtration flux ($0.2 \times 10^{-5} \text{ m.s}^{-1}$) in single and mixed solutions at three concentrations using Eq. (V.11) and the experimental ones versus solution pH. The values of correction parameter α used in the calculation are obtained from Eq. (V.12), considering pK_{eff} values equal to 5.75, 5.80, and 5.44 for the concentration of 100mM, 200mM, and 500mM respectively. One can observe that the calculated retentions fit well with the experimental ones.

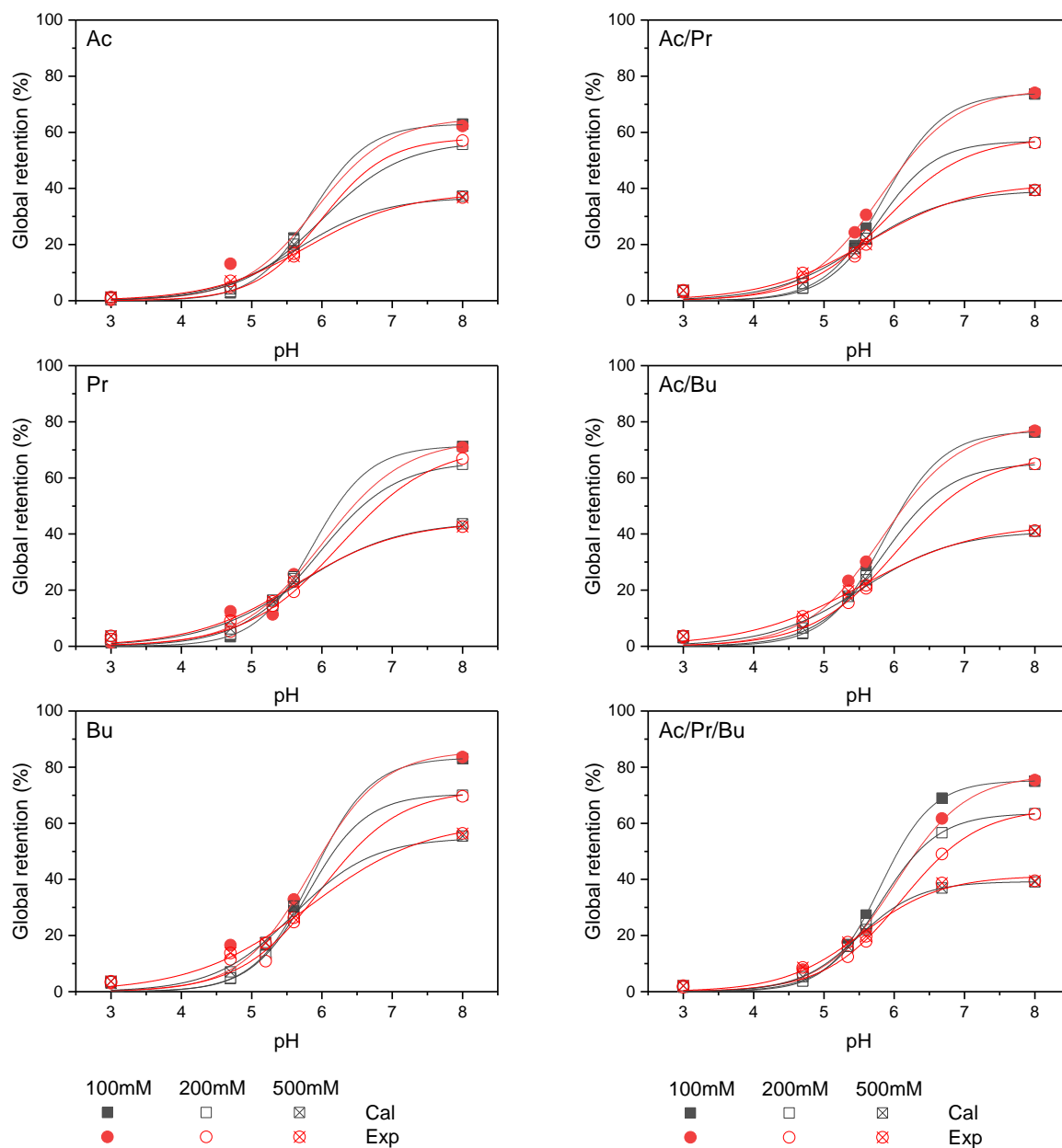


Figure V-24 Calculated global retentions take the dissociation of the membrane into consideration (pK_a -eff of the membrane are 5.80, 5.75, and 5.44 respectively for 100mM, 200mM, and 500mM) compared with experimental obtained global retention of VFAs single, binary, and ternary solutions at different solution pH and varying total concentration, filtration flux= $0.2 \times 10^{-5} \text{ m.s}^{-1}$. Results obtained using NF-45 membrane.

The pK_{eff} values obtained from the fitting are correlated to the pK_a values of the membrane functional groups. The pK_{eff} values (from 5.44 to 5.80) obtained from the fitting are within the range of the membrane pK_a values previously reported. Indeed, for carboxylic functional groups on polyamide films, pK_a values from 5 to 9 were obtained by contact angle titration [167]. Furthermore, the first pK_a values reported for five different NF/RO membranes with polyamide active layer using heavy ions probes were between 5.23 and 5.72 [156,158]. Current results indicate that the retention of charged solute could be directly related to the dissociation of membrane functional groups that determines the membrane charge.

It was also reported in previous work that the experimental dissociation curves were broadened compared with simulated ones [167]. Current results also show the broadening of the correction parameters versus solution pH compared with simulated dissociation curves (see Figure V-23b). This could be due to that carboxylic functional groups on the NF membrane have different pK_a values, as suggested in ref. [156] and [167]. The different pK_a values observed for the carboxylic functional groups on the membrane could occur due to the site-site interactions between functional groups on the polymer chains, which may be related to the low dielectric constant within the aliphatic chain and/or inside the confined membrane pores [156,204,205].

In addition, the three different pK_{eff} values (5.4 for 500mM and 5.75 for 100mM, and 5.80 for 200mM) obtained for three total concentrations seem indicate that the membrane/solute charge interaction is concentration-dependent. This could be due to the ionization of functional groups. Indeed, as previously mentioned concerning VFAs, the ionization constant of weak acid decreases with ionic concentration according to Debye–Hückel law [206] so that a lower pK_a value can be observed at higher ionic concentration. Current result is in agreement with this trend.

V.3 Conclusion

Solution pH as well as ionic concentration have significant influence for the nanofiltration of weak acids. Solution pH can change the ratio of dissociated/undissociated weak acids, as well as modify the membrane charge. Ionic concentration can screen the charge interactions between charged membrane and dissociated weak acids. Current work investigated the influence of both pH and concentration on the retention of VFAs in single and mixed solutions.

It was observed that VFAs retentions increase with either filtration flux or solution pH. Retentions of VFAs increase with solution pH follows the dissociation curves of VFAs. Then,

retentions of VFAs decrease when the concentration increases, showing the influence of screening effect. This influence is nearly negligible at pH 3, then becomes stronger when the solution pH increases. Besides, the permeate proportion of Ac increases while the permeate proportion of Bu decreases when the solution pH increases, due to the co-ions competition. However, the proportion of Pr in the permeate is nearly unchanged whatever the solution pH.

Furthermore, based on the assumption that the dissociated and undissociated VFAs transfer through the membrane independently, calculation of VFAs retentions at different solution pH and concentrations for a given filtration flux was carried out. By only considering the dissociation of VFAs, the calculated retention curves were higher and paralleled to the experimental ones, indicate there is an additional influence of solution pH.

On the one hand, increasing the pK_a values of the VFAs by 1.24 units, the calculated retention curves can fit the experimental ones. Based on the knowledge that the dielectric constant in a confined space can decrease, and that the pK_a of VFAs increases when the dielectric constant in the solution decreases, this explanation could be partially realistic. Further calculation also showed that when the filtration flux increase, the experimental retention curves are more close to the theoretical ones, i.e. the fitted pK_a becomes close to the theoretical value.

On the other hand, considering a correction parameter related to the membrane charge, the calculated retention curves can also be in agreement with the experimental ones. The correction parameters can be fitted by a constant value (namely pK_{eff}) for each concentration. The obtained pK_{eff} values are 5.75, 5.80, and 5.44 for VFAs solutions at the total concentration of 100mM, 200mM, and 500 mM respectively. Those values (5.44-5.80) observed are within the range of the pK_a values (5-9) for carboxylic functional groups on polyamide films reported previously. Therefore, this explanation could also be realistic.

The current work discussed the VFAs retention through a simple model which can be applied to single and mixed VFAs solutions, the different possible mechanisms for the influence of solution pH on VFAs retention were discussed. However, since the influence of pH involves the dissociation of VFAs as well as of the membrane, the influence of each cannot be distinguished. Further work is still required to reveal the different mechanisms and to which extent can those mechanisms influence the retention of electrolytes.

VI.

Chapter VI
NF of VFAs fermentation broths

This chapter investigated the retention and separation performance of nanofiltration process on a real fermentation broth at different pH, aim to explore the possible treatment.

The possible applications of VFAs are introduced in Chapter I, it is reported that higher proportion of butyric acid is more favorable for PHA (polyhydroxyalkanoates) production [91]. On the contrary, butyric acid is considered as unfavorable for energies and biofuel applications, as it can reduce the degradation rate for MFC (microbial fuel cell) process [81], and reduce the production of microbial lipids [84,85]. Furthermore, it is observed that, in the fermentation broth, organic impurities such as ethanol and methanol can hinder the following applications such as PHA fermentation [29,30].

Then, there are three main objectives for the NF process for the treatment of fermentation broth containing VFAs. Firstly, inorganic ions like Cl^- are generally unfavorable components for VFAs valorization, the removal of Cl^- by NF is considered. Then, it is more favorable to change the proportions of acetic, propionic, and butyric acids according to the requirement of the following applications. Finally, it is necessary to extract VFAs and remove hindering organics (i.e., ethanol and methanol).

In the current Chapter, two NF membranes, namely XLE and NF-45, are used. As introduced in Chapter II, XLE membrane is much tight than NF-45 membrane, thus XLE membrane could be beneficial for the extraction of VFAs and remove the impurities (e.g., ethanol), while NF-45 could be used for the modification of VFAs composition.

The experimental investigation is firstly applied to synthetic broths with composition and pH close to the real fermentation broth. Then, a real fermentation broth contains VFAs is filtrated. The results obtained in previous Chapters are also used for comparison. The retentions of individual solutes in mixed solutions, synthetic broths and real fermentation broth by the two membranes are discussed. The proportions of individual solutes in the permeate are investigated as well. Then, the performances of the two membranes on the modification of feed and permeate proportions for the synthetic and real broths are further compared, and the possible applications of NF on the treatment of VFAs fermentation broth are given.

VI.1 Individual solutes retentions in synthetic and real fermentation broths

VI.1.1 Individual solutes retentions in synthetic broths

The experimental investigation is firstly carried out with synthetic broths with similar compositions as the real fermentation broth. The composition of the VFAs real fermentation broth is shown in Table VI-1. It mainly contains Ac, Pr, Bu, and Cl⁻, the cations compositions are mainly Na⁺ and Ca²⁺, with trace amount of NH₄⁺ and K⁺.

As already mentioned in Chapter II, the TOC of VFAs is calculated from the concentration of VFAs in the real fermentation broth obtained using HPLC, then the TOC of organic matters/impurities (OM) is the TOC other than the TOC of VFAs (TOC- TOC_{VFAs}). From the composition obtained from HPLC analysis, ethanol is the main contributor of the TOC of OM (244 mg.L⁻¹ of TOC_{ethanol} out of 334mg.L⁻¹ TOC_{OM}, 73%).

Table VI-1 Composition of the real fermentation broth

Organics		Inorganics	
Components	Concentration(mM)	Components	Concentration (mM)
Ac	44.41	Cl ⁻	28.96
Pr	30.76	SO ₄ ²⁻	0.32
Bu	39.96	Na ⁺	46.34
Ethanol	10.17	NH ₄ ⁺	10.96
Butanol	1.72	K ⁺	3.98
		Ca ²⁺	24.09
Total VFAs Concentration (mM)	115.13	Total cations concentration (mEq.L⁻¹)	109.46
TOC (mg.L⁻¹)	4425.17		
TOC_{VFAs} (mg.L⁻¹)	4091.38		
TOC_{OM} (mg.L⁻¹)	333.79		

The compositions of the 6 synthetic broths are given in Table VI-2. Two membranes, i.e., XLE and NF-45 membranes, are used in the experimental investigation. The proportion of Ac:Pr:Bu for synthetic broths (i.e., Syn 1, Syn 2, and Syn 3) filtrated by XLE membrane is 1:1:1, the total VFAs concentration (117 mM) is similar to that of the real fermentation broth (115 mM). Then 24mM of NaCl and 24mM of CaCl₂ are added respectively in order to simulate the influence of inorganic salts. The chosen VFAs proportion (1:1:1) for the synthetic broths can be compared with the ternary solutions with identical VFAs proportion. The proportion of Ac:Pr:Bu for synthetic

broths (i.e., Syn 4, Syn 5, and Syn 6) that filtrated by NF-45 membrane is 45:31:40, the same as that for the real fermentation broth, in order to compare the permeate proportions between synthetic and real fermentation broths.

Table VI-2 Compositions and pH values of the synthetic fermentation broths

Components	pH 5.7 and 8 (XLE)			pH 5.7 (NF-45)		
	Syn 1	Syn 2	Syn 3	Syn 4	Syn 5	Syn 6
Ac (mM)	39	39	39	45	45	45
Pr (mM)	39	39	39	31	31	31
Bu (mM)	39	39	39	40	40	40
NaCl (mM)		24			24	
CaCl ₂ (mM)			24			24
Total VFAs concentration (mM)	117	117	117	116	116	116

VI.1.1.1 Nanofiltration using XLE membrane

Figure VI-1 and Figure VI-2 show the retentions versus filtration flux for all the anions in the synthetic broths at acidic (pH 5.7) and alkaline (pH 8) conditions by XLE membrane.

One can observe that the retentions of VFAs at acidic condition are lower than the retentions at alkaline condition. Indeed, retentions of Ac, Pr, and Bu at pH 5.7 without the addition of salts (Syn1) for the filtration flux of $1 \cdot 10^{-5} \text{ m}\cdot\text{s}^{-1}$ are 91%, 93%, and 96% respectively, while the retentions of VFAs at pH 8 for the same filtration flux are all above 98%. On the other hand, the retention of Cl⁻ at pH 5.7 is lower than that at pH 8, especially at low filtration flux.

Then, it is shown that the differences between individual VFAs retentions without and with the addition of inorganic salts at pH 5.7 are lower than 5%, especially at high filtration flux. Similar phenomenon is found for VFAs retentions at pH 8. Current observation shows that the addition of NaCl and CaCl₂ can only influence the retention of VFAs to a limited extent. This result is in agreement with that observed for NF-45 membrane in Chapter IV.

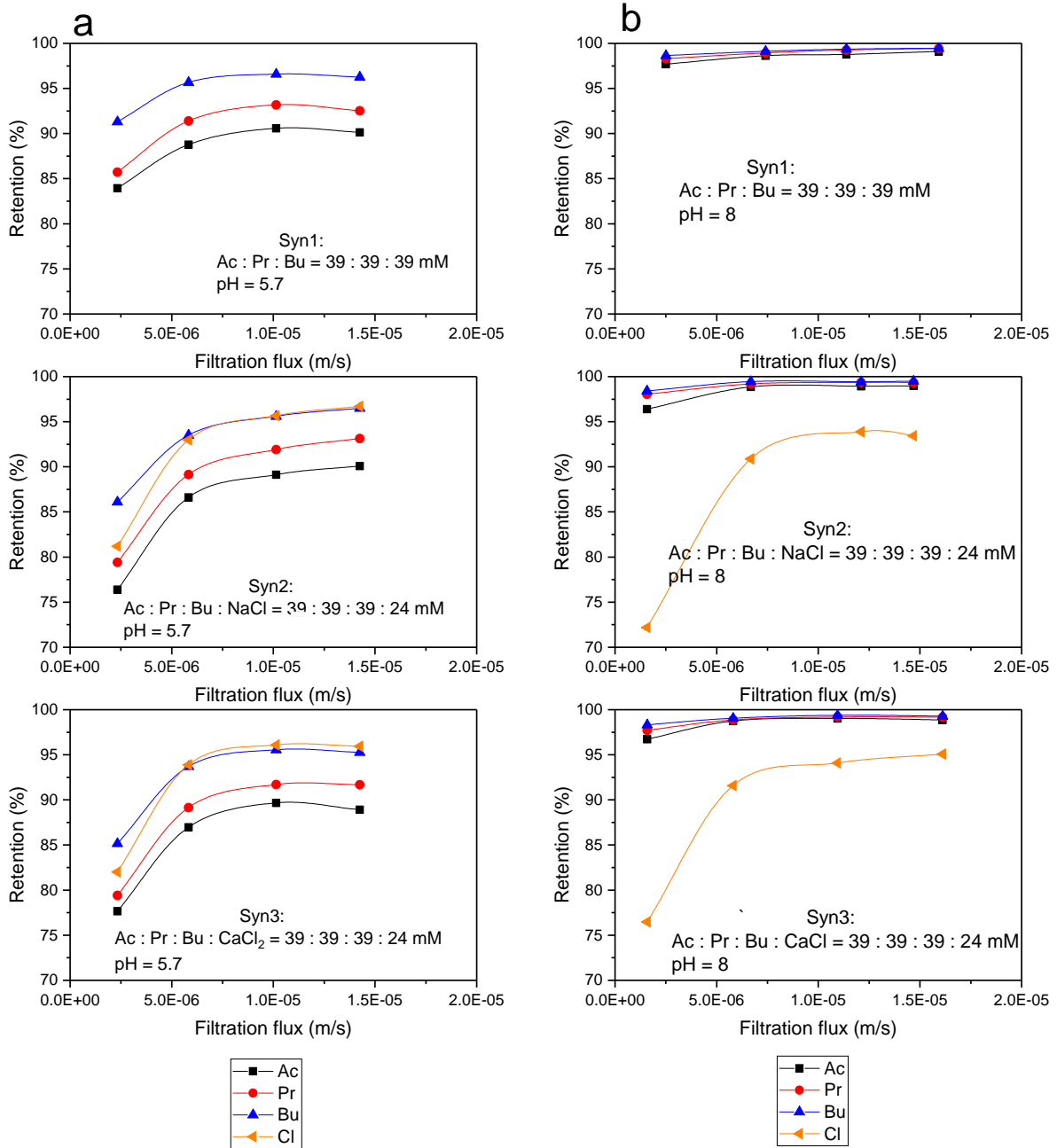


Figure VI-1 The retentions of all anions in the synthetic solutions versus filtration flux (a) pH 5.7, (b) pH 8. Membrane used: XLE membrane, VFAs feed proportions: Ac:Pr:Bu=1:1:1.

