MICELLAR ENHANCED ULTRAFILTRATION WITH NONIONIC SURFACTANTS (MEUF)

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MICELLAR ENHANCED ULTRAFILTRATION WITH NONIONIC SURFACTANTS (MEUF)

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

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ABSTRACT

MICELLAR ENHANCED ULTRAFILTRATION WITH NONIONIC SURFACTANTS (MEUF)

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Butanol is a versatile chemical used in many different fields such as electronics, cosmetics, and textiles, and the synthesis of many other chemicals. In fermentative butanol production, in addition to butanol; acetone and ethanol are released in the aqueous environment, too. To separate butanol from this mixture, which is called the ABE mixture, different methods are available. The project's main purpose is to develop an alternative method to these separation techniques by using Micellar Enhanced Ultrafiltration (MEUF) method.

In the MEUF method, above certain surfactant concentration and solution temperature values, aggregates are formed. These aggregates, called micelles, trap small organic substances within. Then, using ultrafiltration membranes with a pore size much larger than the materials to be separated, organic materials trapped inside the micelles are separated from the rest of the solution. In this study, non-ionic surfactants called Pluronics were used.

Firstly, based on the permeate flow rate and the surfactant's rejection values; membrane selections were carried out (1 kDa ultrafiltration membrane and NF90 as nanofiltration membrane) and the optimum operating pressure of the selected membrane was determined as 3 bar. Then, rejection performance of butanol was determined by using Pluronic F127, P123, L101, and L61 nonionic surfactants and their mixtures of different concentrations. When 1kDa membrane is used, the solution of 6.21wt.% P123 + 0.5wt.% L101 exhibited the best butanol separation performance. When NF90 membrane is used, solutions containing in addition to 1wt.% L101; 3 and 1wt.% P123 had exhibited the best butanol separation performances. When the separation of butanol from ABE mixture was tested with 1wt.% P123 + 1wt.% L101 among the best butanol separation performing surfactant couples, approximately 1.35% acetone, 68.19% butanol, and 26.87% ethanol rejection were obtained. Also, when the separation was tested with 6.21wt.% P123 + 0.5.% L101, rejections were approximately 23.44% for acetone, 66.09% for butanol, and 19.97% for ethanol. When process calculations were conducted for a three-stage filtration, based on result of the ABE experiments with 1 kDa membrane and Pluronic P123 wt.%: L101 wt.% = 6.21:0.5, at the end of the third stage; acetone, butanol, and ethanol concentrations are expected to be 5.9, 74.2, 6.1 g/L, respectively. On the other hand, for the NF90 membrane and Pluronic P123 wt.%: L101 wt.% = 1:1, concentrations of 5.3, 99, 7.9 g/L would be expected, respectively.

Keywords: Micellar Enhanced Ultrafiltration, Butanol, Pluronic, Surfactant, ABE Fermentation.

ÖZ

İYONİK OLMAYAN YÜZEY AKTİF MADDELERLE MİSEL DESTEKLİ ULTRAFİLTRASYON (MEUF)

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Bütanol elektronik, kozmetik ve tekstil gibi birçok farklı alandaki kimyasal süreçlerde ve diğer pek çok kimyasalın sentezinde kullanılan çok yönlü bir kimyasaldır. Fermantasyon ile yapılan bütanol üretim yöntemlerinde, fermantasyon sonucunda sulu ortamda bütanolün yanı sıra aseton ve etanol de açığa çıkmaktadır. ABE karışımı olarak adlandırılan bu karışımdan bütanolü ayırmak için kullanılan farklı yöntemler mevcuttur. Projenin temel amacı ise Misel Destekli Ultrafiltrasyon (MEUF) yöntemini kullanarak bu ayırma yöntemlerine alternatif bir yöntem geliştirmektir.

MEUF yöntemi; yüzey aktif maddelerin (YAM) kullanımı ile belirli konsantrasyonların ve sıcaklık değerlerinin üzerinde misel adı verilen agregaları oluşturarak küçük organik maddeleri bu agregaların içine hapseder. Böylece ayrıştırılmak istenen malzemelerden çok daha büyük gözenek boyutuna sahip ultrafiltrasyon membranlarını kullanarak YAMların içine hapsedilen organik malzemeleri, çözeltinin geri kalanından ayırır. Çalışmada Pluronic adı verilen iyonik olmayan yapıda YAMlar kullanılmıştır.