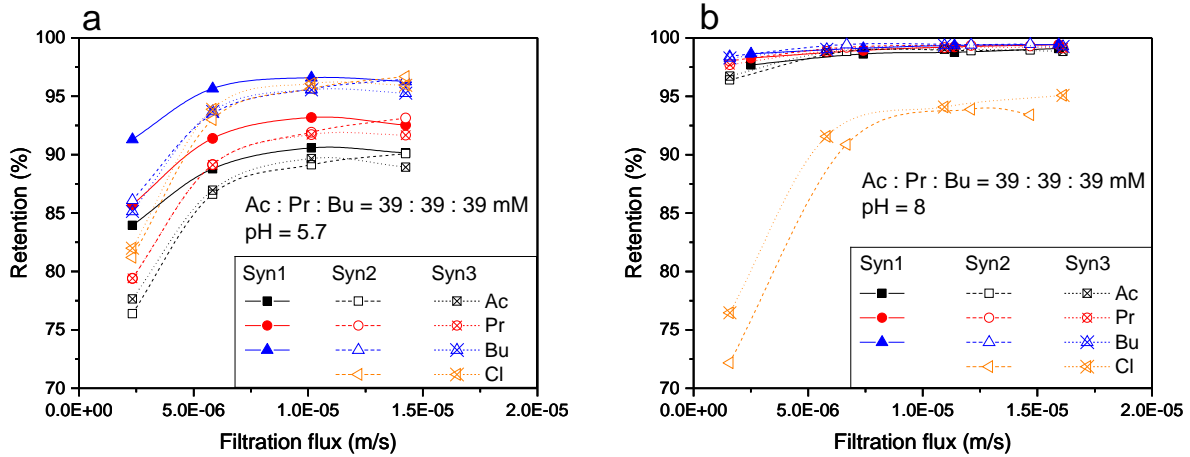


Figure VI-2 Comparison of the retentions of all anions in the synthetic solutions without and with salts (a) pH 5.7, (b) pH 8. Membrane used: XLE membrane, VFAs feed proportions: Ac:Pr:Bu=1:1:1.

Furthermore, it is observed that the retention sequence of the four solutes is $Cl^- < Ac^- < Pr^- < Bu^-$ at pH 8, the same as that observed in Chapter IV using NF-45. However, at pH 5.7, the retention sequence of the four anions changed to $Ac^- < Pr^- < Bu^- \approx Cl^-$, reverse sequence is observed between the retentions of VFAs and Cl^- .

It is discussed in Chapter V that the solution pH has a significant influence for the retention of VFAs. At diluted solutions, the retention of dissociated VFAs is much higher than the retention of the undissociated ones, due to the charge effect. Then, the retention of VFAs observed at pH 5.7 is a combination of the retentions of undissociated and dissociated VFAs. The increase of solution pH increases VFAs retention, due to a higher proportion of dissociated VFAs as well as higher membrane charge.

In order to figure out the retentions of dissociated and undissociated VFAs, a calculation based on VFAs dissociation and electroneutrality both in the feed and permeate is carried.

Firstly, the dissociation of the three VFAs all depend on the dissociation constant of each VFA and H^+ concentration in the solution, both in the feed and permeate. In the mixed solution, H^+ concentration is the same for the three VFAs. The dissociation of the three VFAs at given H^+ concentration in the feed or permeate can be given in Eq. (VI.1).

$$[H^+] = \frac{K_{a_{Ac}} \times \{[Ac] - [Ac^-]\}}{[Ac^-]} = \frac{K_{a_{Pr}} \times \{[Pr] - [Pr^-]\}}{[Pr^-]} = \frac{K_{a_{Bu}} \times \{[Bu] - [Bu^-]\}}{[Bu^-]} \quad (VI.1)$$

Then, the concentration of anions and cations in the solution are equal. The concentration of H^+ and OH^- is negligible (concentration of H^+ is lower than 10^{-2} mM at pH 5.7, and

concentration of OH^- is about 10^{-3} mM at pH 8, more than two magnitudes lower than the concentration of solute). Then, the electroneutrality in the feed and permeate is given in Eq. (VI.2).

$$[Na^+] + [Ca^{2+}] = [Ac^-] + [Pr^-] + [Bu^-] \quad (VI.2)$$

$[H^+]$ concentration of H^+ in the feed or permeate

K_{aAc} , K_{aPr} , K_{aBu} the dissociation constant of Ac, Pr, and Bu respectively, in the feed or permeate.

$[Ac]$, $[Pr]$, $[Bu]$ the concentrations of both dissociated and undissociated Ac, Pr, Bu, respectively, in the feed or permeate.

$[Ac^-]$, $[Pr^-]$, $[Bu^-]$ the concentration of dissociated Ac, Pr, Bu, respectively, in the feed or permeate.

$[Na^+]$, $[Ca^{2+}]$ the concentration of Na^+ and Ca^{2+} , in the feed or permeate.

In Eqs. (VI.1) and (VI.2), the three variables are $[Ac^-]$, $[Pr^-]$, and $[Bu^-]$, the input parameters ($[Ac]$, $[Pr]$, $[Bu]$, $[Na^+]$, and $[Ca^{2+}]$) can be experimentally obtained by HPLC analysis.

By solving Eqs. (VI.1) and (VI.2) using Matlab, the concentrations of dissociated VFAs, i.e., $[Ac^-]$, $[Pr^-]$, and $[Bu^-]$, in the feed and permeate are obtained. Then, the concentration of undissociated VFAs in the feed and permeate are obtained by mass balance.

Then, from the concentrations of individual dissociated and undissociated VFAs in the feed and permeate, the retentions of individual dissociated and undissociated VFAs can be calculated using Eq. (II.2).

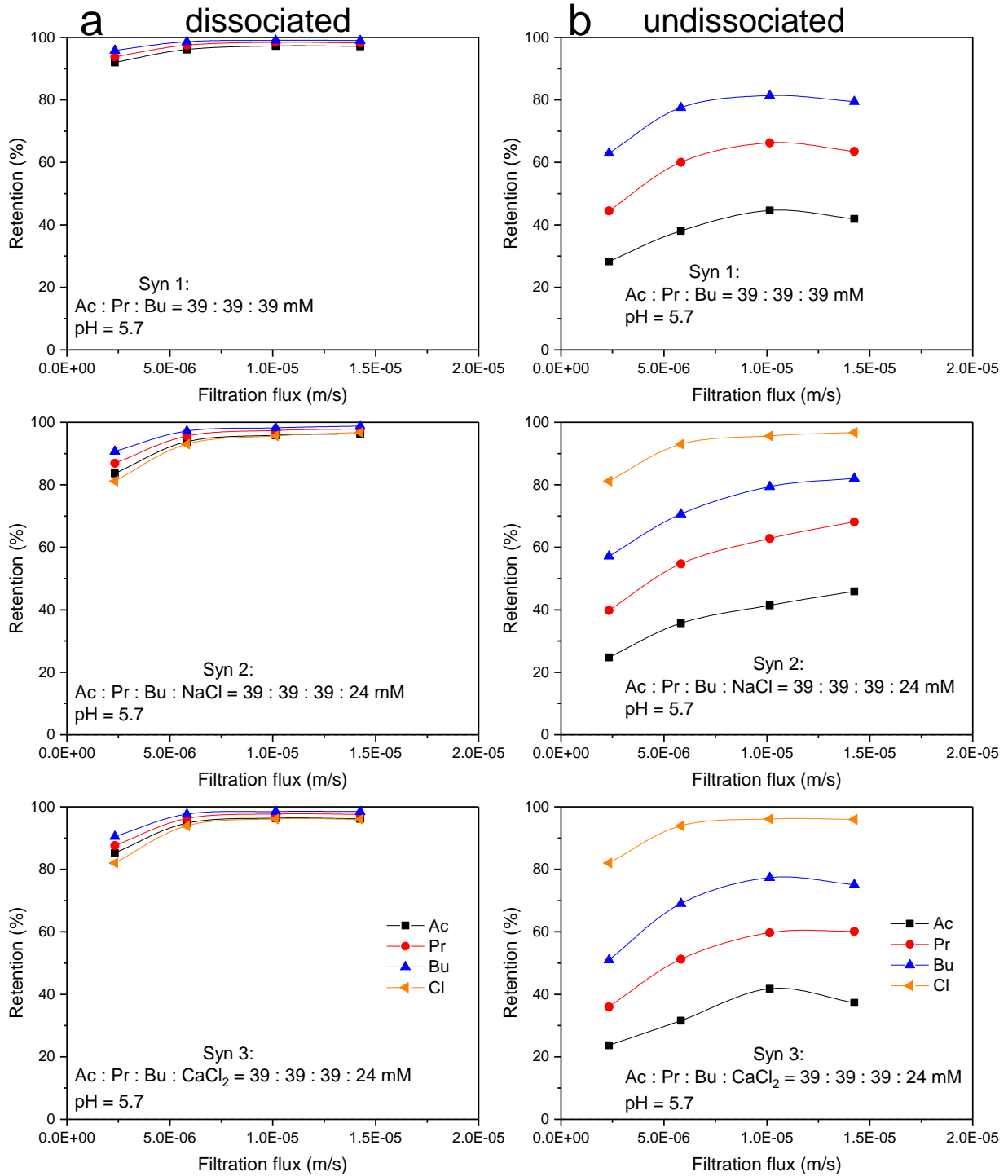


Figure VI-3 Retentions of (a) dissociated VFAs, (b) undissociated VFAs in the synthetic solutions without and with salts. Retention of Cl⁻ is also given as reference. Using XLE membrane for synthetic solutions Syn1, Syn2, and Syn3 at solution pH 5.7. VFAs feed proportions: Ac:Pr:Bu=1:1:1.

Figure VI-3 gives the retentions of individual dissociated and undissociated VFAs in the synthetic broths (Syn1, Syn2, and Syn3) at pH 5.7.

One can observe that the retention sequence of dissociated VFAs in the system is $\text{Ac}^- < \text{Pr}^- < \text{Bu}^-$, and for the undissociated VFAs, the retention sequence is $\text{Ac} < \text{Pr} < \text{Bu}$, both following their MWs. Then, it is found that the retention of Cl^- is lower than the retention of dissociated VFAs but higher than the retentions of undissociated VFAs.

Therefore, considering the retention sequence of the dissociated forms, the sequence of anions is $\text{Cl}^- < \text{Ac}^- < \text{Pr}^- < \text{Bu}^-$ at pH 5.7 using XLE membrane, following their MWs. This sequence is the same as that obtained at pH 8 by XLE membrane and NF-45 membrane (reported in Chapter IV).

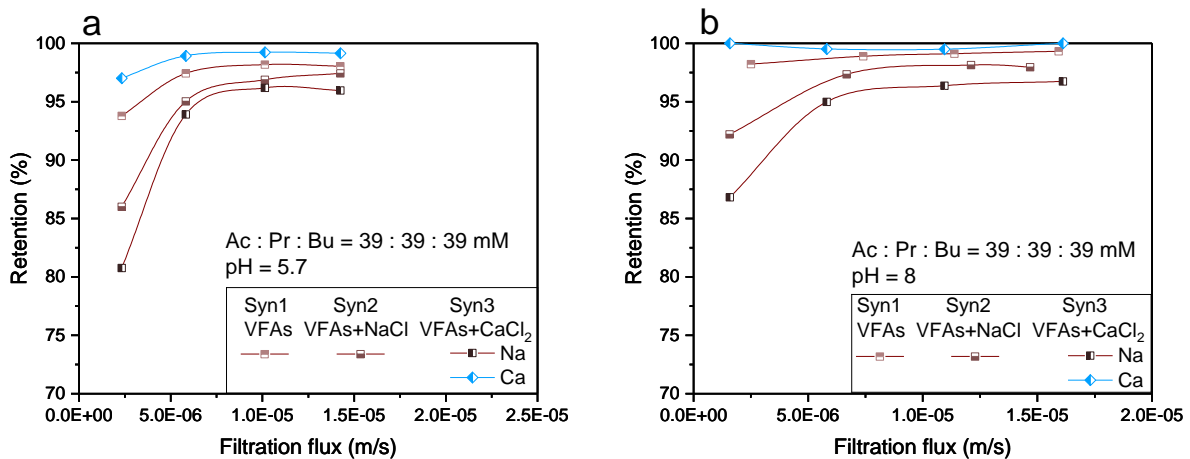


Figure VI-4 The retentions of all cations versus filtration flux in the synthetic solutions using XLE membrane at (a) pH 5.7 (b) pH 8. VFAs feed proportions: Ac:Pr:Bu=1:1:1.

The retentions of all the cations in the synthetic broths at acidic (pH 5.7) and alkaline (pH 8) conditions are given in Figure VI-4. Similar to the retention of VFAs, the retention of Na^+ and Ca^{2+} at pH 5.7 is lower than that at pH 8, especially at low filtration flux. For the synthetic broth with the addition of CaCl_2 , the retention sequence is $\text{Na}^+ < \text{Ca}^{2+}$, the same as that reported in Chapter IV with NF-45 membrane.

Then, one can observe that, as the total concentration increases from 117mM (Syn1, VFAs without salts) to 141mM (Syn2, VFAs+NaCl), the retention of Na^+ slightly decreases, showing the influence of screening effect. Then, in the presence of Ca^{2+} (Syn3, VFAs+ CaCl_2 , ionic concentration $165\text{mEq}\cdot\text{L}^{-1}$), the retention of Na^+ decreases more compared to other compositions, this observation could be due to the influence of both screening effect and co-ions competition.

This phenomenon is in agreement with the results previously observed using NF-45 membrane in Chapter IV.

VI.1.1.2 Nanofiltration using NF-45 membrane

The synthetic broths are prepared according to the composition of VFAs in the real fermentation broth (Ac:Pr:Bu=45:31:40 mM), then NaCl and CaCl₂ are added respectively to simulate the influence of Cl⁻ and Ca²⁺ (namely, Syn4, Syn5, and Syn6), at the same pH as the real broth (pH 5.7).

Figure VI-5 and Figure VI-6 give the retentions of all the anions and cations versus filtration flux with the synthetic broths at pH 5.7.

One can observe that the retention sequence for VFAs and Cl⁻ is Cl⁻<Ac<Pr<Bu. This retention sequence is the same as that observed for mixed solutions (i.e., VFAs+NaCl and VFAs+CaCl₂) at pH 8 reported in Chapter IV. The sequence observed at pH 5.7 is not differed from that observed at pH 8 as that reported previously using XLE membrane. This could be due to that the retention of Cl⁻ using NF-45 membrane (15% at filtration flux = 1×10^{-5} m/s, pH 5.7) is much lower than that using XLE membrane (95% at filtration flux = 1×10^{-5} m/s, pH 5.7), a lower pH value is required to obtain the reverse trend.

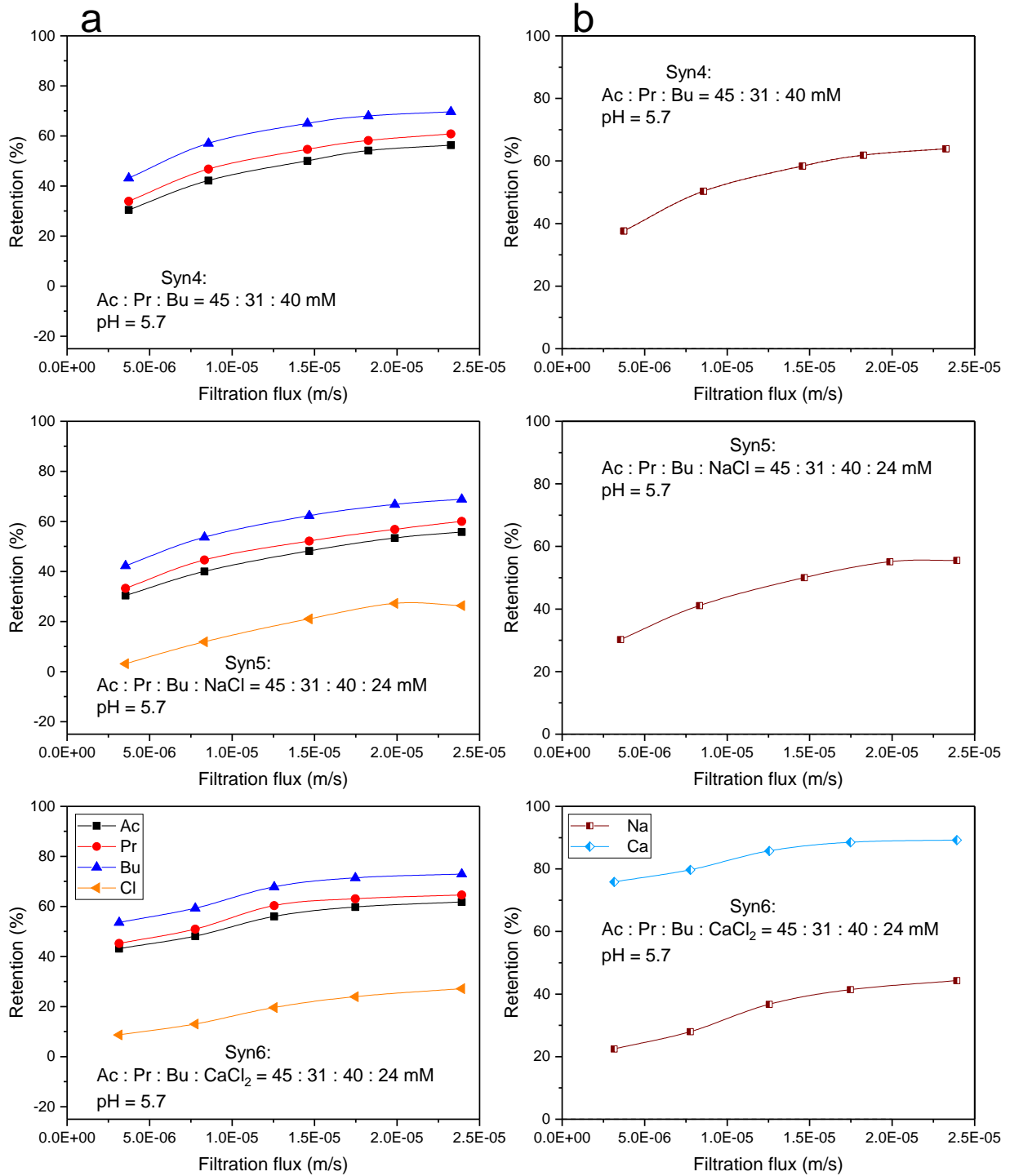


Figure VI-5 The retentions of all anions (a) and all cations (b) in the synthetic broths with and without salts, using NF-45 membrane at pH 5.7. VFAs feed proportions: Ac:Pr:Bu=45:31:40.

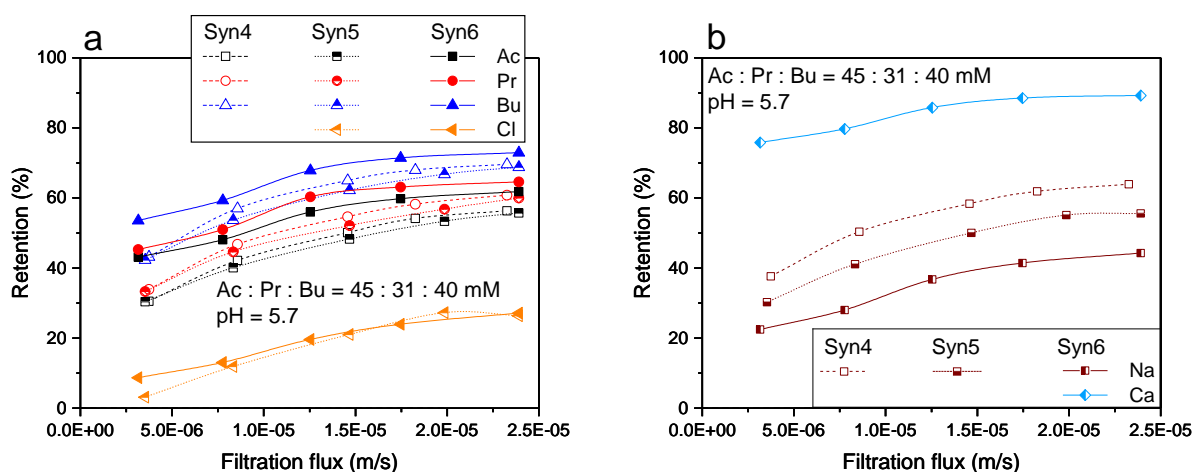


Figure VI-6 Comparison of the retentions of all anions (a) and all cations (b) in the synthetic broths with and without salts, using NF-45 membrane at pH 5.7. VFAs feed proportions: Ac:Pr:Bu=45:31:40.

Then, it is observed that the retentions of VFAs in synthetic broths without salts (Syn4) and with addition of NaCl (Syn5) are similar. However, with the addition of CaCl₂ (Syn6), the retentions of VFAs slightly increased. Nevertheless, the differences between the retentions of VFAs for the three synthetic broths are below 10%, except for the conditions at the lowest filtration flux. This indicates that the influence of inorganic salts on VFAs retentions is not significant, as already concluded in Chapter IV.

For the retentions of cations, one can observe that as the concentration of synthetic broths increases from 116mM (Syn4, VFAs without salts), 140mM (Syn5, VFAs+NaCl), to 164mEq.L⁻¹ (Syn6, VFAs+CaCl₂), the retention of Na⁺ decreases gradually.

Indeed, in synthetic broths Syn4 and Syn5, Na⁺ is the only cation in the solution, while in the synthetic broth Syn6, both Na⁺ and Ca²⁺ are presented. The decrease of Na⁺ retention in synthetic broth Syn5 compared to Syn4 could be due to the screening effect, since the total concentration increases from 116mM to 140mM. Then, the decrease of Na⁺ retention in synthetic broth Syn6 could be due to the combination of screening effect and co-ions competition between Na⁺ and Ca²⁺. Current observation is in agreement with the result obtained using XLE membrane. Similar observations are reported in Chapter IV and ref. [147].

VI.1.2 Individual solutes retentions in the real fermentation broth

VI.1.2.1 Nanofiltration using XLE membrane

The previous investigation has shown that the XLE membrane has higher retention of VFAs than the NF-45 membrane at both pH 5.7 and pH 8. When operated at pH 8, retentions of all the VFAs are higher than 98% and nearly no retention difference between VFAs is observed. Therefore, it is difficult to compare the individual solutes retentions at pH 8. In the following section, the investigation of XLE membrane with the real fermentation broth is only made at the initial pH (pH 5.7).

The retentions of all the anions and cations in the real fermentation broth at the initial pH (pH 5.7) are given in Figure VI-7. The concentration of K^+ in the permeate is below the detection limit of the analytical method, thus the retention of K^+ is not shown.

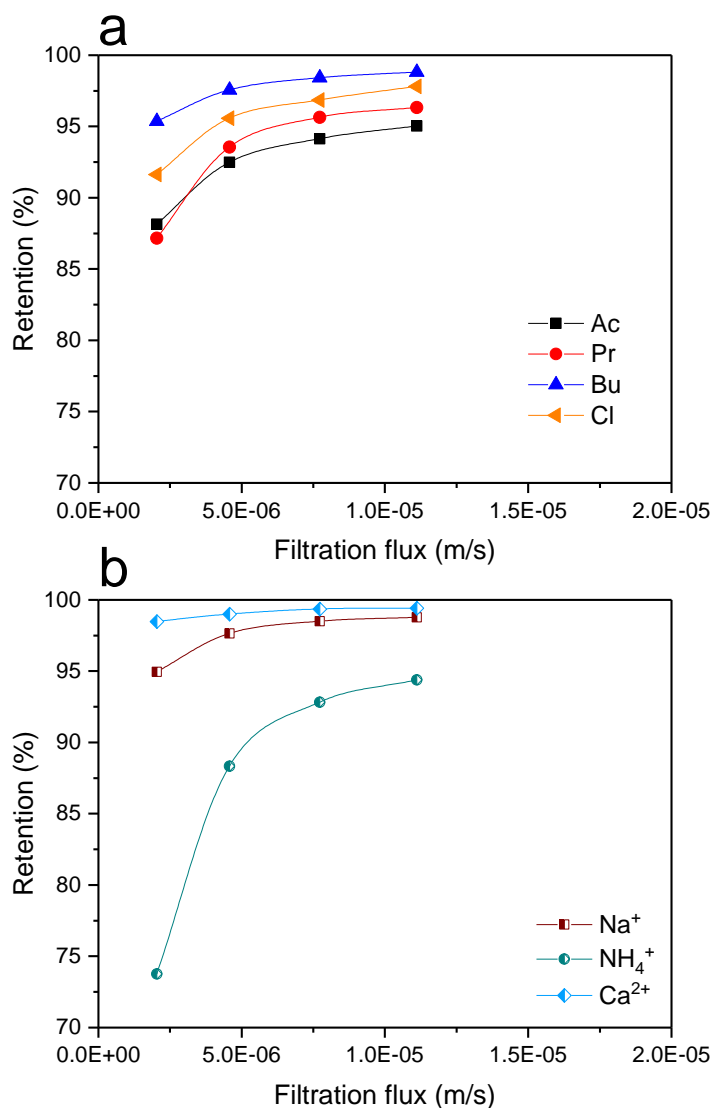


Figure VI-7 Retentions of all the anions (a) and cations (b) in the real fermentation broth using XLE membrane at pH 5.7. The compositions of the real fermentation broth are Ac:Pr:Bu:Cl = 45:31:40:29 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 46:11:4:24 mM for anions and cations respectively.

The retentions of Ac, Pr, and Bu in the real fermentation broth are 95%, 96%, and 99% respectively, at a filtration flux of $1 \times 10^{-5} \text{ m.s}^{-1}$, slightly higher than those in synthetic broths (about 90%, 93%, and 96% for Ac, Pr, and Bu respectively, filtration flux = $1 \times 10^{-5} \text{ m.s}^{-1}$). The retention sequence of VFAs and Cl⁻ is Ac < Pr < Cl⁻ < Bu, the same as that observed in synthetic broths.

For the cations, the retention of the divalent ion, Ca²⁺, observed the highest among all the cations, followed by Na⁺ and NH₄⁺. The retention sequence of all the cations is NH₄⁺ < Na⁺ < Ca²⁺.

The retentions of all the anions and cations are similar to those in the synthetic broths, indicating that the presence of other impurities (e.g. ethanol and butanol) has no significant influence on the retentions of the main components.

VI.1.2.2 Nanofiltration using NF-45 membrane

In Chapter V, it is shown that the retentions of VFAs using NF-45 membrane are significantly influenced by solution pH, high pH is beneficial for VFAs retention as well as separation. Therefore, the following investigations on the real fermentation broth using NF-45 membrane are operated at increasing solution pH (i.e., 5.7, 6.6, and 8.2).

As mentioned in Chapter II, the same batch of VFAs real fermentation broth is used for the experiments using both XLE and NF-45 membranes. The volume of the VFAs real fermentation broth (about 800 mL) is not enough for all the experiments and the retentate and permeate has to be recycled after each experiment.

The real fermentation both at the initial pH (pH 5.7) used for NF-45 membrane was recycled from the retentate and permeate of the previous filtration using XLE membrane. Then, after the filtration using NF-45 membrane, the permeate and retentate were recycled again. The recycled real fermentation broth was adjusted to pH 6.6 using NaOH solution, and filtration is carried out using the pH adjusted real fermentation broth. Finally, the recycled real fermentation broth was adjusted to pH 8.2 and the last filtration is applied using NF-45 membrane.

Due to the recycle and reuse, the compositions of the real fermentation broth slightly modified between different experiments. However, the modification of the compositions between all the four experiments is below 2%.

The retentions of all the anions and cations in the real fermentation broth at pH 5.7, 6.6, and 8.2 are given in Figure VI-8, and the comparison of individual ions retentions at the three pH values are given in Figure VI-9.

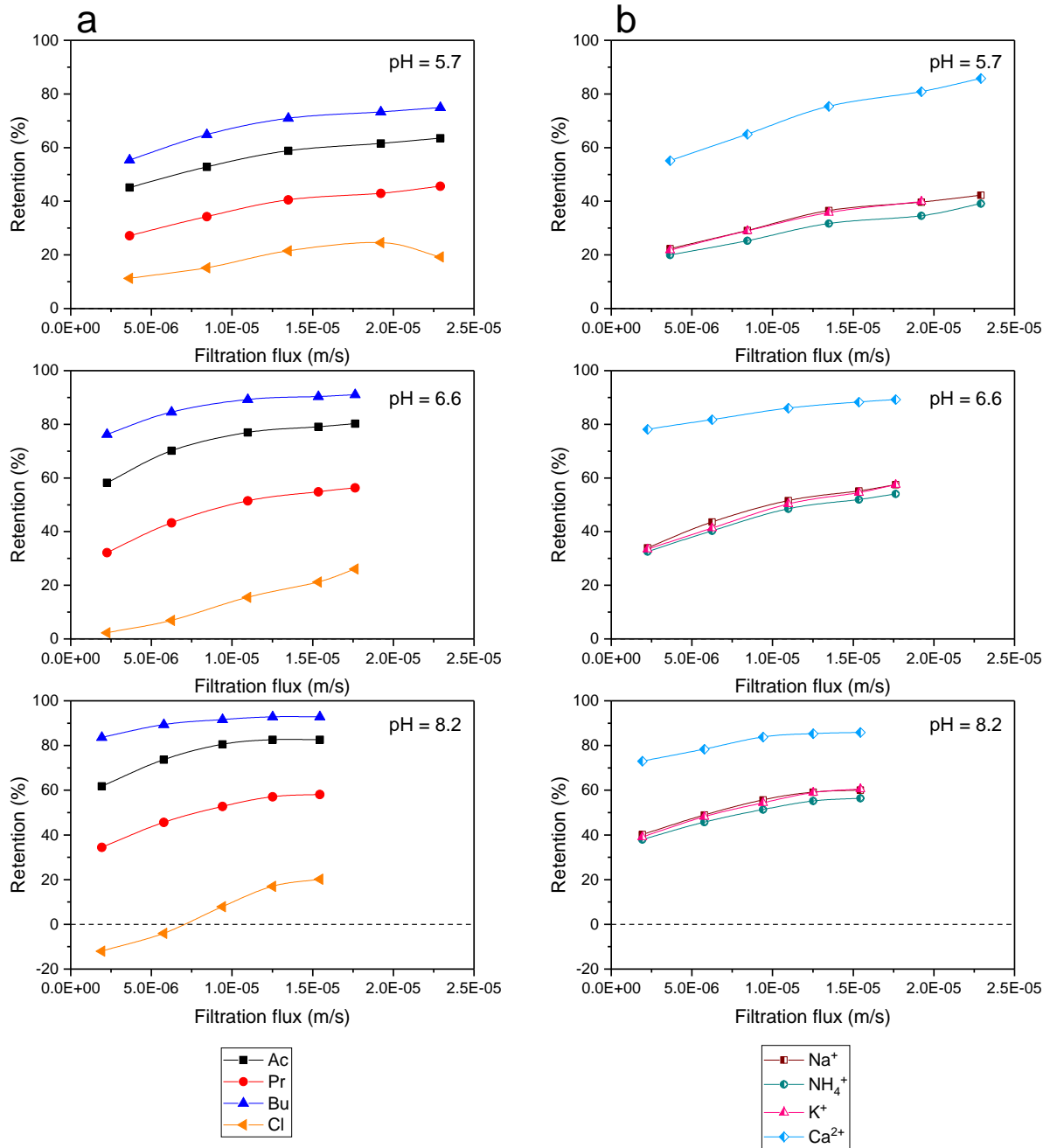


Figure VI-8 Retentions of all the anions (a) and cations (b) in the real fermentation broth at pH 5.7, 6.6, and 8.2 using NF-45 membrane. The compositions of the real fermentation broth are Ac:Pr:Bu:Cl = 45:31:43:27 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 51:11:4:25 mM at pH 5.7, Ac:Pr:Bu:Cl = 43:33:40:26 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 56:11:4:27 mM at pH 6.6, and Ac:Pr:Bu:Cl = 44:30:41:25 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 57:11:4:27 mM at pH 8.2, for anions and cations respectively.

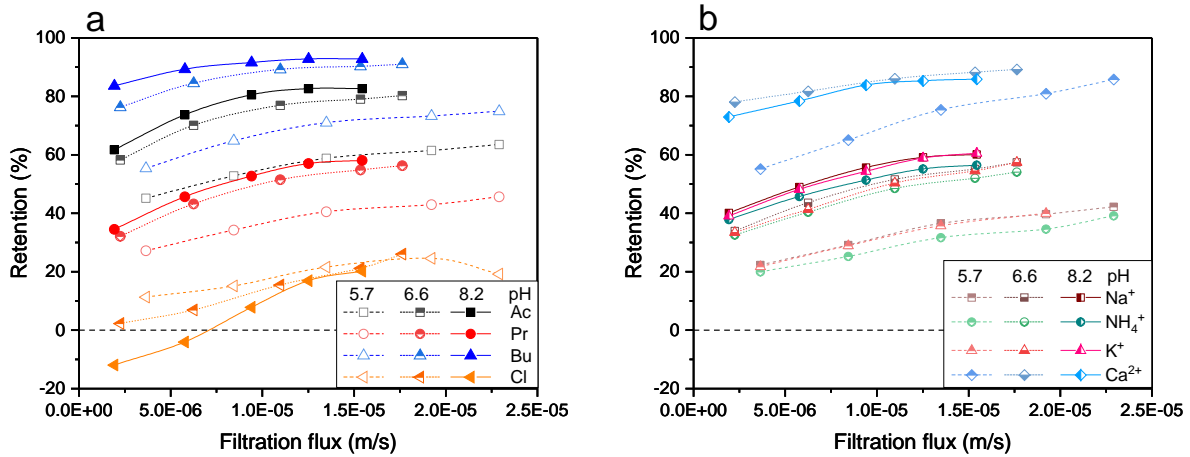


Figure VI-9 Comparison of the retentions of all the anions (a) and cations (b) in the real fermentation broth at pH 5.7, 6.6, and 8.2 using NF-45 membrane. The compositions of the real fermentation broth are Ac:Pr:Bu:Cl = 45:31:43:27 mM, and $\text{Na}^+:\text{NH}_4^+:\text{K}^+:\text{Ca}^{2+} = 51:11:4:25$ mM at pH 5.7, Ac:Pr:Bu:Cl = 43:33:40:26 mM, and $\text{Na}^+:\text{NH}_4^+:\text{K}^+:\text{Ca}^{2+} = 56:11:4:27$ mM at pH 6.6, and Ac:Pr:Bu:Cl = 44:30:41:25 mM, and $\text{Na}^+:\text{NH}_4^+:\text{K}^+:\text{Ca}^{2+} = 57:11:4:27$ mM at pH 8.2, for anions and cations respectively.

For the retentions of anions, it is observed that the retention sequence in the real fermentation broth is $\text{Cl}^- < \text{Pr}^- < \text{Ac}^- < \text{Bu}^-$, for the three pH values investigated. The retention sequence of Ac and Pr is altered compared to that in ternary solutions and synthetic solutions ($\text{Ac}^- < \text{Pr}^- < \text{Bu}^-$).

According to the composition of the real fermentation broth, ethanol is the major component beside VFAs. Experiments for VFAs ternary solutions with the addition of 10mM and 50mM of ethanol were carried out at pH 5.7, in order to test if the presence of ethanol can influence the retention sequence between Ac and Pr. However, the experimental results show that no reverse sequence between the retentions of Ac and Pr is observed.

The alteration of retention sequence of Ac and Pr in a real fermentation broth was also reported by Xiong et al., using Desal DK and DL membrane to filtrate digested liquor at a solution pH of 7 [6]. The mechanism of the alteration in retention sequence is unknown and deserves further investigation.

Then, the retentions of VFAs gradually increase when the solution pH increase from 5.7, 6.6, to 8.2. Meanwhile, the retention of Cl^- continuously decreased when pH increase, a negative value of Cl^- retention is observed at low filtration flux at pH 8.2.

The increase of VFAs retentions and decrease of Cl^- retention when solution pH increases shows the enhancement of co-ions competition between VFAs^- and Cl^- . As discussed in Chapter

IV, this is due to the dissociation of VFAs as well as to the increase of the pH-induced membrane surface charge. A similar observation was reported in ref. [146] too.

For the cations, the retention sequence in the real fermentation broth is $\text{NH}_4^+ < \text{Na}^+ \approx \text{K}^+ < \text{Ca}^{2+}$, at the three pH values investigated (Figure VI-8b). The divalent cation, Ca^{2+} has much higher retention than monovalent cations (Na^+ , K^+ , and NH_4^+). When the solution pH increases, the retentions of the monovalent cations gradually increase. Meanwhile, the retention of Ca^{2+} increases with pH from 5.7 to 6.6, then remains nearly constant when solution pH increases to 8.2. The retention sequence of Ca^{2+} and Na^+ is the same as that observed in single and mixed solutions in Chapter IV (i.e., $\text{Na}^+ < \text{Ca}^{2+}$).

VI.1.3 Removal of organic impurities from the real fermentation broth

The real fermentation broth contains many organic matter/impurities (e.g., ethanol and butanol, as shown in Table VI-1), which could hinder the downstream processes such as PHA production. The TOC of the real fermentation broth can be experimentally obtained (namely TOC), the compositions of VFAs can be also obtained by HPLC analysis. Therefore, the TOC due to the organic matter/impurities (OM) can be obtained as the difference of TOC and the theoretical TOC values of the three VFAs obtained from HPLC (i.e., $\text{TOC}_{\text{OM}} = \text{TOC} - \text{TOC}_{\text{VFAs}}$).

The concentrations of total organic carbon (TOC) in the feed, permeate, and retentate of the real fermentation broth using XLE membrane are measured, and the concentrations are given in Table VI-3. The TOC analysis for the feed, permeate, and retentate of real fermentation broth using NF-45 membrane is not obtained due to that the samples were improperly stored.

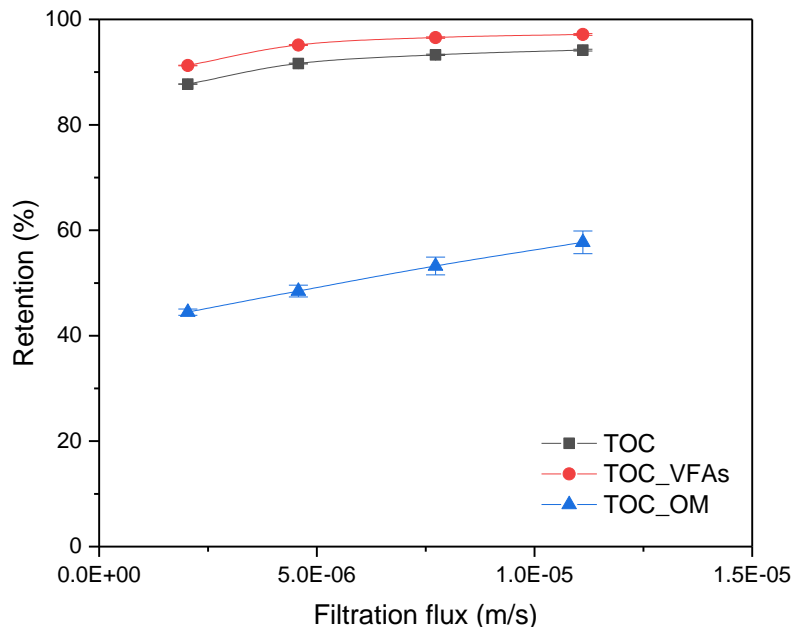
One can observe that VFAs holds more than 90% of the TOC in the real fermentation broth. Then the contribution of VFAs on the TOC in the permeate decrease rapidly as the transmembrane pressure increase. At the transmembrane pressure of 20bar, the contribution of VFAs on the TOC in the permeate is only about 45%.

Table VI-3 Total organic carbon (TOC) in the feed, permeate, and retentate of real fermentation broth using XLE membrane.

Samples	TOC (mg/L)		
	TOC	TOC _{-VFAs}	TOC _{-OM}
Feed	4425±0	4091±0	334±0
8 bar	543±0	358±2	185±2
12 bar	371±0	199±4	172±4
Permeate	298±0	142±6	156±6
20 bar	258±0	117±7	141±7
Retentate	5054±0	4767±0	287±0

The retentions of the TOC of the real fermentation broth (TOC), the TOC of the three VFAs (TOC_{VFAs}), and the TOC of the organic matters/impurities (TOC_{OM}) are given in Figure VI-13.

It is observed that the retention sequence of the TOC of the real fermentation broth, the TOC of the three VFAs, and the TOC of the organic matters/impurities is TOC_{OM}<TOC< TOC_{VFAs}. At the filtration flux of 1×10^{-5} m/s, the retention of TOC_{OM}, TOC, and TOC_{VFAs} are 57%, 94%, and 97% respectively. The retentions of the TOC of the real fermentation broth and the TOC of VFAs are much higher than the retention of TOC_{OM}. This result indicate that it is possible to reject VFAs while remove OM in the retentate.

**Figure VI-10** The retentions of the TOC of real fermentation broth (TOC_{all}), the TOC of the three VFAs (TOC_{VFAs}), and the TOC of the organic matters/impurities (TOC_{VFAs}) using XLE membrane at pH 5.7.

VI.2 Proportions of individual solutes in the permeate of synthetic and real fermentation broths

Following the results of the previous chapters, it is concluded that for a given solute proportion in the feed, there is a fixed solute proportion in the permeate when the filtration flux is higher than a certain value, both for NF-45 membrane and XLE membrane at different pH values investigated. In this section, this finding will be checked with synthetic and real fermentation broths.

VI.2.1 Synthetic fermentation broths

The permeate proportions of all the anions in the six synthetic broths versus filtration flux using XLE and NF-45 membranes at pH 5.7 are given in Figure VI-11. For the six synthetic broths, the VFAs feed proportions are Ac:Pr:Bu=1:1:1 for Syn1, Syn2, and Syn3 filtrated by XLE membrane, and Ac:Pr:Bu=45:31:40 for Syn4, Syn5, and Syn6 filtrated by NF-45 membrane. The addition of NaCl and CaCl₂ changes the feed composition but does not change the VFAs proportion.

One can observe that, for a given solute proportion in the feed, it seems that a given solute proportion in the permeate is obtained, except for low filtration flux, both for VFAs and Cl⁻.

In the permeate of XLE membrane, the proportion of Ac increases compared to that in the feed, while the proportion of Bu and Cl⁻ decrease compared to their proportions in the feed; the proportion of Pr in the permeate only slightly increases compared to that in the feed (Figure VI-11a). In the permeate of NF-45 membrane, the proportions of Ac, Pr, and Bu increase and decrease following the same trend as that in the permeate of XLE membrane. However, the proportion of Cl⁻ increases compared to that in the feed.

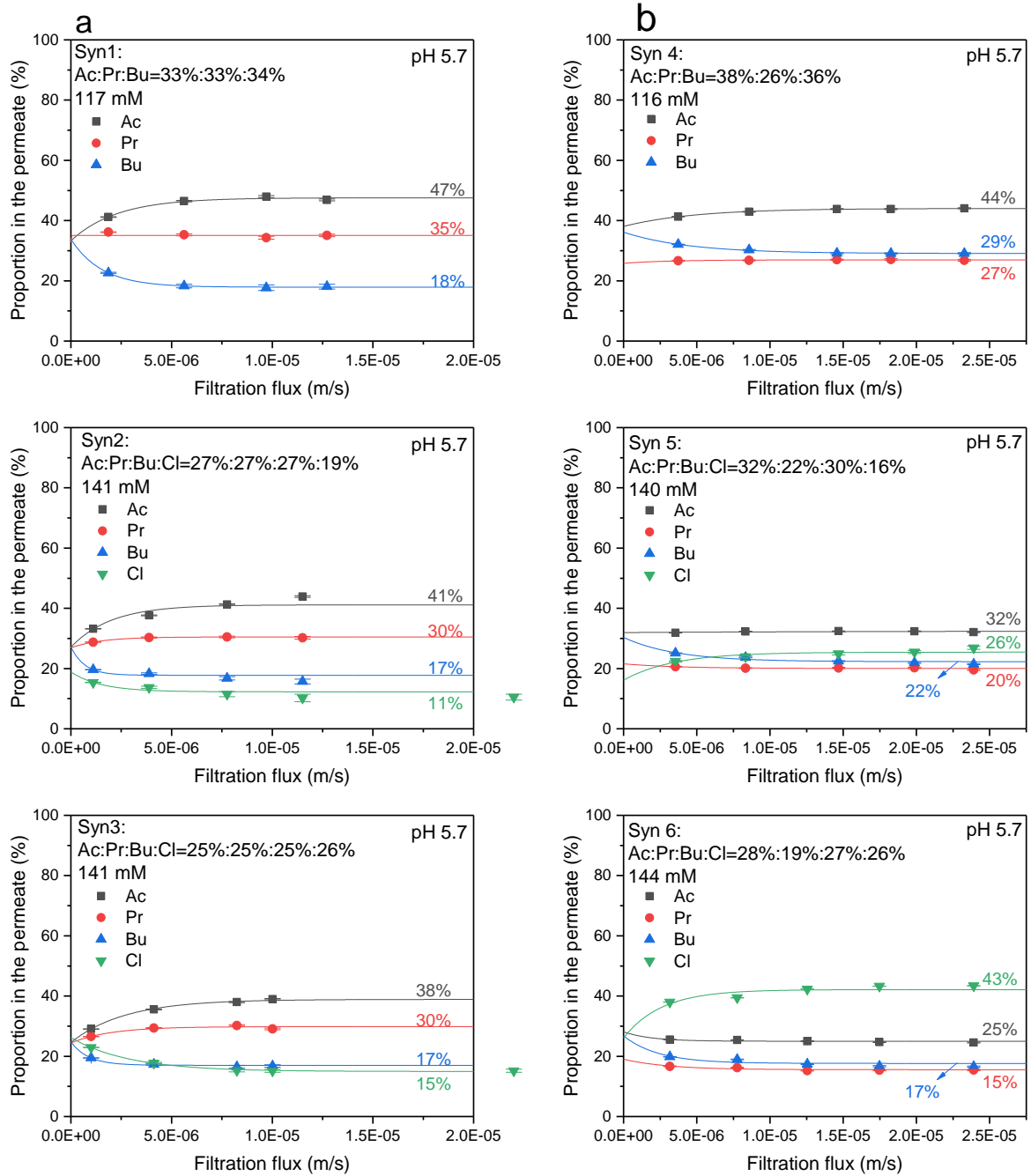


Figure VI-11 Individual solutes proportions in the permeate for the six synthetic broths (Syn1 and Syn4, NaVFAs, Syn2 and Syn5, NaVFAs+NaCl, Syn3 and Syn6, NaVFAs+CaCl₂) at pH 5.7, using (a) XLE membrane (b) NF-45 membrane. Proportions of Ac:Pr:Bu are 1:1:1 for Syn1, Syn2, and Syn3, and 45:31:40 for Syn4, Syn5, and Syn6. 24 mM NaCl is added in Syn2 and Syn4, then 24 mM of CaCl₂ is added in Syn3 and Syn6.

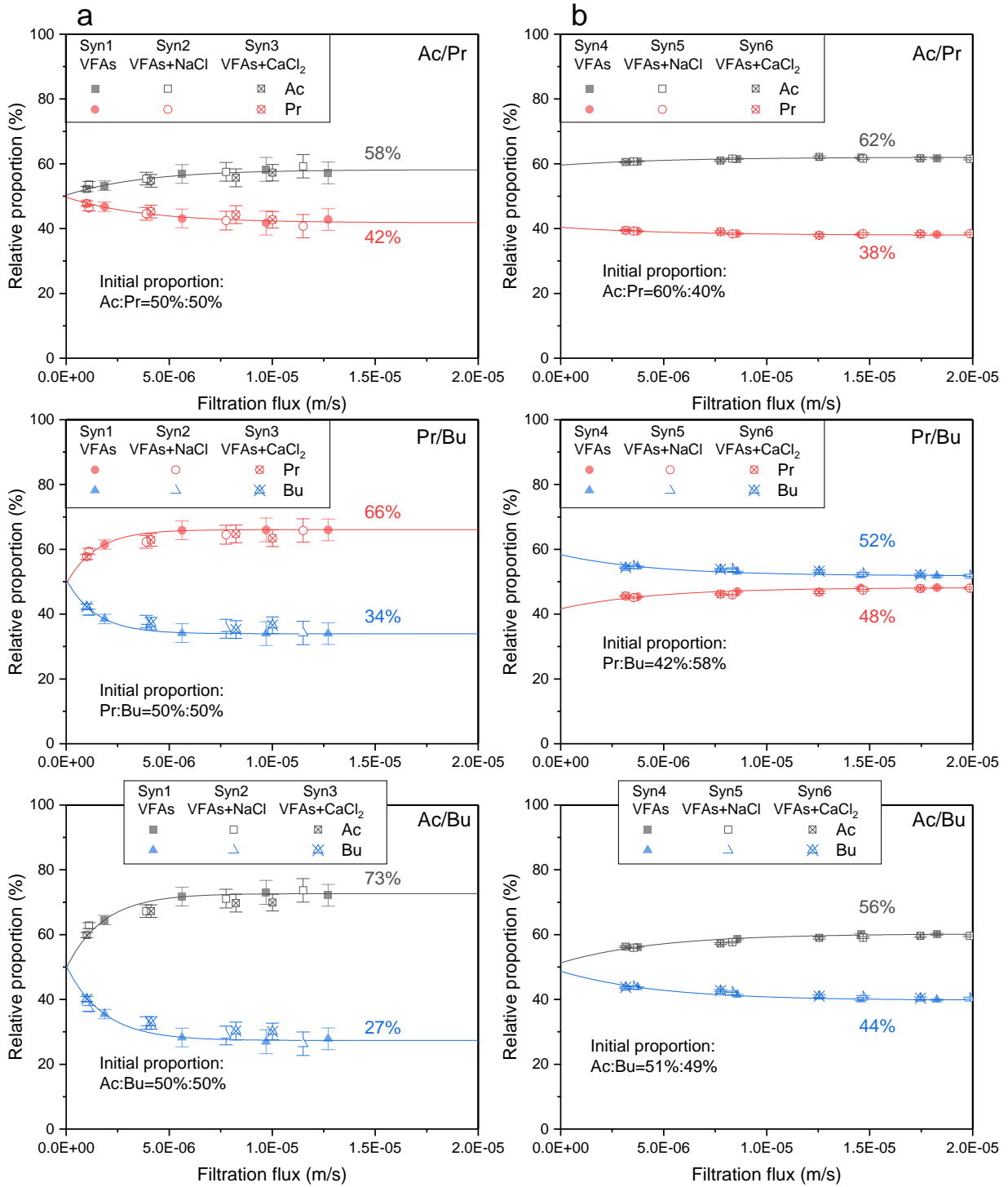


Figure VI-12 Relative VFAs proportions in the permeate versus filtration flux for the six synthetic broths (Syn1 and Syn4, NaVFAs, Syn2 and Syn5, NaVFAs+NaCl, Syn3 and Syn6, NaVFAs+CaCl₂) at pH 5.7, using (a) XLE membrane (b) NF-45 membrane. The initial proportion is given for each condition.

The relative proportions of VFAs is considered to compare the performance of the two membranes on the separation of VFAs. The relative proportion is defined in Chapter II using Eqs. (II.6), (II.7), (II.8), and (II.9). Then, the relative proportions of Ac, Pr, and Bu in the permeate versus filtration flux for the couples of Ac/Pr, Pr/Bu, and Ac/Bu using XLE and NF-45 membranes are given in Figure VI-12.

Considering the couple of Ac/Pr, one can observe that the relative proportion of Ac increases in the permeate compared to that in the feed, while the relative proportion of Pr decreases in the permeate compared to that in the feed, when filtration flux increase. The relative proportions of Ac and Pr in the permeate both reaches a plateau when the filtration flux is higher than a certain value. This observation is found in the permeate of both XLE and NF-45 membranes for the synthetic broths without and with salts. And the same results are observed for the couples of Pr/Bu and Ac/Bu too. Current observation indicates that relative proportions of solutes in the permeate mainly depends on the relative feed proportions, and the addition of inorganic salts does not influence the relative proportion in the permeate. This result is in agreement with that observed in Chapter IV using NF-45 membrane at pH 8,

Then, one can observe that the relative proportion of Ac for the couple of Ac/Pr increases from 50% in the feed to 58% in the permeate (at the plateau value) using XLE membrane. However, for NF-45 membrane, the relative proportion only slightly increased from 60% in the feed to 62% in the permeate (at the plateau value). Similar observations can be found for the couples of Pr/Bu and Ac/Bu. These results indicate that at pH 5.7, XLE membrane can be more efficient to modify the VFAs proportion in the permeate compared to NF-45 membrane.

The proportions of cations (Na^+ and Ca^{2+}) in the permeate of synthetic broths Syn3 and Syn6 using XLE and NF-45 membranes versus filtration flux are given in Figure VI-13.

As observed for anions, the proportion of Na^+ in the permeate increases while the proportion of Ca^{2+} decreases with filtration flux, reached a plateau when the filtration flux is higher than a certain value. In addition, one can observe that with the feed proportions of Na^+ and Ca^{2+} similar in Syn3 and Syn6 (67%:33% and 69%:31% respectively), the same proportion in the permeate ($\text{Na}^+:\text{Ca}^{2+}=91\%:9\%$) is observed using both XLE and NF-45 membranes. This shows that the two membranes have similar capabilities to the modification of Na^+ and Ca^{2+} proportions, when the filtration flux is higher than a certain value.

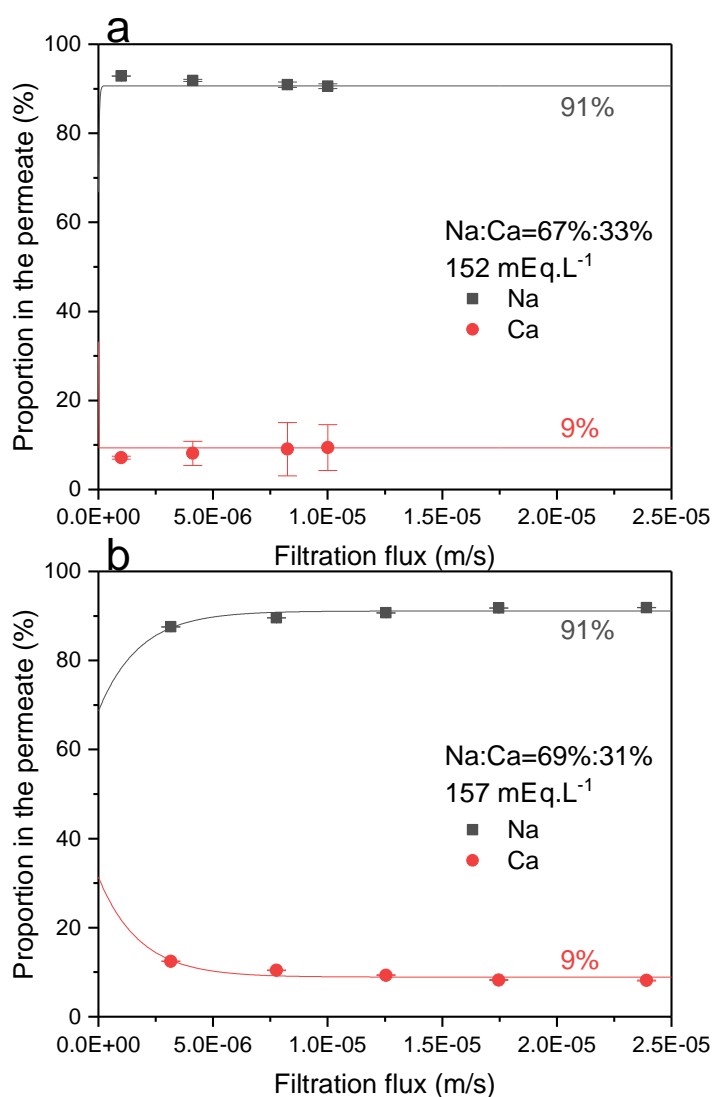


Figure VI-13 Proportion of cations in the permeate for synthetic broths (Syn3 and Syn6, NaVFAs+CaCl₂), using (a) XLE membrane, (b) NF-45 membrane. The proportion of cations in the feed are given for each condition.

VI.2.2 Real fermentation broth

The proportions of individual anions and cations in the permeate of the real fermentation broth versus filtration flux using XLE membrane are given in Figure VI-14.

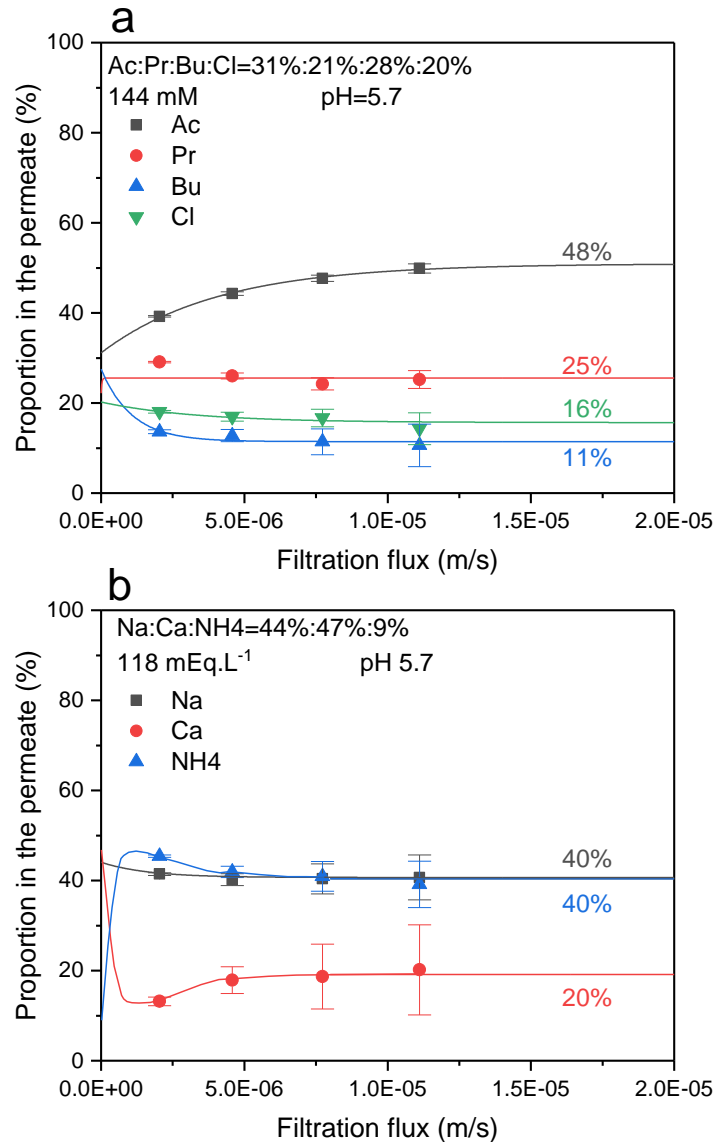


Figure VI-14 Solutes proportions in the permeate of the real fermentation broth versus filtration flux using XLE membrane, (a) anions, (b) cations. The compositions of the real fermentation broth are Ac:Pr:Bu:Cl = 45:31:30:29 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 46:11:4:24 mM for anions and cations respectively.

It is observed that the proportions of Ac increase, Bu and Cl⁻ decrease, while Pr remain nearly constant when the filtration flux increases. The proportions of all the anions reach constant values when the filtration flux is higher than a certain level, as observed for synthetic broths.

For the cations, it is shown that the proportion of Na⁺ decreases when the filtration flux increases, reached a constant proportion of 40% when the filtration flux is higher than a certain value. This result is in agreement with that observed for synthetic broths.

However, the proportions of Ca^{2+} and NH_4^+ show different behaviors. The proportion of Ca^{2+} in the permeate is much lower than that in the feed, while the proportion of NH_4^+ in the permeate is much higher than that in the feed. When the filtration flux increases, the permeate proportion of Ca^{2+} increases, meanwhile the permeate proportion of NH_4^+ decreases before reach a constant proportion when the filtration flux is higher than a certain value. This behavior is also observed for the proportions of cations in the permeate of synthetic broth (Syn 3, shown in Figure VI-13).

For NF-45 membrane, it is always observed that the differences between the individual solutes proportions in the permeate continuously increase when the filtration flux increase, and reached a constant value when the filtration flux is higher than a certain value. The same observation is found for anions using XLE membrane. However, when the proportion of cations in the permeate is considered using XLE membrane, it seems that different behavior is observed. The differences between individual cations proportions in the permeate firstly reach the highest value at the lowest filtration flux investigated, then decrease when the filtration flux increase, before reaching a constant value when the filtration flux is higher than a given level. This abnormal behavior requires further investigation.

The anions and cations proportions in the permeate of the real fermentation broth using NF-45 membrane at pH 5.7, 6.6, and 8.2 are given in Figure VI-15.

As for synthetic broths, one can observe that the proportions of individual anions in the permeate change with filtration flux, the proportion of Cl^- and Pr increase while the proportions of Ac and Bu decrease, reach a plateau when the filtration flux is higher than a certain value for the three pH investigated.

For the cations, the proportions of monovalent cations, Na^+ , NH_4^+ , and K^+ in the permeate all increase, while the proportion of Ca^{2+} decreases, for the three pH investigated. It is noticed that except for the proportions of Na^+ and Ca^{2+} in the permeate at pH 5.7, a constant proportion is observed for each cation when the filtration flux is higher than a given value.

In addition, one can observe that when the solution pH increases, the filtration flux required to obtain the constant permeate proportion significantly decreases from more than $1.25 \times 10^{-5} \text{ m.s}^{-1}$ at pH 5.7, to about $0.5 \times 10^{-5} \text{ m.s}^{-1}$ at pH 8.2. This is in agreement with what was observed for VFAs ternary solutions in Chapter V.

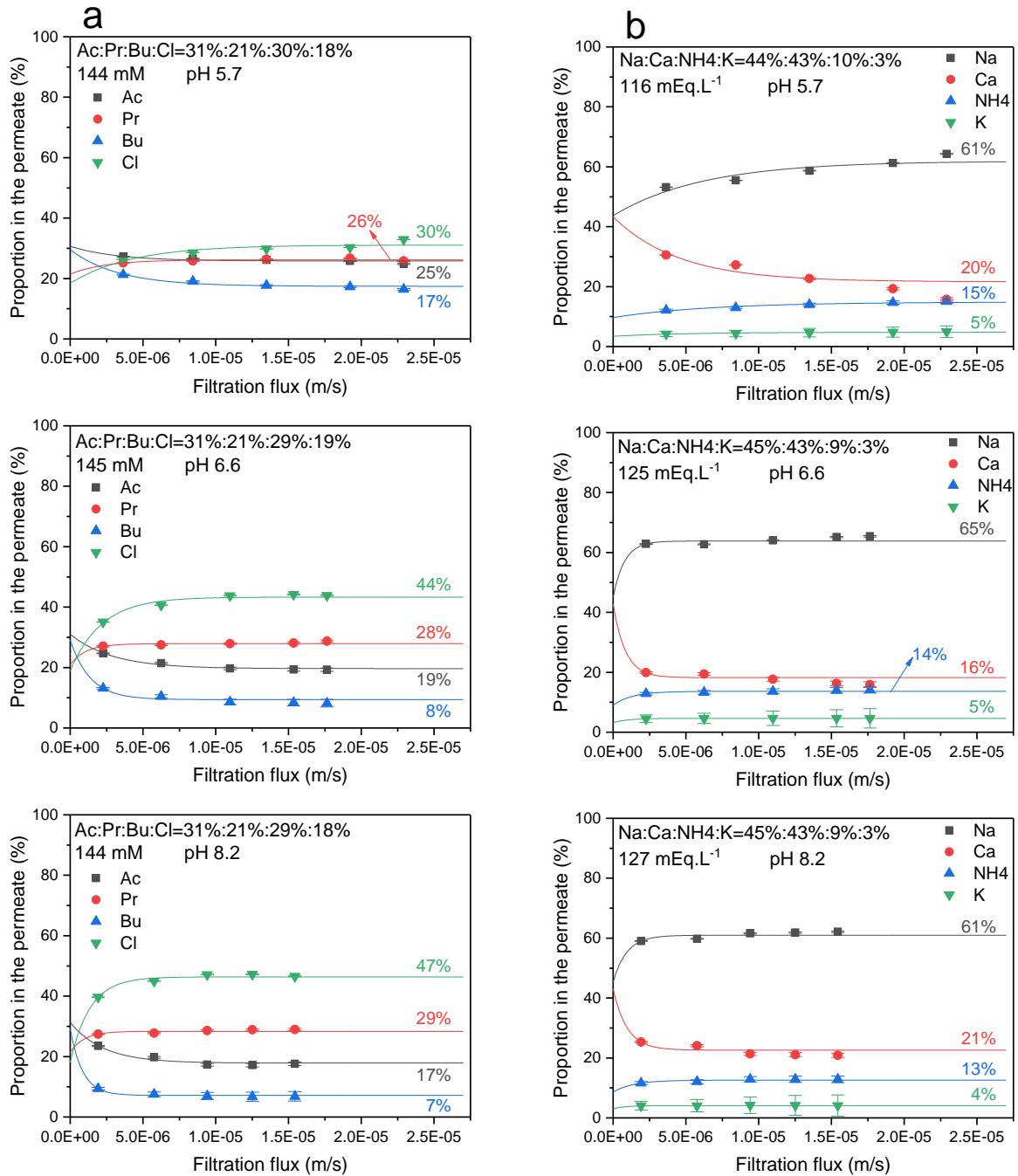


Figure VI-15 Solutes proportions in the permeate of NF-45 membrane for the real fermentation broth at three pH values, (a) anions (b) cations. The compositions of the real fermentation broth are Ac:Pr:Bu:Cl = 45:31:43:27 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 51:11:4:25 mM at pH 5.7, Ac:Pr:Bu:Cl = 43:33:40:26 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 56:11:4:27 mM at pH 6.6, and Ac:Pr:Bu:Cl = 44:30:41:25 mM, and Na⁺:NH₄⁺:K⁺:Ca²⁺ = 57:11:4:27 mM at pH 8.2, for anions and cations respectively.

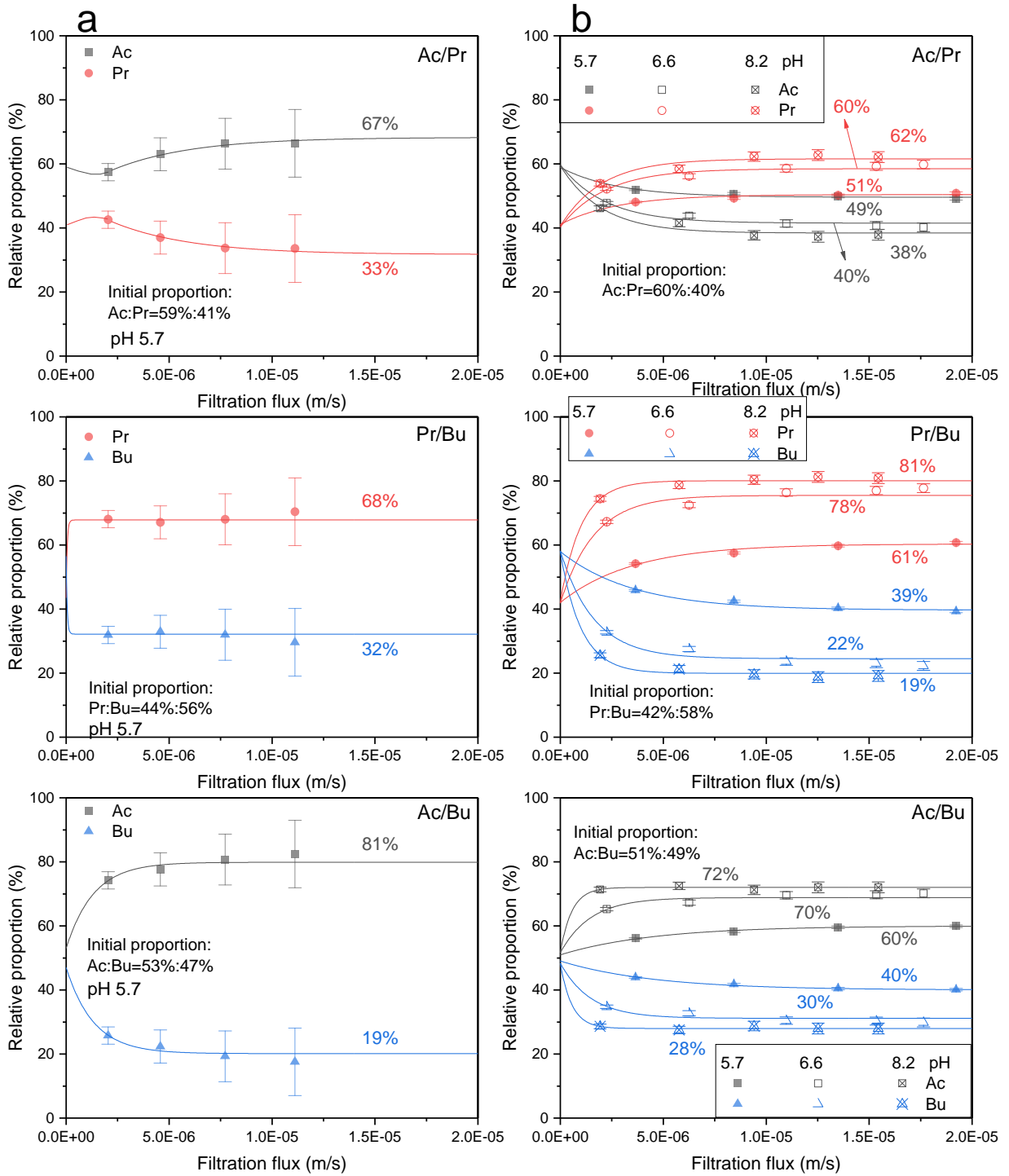


Figure VI-16 Relative VFAs proportions in the permeate versus filtration flux for the real fermentation broth at pH 5.7, 6.6, and 8.2, using (a) XLE membrane (b) NF-45 membrane. The relative proportion in the feed is given for each condition.

The relative proportion of VFAs in the permeate of XLE and NF-45 membranes for the real fermentation broth are given in Figure VI-16.

For the permeate of XLE membrane, one can observe that the proportion of Ac increases, while the proportion of Pr decreases when the filtration flux increases for the couple of Ac/Pr. However, the reverse trend is observed for the couple of Ac/Pr in the permeate of NF-45 membrane, the proportion of Pr increases while the proportion of Ac decreases when the filtration flux increases. For the couples of Pr/Bu and Ac/Bu, the proportion of Bu decreases in the permeate while the proportions of Pr and Ac increase in the permeate when the filtration flux increases, for the permeates of both XLE and NF-45 membranes.

For the permeate of NF-45 membrane, one can observe that when the pH increases from 5.7, 6.6, to 8.2, the differences between the relative proportions of VFAs in the permeate enlarged. For the same VFAs feed proportions, the higher the difference between VFAs proportions in the permeate, the better the separation. Therefore, this observation indicates that best separation between VFAs is observed at the highest pH for NF-45 membrane.

For a given feed composition, the previous investigation has shown that the best separation is obtained when the permeate proportion reaches the plateau value. Therefore, the following discussion and comparison use the relative proportions at the plateau value.

To compare the performances of the two membranes for VFAs separation in the synthetic solutions/broths and real fermentation broth, the relative proportions of individual VFA in the permeate (at the plateau value) versus that in the feed are given in Figure VI-17. For XLE membrane, synthetic and real fermentation broths at pH 5.7 are compared. For NF-45 membrane, synthetic broths at pH 5.7, as well as the real fermentation broth at pH 5.7, 6.6, and 8.2 are compared. The results for synthetic solutions with and without the addition of salts at pH 8 using NF-45 membrane shown in Chapter IV are also given for comparison.

The relative proportions of two solutes in the feed and permeate represent the separation performance of NF on the two solutes. Indeed, as defined, the separation factor between the two solutes can be calculated from their proportions in the feed and permeate use Eq.(II.11). Therefore, for a given feed proportion, the separation factor is the quotient of the relative proportions of the two solutes in the permeate, the more difference between the proportions of the two solutes in the permeate, the higher the separation performance.

For the results using XLE membrane at pH 5.7, one can observe that the relative proportions of Ac and Pr in the feed and permeate of synthetic and real fermentation broths for the couple of Ac/Pr can be fitted with one single curve. Then, when the relative proportions of Bu in the feed are about 50%, the proportions of Bu in the permeate obtained for the real fermentation broth are about 10% and 6% lower than that observed for synthetic broths, for the couples of Pr/Bu and Ac/Bu respectively.

For the results using NF-45 membrane at various pH values, firstly, it is observed that the relative proportions of Ac and Pr in the feed and permeate in the real fermentation is the reverse compared to that in the synthetic broths for the couple of Ac/Pr.

At pH 5.7 and pH 8, one can observe that the relative proportions of Pr and Ac in the permeate of the real fermentation broth are always higher than those observed in the synthetic solutions/broths. The improvement for the couple Pr/Bu is much significant compared to that of the couple of Ac/Bu. Indeed, for the couple of Ac/Bu, the relative proportions of Ac and Bu in the feed and permeate for synthetic solutions/broths and the real fermentation broth are similar both for pH 5.7 and 8.

Current results show that the performance of XLE membrane on the separation of VFAs is similar for synthetic and real fermentation broths. The presence of organic and inorganic components in the real fermentation broth does not influence the separation performance of XLE membrane on VFAs. For NF-45 membrane, the separation performance between Ac and Bu is nearly the same for synthetic and real fermentation broths at pH 5.7 and 8, showing the negligible influence of organic and inorganic components in the real fermentation broth. However, the mass transfer of Pr is greatly improved in the real fermentation broth, meaning that there is an additional mechanism improving the membrane separation performance (i.e., the enhancement of the transfer of Pr in real fermentation broth compared to that in synthetic solutions).

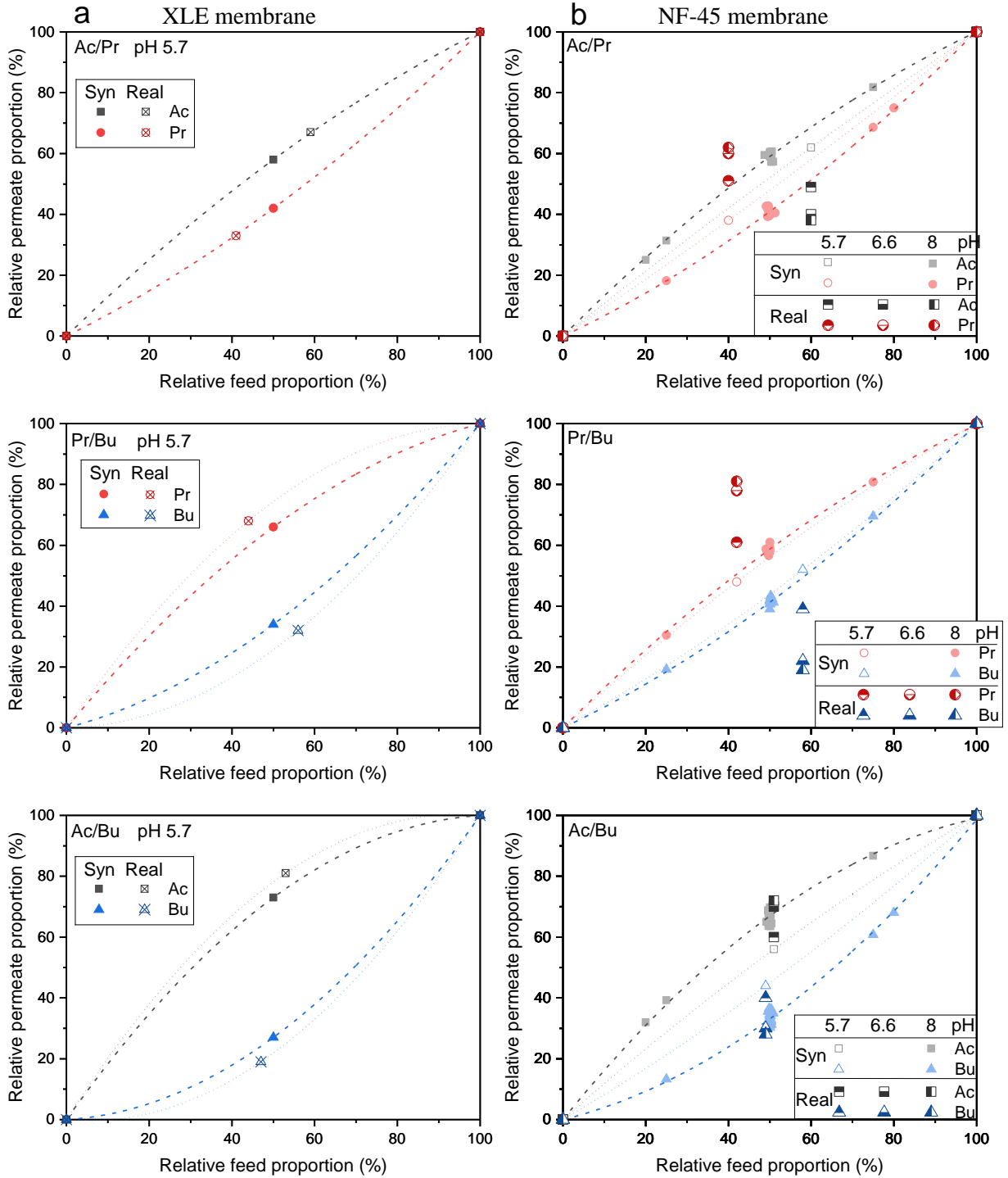


Figure VI-17 Relative proportions of VFAs in the permeate versus relative proportions of VFAs in the feed for synthetic solutions/broths and the real fermentation broth using (a) XLE membrane (b) NF-45 membrane. For XLE membrane, the pH for synthetic and real fermentation broths is 5.7. For NF-45 membrane, pH 5.7 and 8 are investigated for synthetic solutions/broths, and pH 5.7, 6.6, and 8.2 are studied for the real fermentation broth.

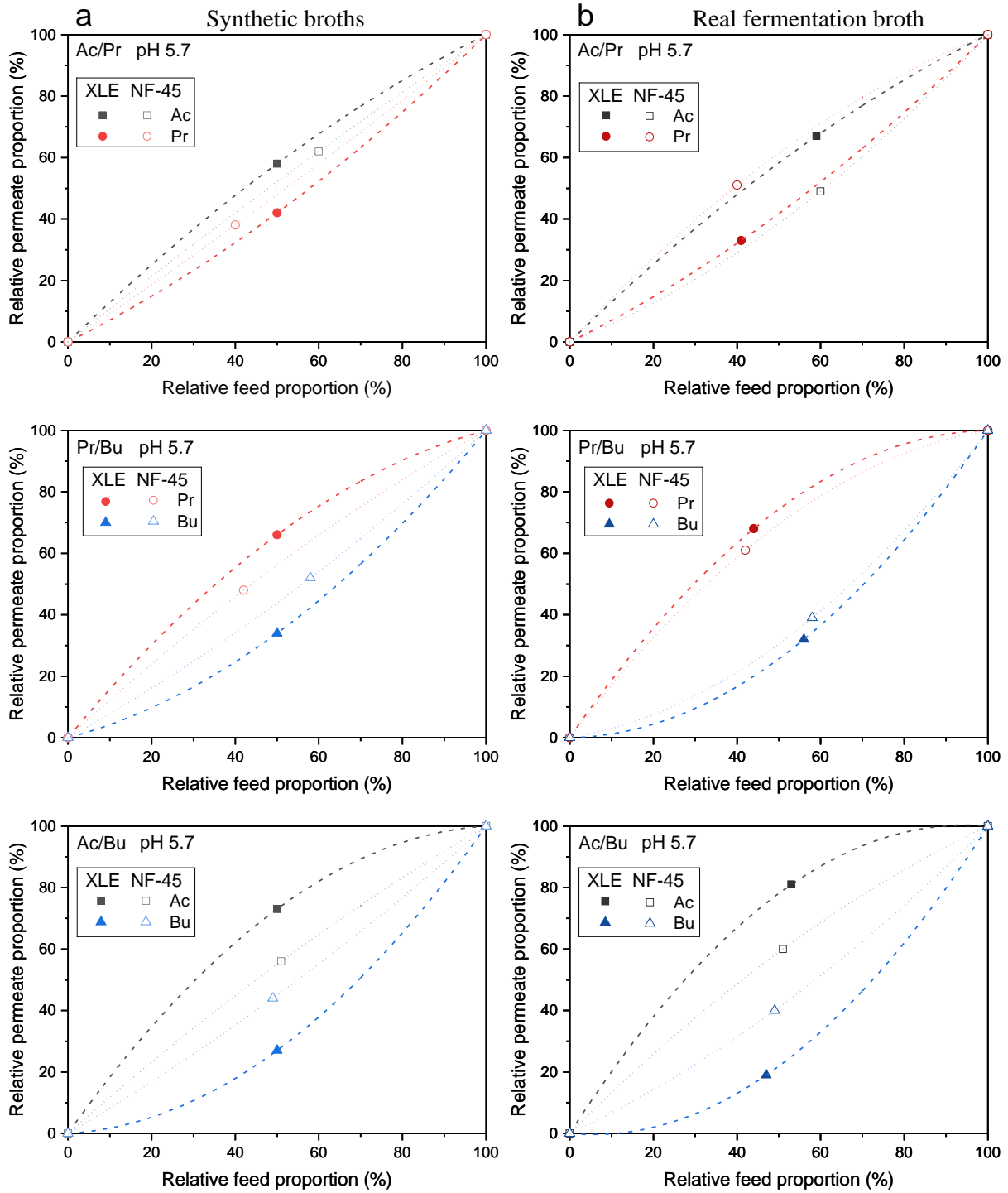


Figure VI-18 Comparison of the relative proportions of VFAs for the (a) synthetic broths and the (b) real fermentation broth in the feed and permeate using XLE and NF-45 membranes at pH 5.7, for the couples of Ac/Pr, Pr/Bu, and Ac/Bu.

The comparison between the relative proportions of VFAs in the feed and permeate for the synthetic and real fermentation broth using XLE and NF-45 membranes at pH 5.7 is given in Figure VI-17. One can observe that, for synthetic broths, the differences between the relative proportions of the two VFAs out of three are higher for XLE membrane for all the three couples compared to NF-45 membrane. Then, for the real fermentation broth, the differences between the relative proportions of the two VFAs out of three are similar for the couples of Ac/Pr and Pr/Bu, for the couple of Ac/Bu, the difference between the permeate proportions of Ac and Bu for XLE membrane is much larger than that of NF-45.

VI.2.3 TOC proportions of VFAs and organic matters/impurities (OM) in the permeate of the real fermentation broth

The proportions of TOC corresponding to VFAs and TOC corresponding to other OM in the permeate versus filtration flux are given in Figure VI-19.

As observed for individual solutes proportion, the proportion of TOC of VFAs decreases while the proportion of TOC of OM increases when the filtration flux increases. The proportions of both VFAs and OM reach a plateau once the filtration flux is higher than a certain value. This observation confirms that, for a mixed solution as complex as a real fermentation broth, when the feed proportion is fixed, one given permeate proportion can be observed when the filtration flux is higher than a certain value.

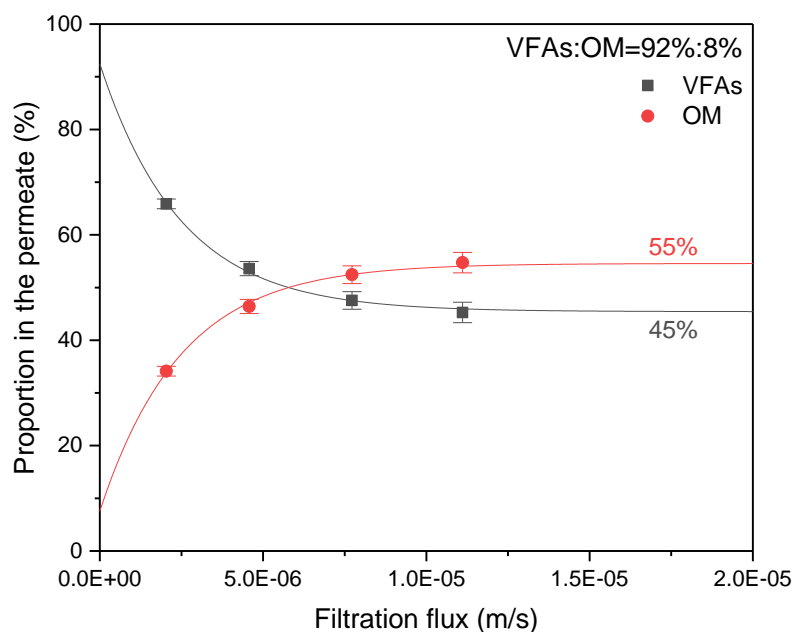


Figure VI-19 TOC of VFAs, and TOC of organic matters (OM) proportions in the permeate of XLE membrane for the real fermentation broth.

One can also observe that the TOC corresponding to VFAs in the permeate are dramatically decreases from 92% in the feed to 45% in the permeate at the plateau value, while the proportion of TOC corresponding to OM increases from 8% in the feed to 55% in the permeate at the plateau value. Then, regarding TOC, NF with XLE membrane provides a retentate significantly enriched in VFAs.

VI.3 Performances of NF for the treatment of VFAs fermentation broth

The applications of NF for the treatment of real fermentation broth containing VFAs can have many possibilities. Three kinds of applications are discussed, which are (1) inorganic salts removal, (2) VFAs composition modification (Individual VFAs separation), and (3) organic matter (OM) removal.

VI.3.1 Case 1: Inorganic salts removal

Inorganic salts are usually unfavorable and even considered as an impediment for biological applications. To remove the inorganic salts, the separation between VFAs (as a total) and Cl^- as well as Ca^{2+} and Na^+ is discussed.

The proportions of VFAs and Cl^- in the feed and permeate (at the constant values), as well as the separation factor between VFAs/ Cl^- are given in Table VI-4. The separation factor between VFAs and Cl^- is calculated using Eq.(II.11). For the results with XLE membrane, VFAs are enriched in the permeate. Therefore, the calculation uses the ratio of VFAs and Cl^- in the permeate divided by the ratio of VFAs and Cl^- in the feed (shown in Eq. (VI.3)). When the feed proportion is the same, the separation factor is the quotient of the proportion of the permeate proportions of VFAs and Cl^- .

$$SF_{(VFAs/Cl^-_{XLE})} = (p_{VFAs}^p/p_{Cl^-}^p)/(p_{VFAs}^f/p_{Cl^-}^f) \quad (\text{VI.3})$$

For the results using NF-45 membrane, the separation factor is obtained using the ratio of VFAs and Cl^- in the feed divided by the ratio of VFAs and Cl^- in the permeate (shown in Eq. (VI.4)).

$$SF_{(VFAs/Cl^-_{NF-45})} = (p_{VFAs}^f/p_{Cl^-}^f)/(p_{VFAs}^p/p_{Cl^-}^p) \quad (\text{VI.4})$$

Table VI-4 Proportions of VFAs and Cl^- in the feed and permeate as well as the separation factor between VFAs/ Cl^- for the real fermentation broth

pH	XLE membrane					NF-45 membrane				
	Feed		permeate		Separation factor	Feed		permeate		Separation factor
	VFAs	Cl^-	VFAs	Cl^-		VFAs	Cl^-	VFAs	Cl^-	
5.7	0.80	0.20	0.84	0.16	1.3	0.82	0.18	0.69	0.31	2.0
6.6						0.81	0.19	0.56	0.44	3.4
8.2						0.82	0.18	0.53	0.47	4.0

One can observe that the proportion of Cl^- decreases in the permeate of XLE membrane (from 20% to 16%), while increases in the permeate of NF-45 membrane, for the three pH values investigated. It is shown that the separation factor between VFAs and Cl^- is 1.3 at initial pH (5.7) using XLE membrane, while increased to 2.0 using NF-45 at the same pH. Then, when the solution pH increases to 6.6 and 8.2, the separation factor between VFAs and Cl^- increases to 3.4 and 4.0 respectively. Current results show that NF-45 has much better separation performance on VFAs and Cl^- compared to XLE membrane.

The proportion of Ca^{2+} and Na^+ in the feed and permeate (at the constant values) as well as the separation factor between $\text{Na}^+/\text{Ca}^{2+}$ are given in Table VI-5. It is observed that the proportion of Na^+ in the permeate increases with the two membranes for all the pH investigated. Then, the

separation factor between Ca^{2+} and Na^+ is 2.3 using XLE membrane, while increases to 3.2 using NF-45 membrane at the initial pH (5.7).

Then, despite the separation factor between Ca^{2+} and Na^+ using NF-45 membrane can vary when the solution pH increases from 5.7, 6.6 to 8.2, it is observed that the proportion of Ca^{2+} and Na^+ in the permeate are $63\% \pm 2\%$ and $19\% \pm 2\%$ respectively. This shows that the pH seems does not influence the separation between Ca^{2+} and Na^+ .

Table VI-5 Proportions of Na^+ and Ca^{2+} in the feed and permeate as well as the separation factor between $\text{Na}^+/\text{Ca}^{2+}$ for the real fermentation broth

pH	XLE membrane					NF-45 membrane				
	Feed		permeate		Separation factor	Feed		permeate		Separation factor
	Na^+	Ca^{2+}	Na^+	Ca^{2+}		Na^+	Ca^{2+}	Na^+	Ca^{2+}	
5.7	0.44	0.47	0.40	0.19	2.3	0.44	0.43	0.61	0.19	3.2
6.6						0.45	0.43	0.65	0.17	3.7
8.2						0.45	0.43	0.62	0.21	2.8

Table VI-6 Proportions of monovalent (i.e., Na^+ , NH_4^+ , and K^+) and divalent (i.e., Ca^{2+}) cations in the feed and permeate as well as the separation factor between monovalent/divalent cations for the real fermentation broth

pH	XLE membrane					NF-45 membrane				
	Feed		permeate		Separation factor	Feed		permeate		Separation factor
	mono	di	mono	di		mono	di	mono	di	
5.7	0.53	0.47	0.81	0.19	3.8	0.57	0.43	0.81	0.19	3.2
6.6						0.57	0.43	0.83	0.17	3.7
8.2						0.57	0.43	0.79	0.21	2.8

Then, considering the separation between monovalent (i.e., Na^+ , NH_4^+ , and K^+) and divalent (i.e., Ca^{2+}) cations, the proportions of monovalent and divalent cations in the feed and permeate for the two membranes at different pH are listed in Table VI-6.

For monovalent cations, one can observe that the proportion in the feed is $55\% \pm 2\%$, then a proportion of $81\% \pm 2\%$ in the permeate is observed for the two membranes at different pH values. The current observation is in agreement with the result observed for synthetic broths (i.e., Syn3 and Syn6) using XLE and NF-45 membranes. It seems that the two membranes have similar performance for the separation of monovalent and divalent cations.

Comparing the results in Table VI-5 and Table VI-6, for NF-45 membrane, it is noticed that the separation performance on $\text{Na}^+/\text{Ca}^{2+}$ and mono/divalent cations are the same. However, for XLE membrane, the separation performance on $\text{Na}^+/\text{Ca}^{2+}$ is lower than that of mono/divalent cations, this is due to the proportion of NH_4^+ increased from 9% in the feed to 40% in the permeate (shown in Figure VI-14).

It is concluded that better separation factors between Cl^-/VFAs and $\text{Na}^+/\text{Ca}^{2+}$ are observed using NF-45 membrane compared to that observed using XLE membrane. Furthermore, increasing the solution pH from 5.7 to 8.2 can double the separation factor between Cl^-/VFAs , while much less influence of solution pH is observed on the separation factor between $\text{Na}^+/\text{Ca}^{2+}$. In general, by using NF-45 membrane, Na^+ and Cl^- in the real fermentation broth is enriched in the permeate, while Ca^{2+} and VFAs^- is enriched in the retentate.

VI.3.2 Case 2: VFAs composition modification

As introduced in Chapter I, VFAs composition is critical for the following applications like PHA (polyhydroxyalkanoates) and bioenergy productions. Higher proportions of Ac and Pr are more favorable for bioenergy production, while higher Bu proportion is beneficial for the production of PHA. In order to compare the ability of the two membranes on the modification of VFAs compositions, the proportions and separation factors between Ac/Pr, Pr/Bu, and Ac/Bu are considered separately.

The separation factor between the two solutes in a couple can be directly calculated from the relative proportions in the feed and permeate, as previously discussed.

The proportions of Ac, Pr, and Bu in the feed and permeate, as well as the separation factors between Ac/Pr, Pr/Bu, and Ac/Bu using the two membranes at different pH values are listed in Table VI-7.

Table VI-7 Proportions of VFAs in the feed and permeate as well as the separation factor between VFAs for the couples of Ac/Pr, Pr/Bu, and Ac/Bu for the real fermentation broth

Couples	pH	XLE membrane					NF-45 membrane				
		Feed		permeate		Separation factor	Feed		permeate		Separation factor
		Ac	Pr	Ac	Pr		Ac	Pr	Ac	Pr	
Ac/Pr	5.7	0.31	0.21	0.56	0.3	1.3	0.31	0.21	0.37	0.38	1.5
	6.6						0.31	0.21	0.35	0.5	2.2
	8.2						0.31	0.21	0.33	0.54	2.4
Pr/Bu	5.7	0.21	0.28	0.3	0.14	2.8	0.21	0.3	0.38	0.25	2.1
	6.6						0.21	0.29	0.5	0.15	4.7
	8.2						0.21	0.29	0.54	0.13	5.8
Ac/Bu	5.7	0.31	0.28	0.56	0.14	3.6	0.31	0.3	0.37	0.25	1.4
	6.6						0.31	0.29	0.35	0.15	2.2
	8.2						0.31	0.29	0.33	0.13	2.4

At the initial pH (5.7), one can observe that the separation factor between Ac/Pr obtained using NF-45 membrane is higher than that obtained using XLE membrane, while the separation factors between Pr/Bu and Ac/Bu shown the reverse. Then, when increasing the solution pH, the separation factors between VFAs observed using NF-45 all increase, the highest values are all observed at pH 8.2.

Figure VI-20 gives the separation factors between Ac/Pr, Pr/Bu, and Ac/Bu in synthetic solutions (Ac:Pr:Bu=33%:33%:33%) and real fermentation broths versus solution pH using XLE and NF-45 membranes. For XLE membrane, one can observe that the separation factors decrease when solution pH increases. The separation factors between VFAs observed with real fermentation broth are higher than those observed with synthetic solutions, except for Ac/Pr. For NF-45 membrane, it is shown that the separation factors increase when the solution pH increases. The separation factors between Ac/Pr and Pr/Bu in the real fermentation broth are much higher than that observed in synthetic solutions. However, the separation factor between Ac/Bu is similar (slightly higher) to that observed in synthetic solutions.

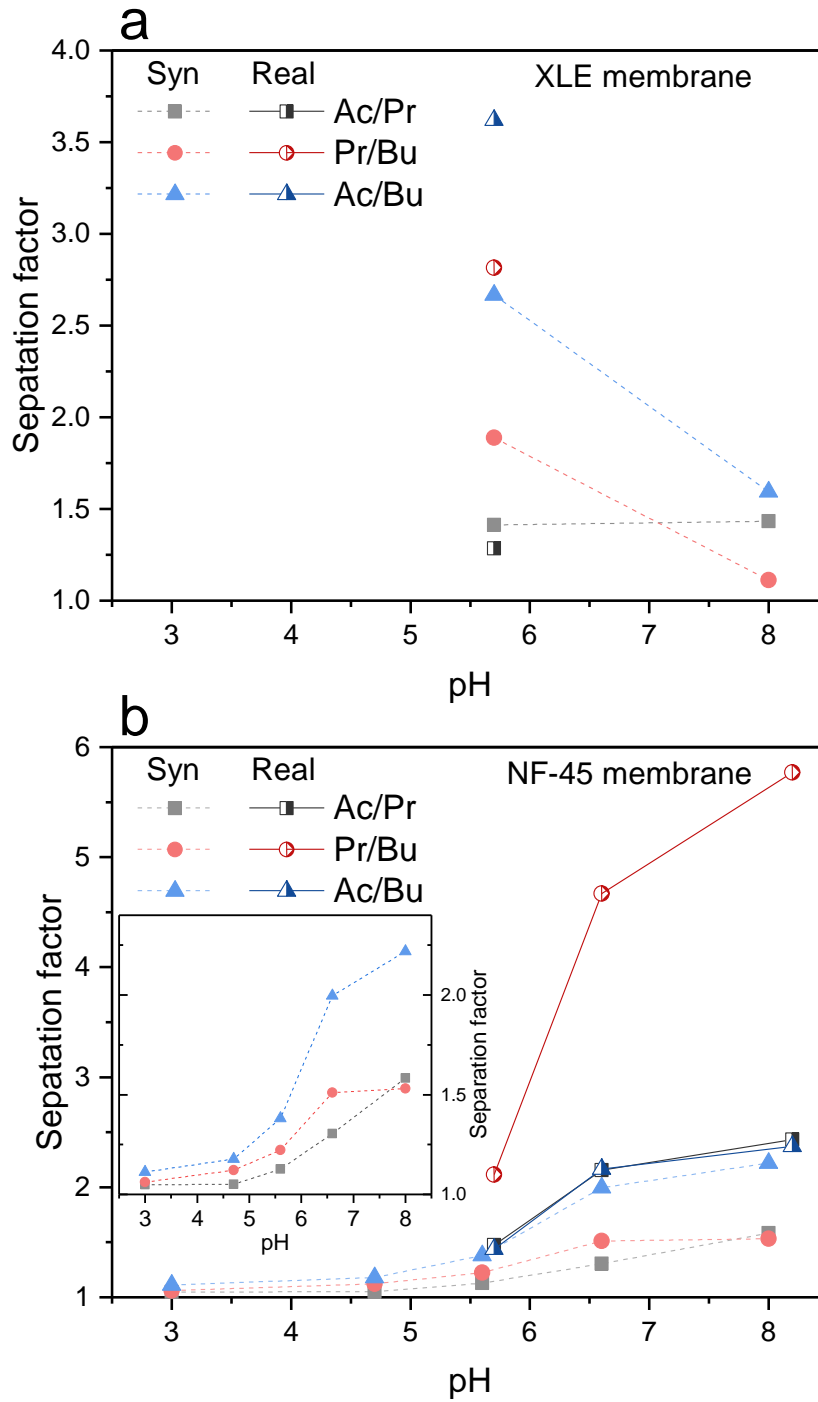


Figure VI-20 Separation factors between Ac/Pr, Pr/Bu, and Ac/Bu in synthetic solutions (Ac:Pr:Bu=33%:33%:33%) and real fermentation broths versus solution pH, (a) XLE membrane, (b) NF-45 membrane. The results obtained using NF-45 membrane for synthetic solutions are zoomed in to identify the individual points.

As previously discussed, the proportion of shorter chained VFAs, i.e., Ac and Pr and longer chained VFAs, i.e., Bu can be used separately, thus it is interesting to consider the separation of the shorter chained VFAs from the longer chained VFAs.

Considering the proportion of Bu and the combined proportion of Ac+Pr, the proportion of shorter and longer chained VFAs in the feed and permeate as well as the separation factor between shorter and longer chained VFAs are given in Table VI-8.

Table VI-8 Proportions of Ac+Pr and Bu in the feed and permeate as well as the separation factor between Ac+Pr and Bu for the real fermentation broth

pH	XLE membrane					NF-45 membrane				
	Feed		permeate		Separation factor	Feed		permeate		Separation factor
	Ac+Pr	Bu	Ac+Pr	Bu		Ac+Pr	Bu	Ac+Pr	Bu	
5.7	0.65	0.35	0.86	0.14	3.3	0.64	0.36	0.75	0.25	1.7
6.6						0.64	0.36	0.85	0.15	3.2
8.2						0.64	0.36	0.87	0.13	3.8

One can observe that the proportion of Ac+Pr is enriched in the permeate, while the proportion of Bu is enriched in the retentate. At initial pH (5.7), the separation factor between Ac+Pr and Bu is better using XLE membrane; then, at pH 8.2, higher separation factor is observed using NF-45 membrane. At the best condition (NF-45 membrane at pH 8.2), the highest separation factor obtained for Ac+Pr and Bu is 3.8.

VI.3.3 Case 3: Organic matters removal

Ethanol and methanol are common by-products during anaerobic fermentation, and they are considered as unfavorable organic matters (OM) for PHA production.

In the previous section, it is shown that the retention of OM (mainly ethanol) is much lower than the retention of VFAs using XLE membrane, then, the OM (other than the TOC of VFAs) is enriched in the permeate and it is possible to remove the OM from the fermentation broth.

Table VI-9 shows the proportions of VFAs and OM (in terms of TOC) in the feed and permeate and the separation factor between VFAs/OM using XLE membrane. The separation factor between VFAs/OM is as high as 14.8, indicating that a good separation between VFAs and OM can be achieved.

Table VI-9 Proportions of VFAs and OM in the feed and permeate as well as the separation factor between VFAs/OM using XLE membrane for the real fermentation broth

pH	XLE membrane				
	Feed		permeate		Separation factor
	VFAs	OM	VFAs	OM	
5.7	0.92	0.08	0.45	0.55	14.8

VI.4 Conclusions

Current Chapter investigated the nanofiltration of synthetic broths containing only VFAs, VFAs with two salts (NaCl and CaCl₂), as well as a real fermentation broth containing anions (Ac, Pr, Bu, and Cl⁻) and cations (Ca²⁺, Na⁺, NH₄⁺, and K⁺) using two NF membranes (XLE and NF-45 membranes). The experiments were operated at various total concentrations and pH values.

The results showed that, the modification of individual VFAs retention due to the influence of the addition of inorganic salts is less than 10%, especially at high filtration flux, for the two membranes investigated. Then, the retentions of individual solutes in the real fermentation broth are slightly higher than that in the synthetic broths, for both membranes.

It was observed that the retention sequence of anions in synthetic broths is Cl⁻<Ac<Pr<Bu, following their molecular weights, for NF-45 membrane at pH 5.7 and 8, as well as for XLE membrane at pH 8. However, compared to other conditions, the retention sequence of VFAs and Cl⁻ altered (i.e., Bu≈Cl⁻>Ac>Pr) for synthetic broths at pH 5.7 using XLE membrane. Further investigation showed that the observed retention of VFAs is a combination of the retentions of dissociated and undissociated VFAs, if only consider the dissociated forms, the retention sequence is Cl⁻<Ac⁻<Pr⁻<Bu⁻, as observed for pH 8.

Then, for XLE membrane, the retention sequence of anions and cations in the real fermentation broths are the same as that in the synthetic broths (i.e., Bu>Cl⁻>Pr>Ac and Ca²⁺>Na⁺). However, for NF-45 membrane, the retention sequence of Ac and Pr was modified (i.e., Bu>Ac>Pr>Cl⁻) in the real fermentation broth compared to that in synthetic broths (i.e., Bu>Pr>Ac>Cl⁻). Similar results were already observed previously. Some experiments (not shown) were carried out to understand the mechanism explaining this modification but no clear explanation was drawn.

With the two types of NF membranes for all the synthetic and real fermentation broths at all the compositions and solution pH values investigated, it was observed that when the filtration flux

is higher than a certain value, the individual solutes proportions in the permeate are constant for a given feed proportion.

Considering the relative proportion of VFAs, the performances of the two membranes for the separation of VFAs in synthetic and real fermentation broths were compared and discussed.

For the XLE membrane, it was observed that the relative proportions of VFAs in the feed and permeate obtained in synthetic and real fermentation broth are similar. For NF-45 membrane, the relative proportions of Ac and Bu for the couple of Ac/Bu are similar for the synthetic and real fermentation broths at pH 5.7 and 8.2. However, the relative proportions of Ac and Pr for the couple of Ac/Pr are the reverse in the real fermentation broth compared to that obtained in synthetic solutions/broths. This is due to the decrease in Pr retention (i.e. increase in Pr transfer) previously reported, and further investigation is required to reveal the mechanism behind.

According to the separation factors between VFAs obtained at the plateau values of VFAs proportions in the permeate, XLE membrane is the better candidate for the separation of VFAs at pH 5.7. In contrast, at pH 8.2, NF-45 membrane has better separation performance compared to XLE membrane.

Besides, it was also noticed that the performance of the two membranes on the separation of monovalent and divalent cation are quite similar, both for synthetic and real fermentation broths. This also deserves further investigation.

Finally, the possible applications of NF for the treatment of real fermentation were discussed. It was observed that NF-45 is the better candidate for inorganic salts removal as well as modification of VFAs composition. At pH 8.2, the separation factor between VFAs and Cl^- is 4.0, and the separation factor between shorter chained VFAs (i.e., Ac and Pr) and longer chained VFAs (i.e., Bu) is 3.8, using NF-45 membrane.

XLE membrane can be used to remove organic matters (OM) from VFAs, a separation factor of 14.8 between OM and VFAs is observed at the best condition.

General conclusions and perspectives

Global change leads to serious environmental problems, which has become an increasing concern for the last decades. Adopt renewable resources such as biomass to replace fossil resources could reduce the carbon emission and it is considered as one of the most beneficial way to slow down the global change.

Volatile Fatty Acids (VFAs) are promising biochemicals that can be used for biodegradable plastics and bioenergy production, and they also have the potential to become chemical building blocks. However, despite VFAs have many perspectives, the recovery and purification of VFAs from raw materials such as a fermentation broth are still challenging and hinder further applications.

Membrane processes are regarded as promising processes for the valorization of VFAs as well as other biomass. The VFAs are monovalent weak electrolytes with increasing molecular weights, and NF is considered as good option to separate individual VFAs. Nevertheless, some bottlenecks regarding the separation performance and mass transfer through the membrane may limit the application of NF for VFAs valorization. The retention of NF membrane on organic solutes depends on filtration flux, ionic concentration, solutes proportions, solution pH, as well as the presence of additional inorganic salts. The interactions between charged solutes as well as that between charged and uncharged solutes need further investigation. Thus, it was difficult to predict and improve the separation performance of NF process on organic solutes.

The objective of the thesis was to investigate the separation and valorization of aqueous solutions containing VFAs using nanofiltration. Synthetic solutions with increasing complexities from single, binary, and ternary solutions of VFAs (i.e., Ac, Pr, and Bu), to mixed solutions containing VFAs and inorganic salts at different compositions were firstly tested, the influence of solution pH on the retention of VFAs was also discussed in order to reveal the mass transfer mechanisms. Then, a real fermentation broth contain VFAs, inorganic salts, as well as organic matters, which was obtained by fermentation of municipal solid waste (MSW), was investigated. Two NF membranes (NF-45 and XLE) were used for the investigation, and the performances of the two membranes on the separation and valorization of VFAs were discussed.

In the first part, synthetic solutions containing dissociated VFAs (pH 8) with various compositions were studied.

It was observed that in mixed solutions, the retention of the more retained solute increases compared to the one in single solution, while that of the less retained one decreases. This is in

agreement with previous reported results. The retention sequence of the three VFAs is $R_{Ac^-} < R_{Pr^-} < R_{Bu^-}$, following their MWs, observed for the two membranes investigated.

Then, it was found that for a given VFAs proportion in the feed, regardless of the total concentration, the proportion of VFAs in the permeate remains constant when the filtration flux is higher than a specific value. The filtration flux required to reach this constant plateau value increases with the increase of total concentration. From the perspective of mass transfer, this observation means that in a mixed solution, the individual charged solute transfer is controlled by the total amount of charge transferred through the membrane (i.e. total solute flux). Indeed, it was found that the individual VFA flux increases linearly with the total solute flux and does not depend on the total concentration but only on the VFAs proportions in the feed. This was observed for the two membranes used. Moreover, for a given feed proportions, it was observed that the permeate proportions are similar for the two membranes, despite their retention on VFAs are different.

Furthermore, the proportion in the feed influences the separation factors between VFAs. For identical proportion of each VFAs in the feed (i.e., Ac:Pr=50%:50% and Ac:Bu=50%:50% in binary solutions and Ac:Pr:Bu=33%:33%:33% in ternary solutions), the highest separation factors between VFAs were obtained. Moreover, for identical feed proportion, the separation factors between VFAs obtained in ternary solutions are always higher than that obtained in binary solutions.

In the second part, more complex solutions containing VFAs with the addition of three inorganic salts (Na_2SO_4 , NaCl, and $CaCl_2$) were further investigated.

The same retention sequence was observed for all the anions ($R_{Cl^-} < R_{Ac^-} < R_{Pr^-} < R_{Bu^-} < R_{SO_4^{2-}}$), and cations ($R_{Na^+} < R_{Ca^{2+}}$), for single and mixed solutions, following their valence and MWs. In the mixed solutions, the retention of the more retained co-ion increases compared to the one in single solution, while that of the less retained one decreases, for all the anions and cations investigated. This results are in agreement with those observed in the first part.

In any condition, it was found that constant permeate proportions for organic and inorganic solutes (anions as well as cations) are obtained for a given feed proportion, when the filtration flux is higher than a certain value. Furthermore, it was concluded that, for any couple of co-ions (Ac/Pr, Pr/Bu, Ac/Bu, VFAs⁻/ SO_4^{2-} or VFAs⁻/Cl⁻) in any mixed solution (binary, ternary, and with the addition of salts), the plateau value of the relative proportion of the individual co-ions in

the permeate is fixed by its proportion in the feed. This conclusion was also extended to couples of cations (e.g., $\text{Na}^+/\text{Ca}^{2+}$).

The separation factors between Ac/Pr, Pr/Bu, and Ac/Bu for the systems of VFAs, VFAs+ Na_2SO_4 , VFAs+ NaCl , and NaVFAs+ CaCl_2 were determined. On the contrary to what was reported in previous studies with mixed solution containing uncharged and charged solutes, it was observed that the addition of both co-ions (anions) and counter-ions (cations) does not have a significant influence on the separation factors between VFAs.

In the third part, single and mixed VFAs solutions at various total concentrations and solution pH were investigated. The influence of solution pH on the retention of VFAs as well as the relative proportions of VFAs was discussed.

It was shown that the solution pH significantly changes the retention of VFAs as well as the permeate proportion of VFAs. However, for any pH value, a constant permeate proportion is observed for a given proportion in the feed when the filtration flux is higher than a specific value. The filtration flux required to reach the plateau value increases when the solution pH decreases.

Then, a model to describe the VFAs retention versus pH was proposed based on the following assumptions: (1) The undissociated and dissociated VFAs transfer through the membrane independently; (2) Retention of HVFAs is that obtained at pH 3 and does not depend on the concentration; (3) Retention of VFAs^- is that obtained at pH 8 at the corresponding ionic concentration. It was shown that the model can describe the retention of VFAs versus solution pH by considering an increase of the VFAs pK_a values by about 1.2 units or a membrane effective pK_a value of about 5.4 to 5.8.

At last, the separation performance of nanofiltration was evaluated. Synthetic broths with the three VFAs and inorganic salts, as well as a real fermentation broth produced from municipal solid waste were investigated.

The retention sequences of the charged solutes in synthetic solutions are $R_{\text{Cl}^-} < R_{\text{Ac}^-} < R_{\text{Pr}^-} < R_{\text{Bu}^-}$ for anions and $R_{\text{Na}^+} < R_{\text{Ca}^{2+}}$ for cations, observed using the two membranes. The same retention sequences were observed for the real fermentation broth, except for the reversed retention sequence between Ac and Pr for NF-45 membrane.

Then, it was found that whatever charged or uncharged solutes, even for unknown organic matters in the real fermentation broth, a constant proportion in permeate is observed when the filtration flux is higher than a certain value. This shows that the plateau value could be related to

the nature of solutes and membranes, and this method could be used to compare the separation performances of different membranes.

Separation factor was used to characterize the separation performance of the two membranes with the real fermentation broth. It was observed that the separation factors between VFAs in the real fermentation broth are higher than those obtained with synthetic solutions. So, there are additional parameters that could influence the separation performance of the nanofiltration process.

It was observed that the NF-45 membrane can more efficiently separate Cl^- from VFAs as well as modify the VFAs proportion in the permeate than XLE membrane. Ac and Pr are enriched in the permeate, while Bu is enriched in the retentate. The XLE membrane has a very high VFAs retention (>95% for all the VFAs). It can modify the proportion of VFAs and other organic matters (OM) in the permeate. Therefore, XLE membrane can be used to concentrate the VFAs fermentation broth and remove the hindering organics such as ethanol.

Besides, for the synthetic and real fermentation broths, it was observed that the proportions of divalent and monovalent cations proportion in the feed and permeate are similar. This indicates that the two membranes have similar abilities for the separation of mono/divalent cations.

This work also points out some interesting perspectives.

In current work, it was found that the solutes proportions in the permeate reached a plateau for VFAs in dissociated and undissociated form. It could be interesting to check if this observation is universal for all the solutes, as well as for different membranes. If it is universal, then this parameter could be used to compare the separation performances of different membranes on specific solutes. Furthermore, nanofiltration of solutions with non-aqueous solvents (e.g., organic solvent nanofiltration) need to be checked.

During the investigation on VFAs retention versus pH, the calculation can be carried out to mixed VFAs solutions by considering VFAs as one single solute. It needs to be checked if this simplification can also apply to other solutes (with more difference in pK_a values).

Besides, investigation of the unexpected Pr transfer in the real fermentation broth when using NF-45 membrane could reveal the additional interactions.

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Nomenclature

List of symbols

J	Filtration flux ($\text{m}\cdot\text{s}^{-1}$)
V	Volume (m^3)
S_m	Active surface of the membrane (m^2)
t	Time (s)
R	Retention (%)
c	Concentration ($\text{mol}\cdot\text{m}^{-3}$, abbreviate as mM)
P	Proportion of the solute (%)

Superscripts & subscripts

glo	Global
$HVFAs$	Undissociated VFAs
$VFAs^-$	Dissociated VFAs
$VFAs$	Dissociated and undissociated VFAs
mix	Mixed solution
sgl	Single solution
HAc	Acetic acid
HPr	Propionic acid
HBu	Butyric acid
Ac^-	Acetate
Pr^-	Propionate
Bu^-	Butyrate
Ac	Acetate/Acetic acid
Pr	Propionate/Propionic acid
Bu	Butyrate/Butyric acid
f	Feed
p	Permeate
r	Retentate
exp	Experimental data
cal	Calculated data
m	Membrane

Abbreviations

NF	Nanofiltration
ED	Electrodialysis
RO	Reverse osmosis
MW	Molecular weight
OM	Organic matter
MSW	Municipal solid waste
Mono	Monovalent
Di	Divalent

Appendix: Chromatograms of VFAs

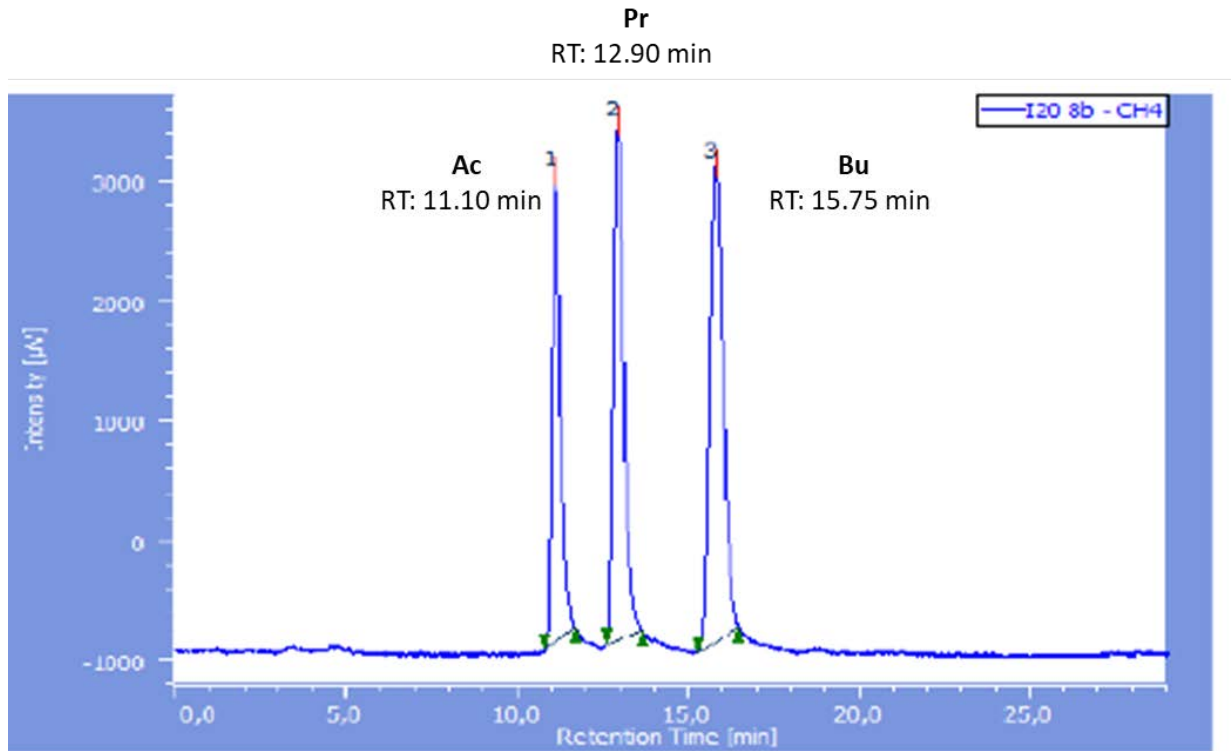


Figure I Chromatogram of the three VFAs with HPLC (Jasco)

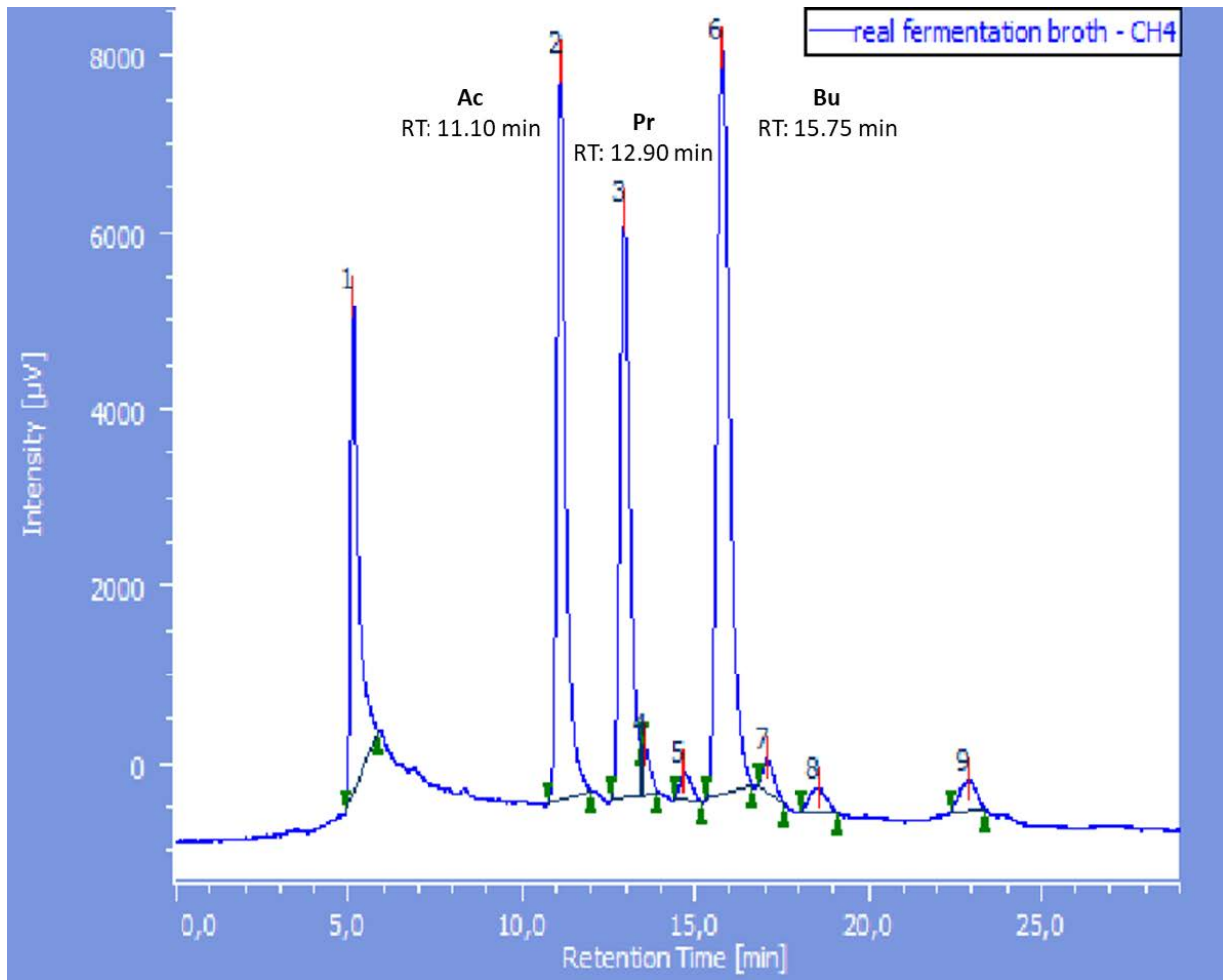


Figure II Chromatogram of the real fermentation broth with HPLC (Jasco)