İlk olarak, sızma akış hızı ve yüzey aktif maddenin reddilme değerlerine dayalı olarak; membran seçimleri yapılmış (1 kDa ultrafiltrasyon membranı ve nanofiltrasyon membranı olarak NF90) ve seçilen membranların optimum çalışma basıncı 3 bar olarak belirlenmiştir. Membran ve basınç seçiminin ardından öncelikle iyonik olmayan YAMlardan Pluronic F127, P123, L101 ve L61 ve bunların farklı konsantrasyonlarında karışımları kullanarak, bütanolün reddedilme performansı belirlendi. En iyi bütanol ayırma performanslarını; 1kDa membran kullanıldığında ağırlıkça %6.21 P123 ve %0.5 L101 içeren karışım, NF90 membranı kullanıldığında ise ağırlıkça %1 L101'e ek olarak; ağırlıkça %3 ve %1 P123 içeren karışımlar sergilemiştir. En iyi performansı gösteren çiftlerden ABE içerisinde ağırlıkça %1 oranında Pluronic P123 ve %1 Pluronic L101 içeren karışımı kullanılarak yapılan ayırma işleminde ise yaklaşık olarak 1.35% aseton, 68.19% bütanol ve 26.87% etanol reddi elde edilmiştir. Ayrıca ağırlıkça 6.21% P123 + 0.5% L101'lik karışım ile yapılan testler sonucunda; 23.44% aseton, 66.09% butanol ve 19.97% ethanol reddi elde edilmiştir. 1 kDa membran ve ağırlıkça %6.21 Pluronic P123 + %0.5 L101 ile yapılan ABE deneylerinin sonucuna göre üç aşamalı bir filtrasyon için proses hesaplamaları yapıldığında: üçüncü aşamanın sonunda aseton, bütanol ve etanol konsantrasyonlarının sırasıyla 5.9, 74.2, 6.1 g/L olması beklenmektedir. Öte yandan, NF90 membran ve ağırlıkça %1 Pluronic P123 + %1 L101 için, sırasıyla 5.3, 99, 7.9 g/L konsantrasyonları beklenir.

Anahtar Kelimeler: Misel destekli ultrafiltrasyon, Bütanol, Pluronic, Yüzey Aktif Madde, ABE Fermantasyonu

To My Big, Lovely Family

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ABBREVIATIONS	
ABE	Acetone, Butanol and Ethanol Solution
BCC	Butanol Capturing Capacity
C	Concentration
CF	Cross-Flow
CGC	Critical Gel Concentration
CGT	Critical Gel Temperature
CMC	Critical Micelle Concentration
CMT	Critical Micelle Temperature
CO_2	Carbon Dioxide
DLS	Dynamic Light Scattering
GC	Gas Chromatography
HLB	Hydrophilic-Lipophilic Balance
IC	Inorganic Carbon
IUPAC	International Union of Pure and Applied Chemistry
KCl	Potassium chloride
MEUF	Micellar Enhanced Ultrafiltration
MWCO	Molecular Weight Cut Off
MF	Microfiltration
NF	Nanofiltration

NTU	Nephelometric Turbidity Units
$NaSO_4$	Sodium Sulfate
NaCl	Sodium Chloride
PPO	Polypropylene Oxide
PEO	Polyethylene Oxide
PES	Polyethersulfone
POE	Polyoxyethylene
RO	Reverse Osmosis
RC	Regenerated Cellulose
T	Temperature
TC	Total Carbon
TCD	Thermal Conductivity Detector
TMP	Transmembrane pressure
TOC	Total Organic Carbon
UF	Ultrafiltration
UP	Pure water
VCF	Volume Concentration Factor

LIST OF SYMBOLS

SYMBOLS	
R	Resistance
J	Permeate Flux
η	Permeate Viscosity
V	Permeate Volume
A_{mem}	Active Membrane Area
t	Time
$R_{filtration}$	Filtration Resistance
$R_{membrane}$	Membrane Resistance
$R_{fouling}$	Fouling Resistance
$R_{irreversible\ fouling}$	Irreversible Fouling Resistance
$R_{reversible\ fouling}$	Reversible Fouling Resistance
K_i	Ratio of Permeate to Retentate Concentration of Compound i
α_{ij}	Selectivity of Compound i over Compound j
$\mathbb{R}_i\%$	% Rejection of Compound i
$C_{F,i}$	Feed Concentration of i in the Feed (or Retentate) Side
$C_{P,i}$	Permeate Concentration of i in the Permeate Side
$C_{R,i}$	Retentate Concentration of i in the Retentate Side (For CF systems)

CHAPTER 1

INTRODUCTION

1.1 Membrane Separation

With a few exceptions, elements and compounds don't exist in nature in a pure form. Hence, for these raw materials to be used efficiently, they must first be subjected to a separation process. One of the areas where separation and concentrate processes are widely used is the chemical industry. In this area, where separation techniques such as distillation, crystallization, adsorption, membrane processes, absorption, stripping, and extraction are widely used, based on the chemical process, approximately 30% - 70% of the total capital cost has spent on the separation and supporting facilities (Agrawal, 2001). Therefore, separation techniques that are cost-effective and have efficient separation performance are the reason for preference in production.

One of the separation techniques used in the chemical industry is membrane separation. This separation technique recently has been used in many areas such as wastewater treatment, gas separation, medical applications, and concentration of pharmaceutical, food, and biotechnology products. Low energy consumption, simple operation, and easy scalability advantages are the main reasons for the separation technique preference (Noble, 2012).

The membrane is a selectively permeable barrier that moderates the permeation of species in a mixture through (Baker, 2004). During the membrane separation process, the solution fed to the system for the separation is named the feed solution. From this feed solution, in the filtration, the stream that passes from the membrane to the other side has been named the permeate. On the other hand, the stream that is rejected and remained on the feed side has been named the retentate (Figure 1.1.1.).

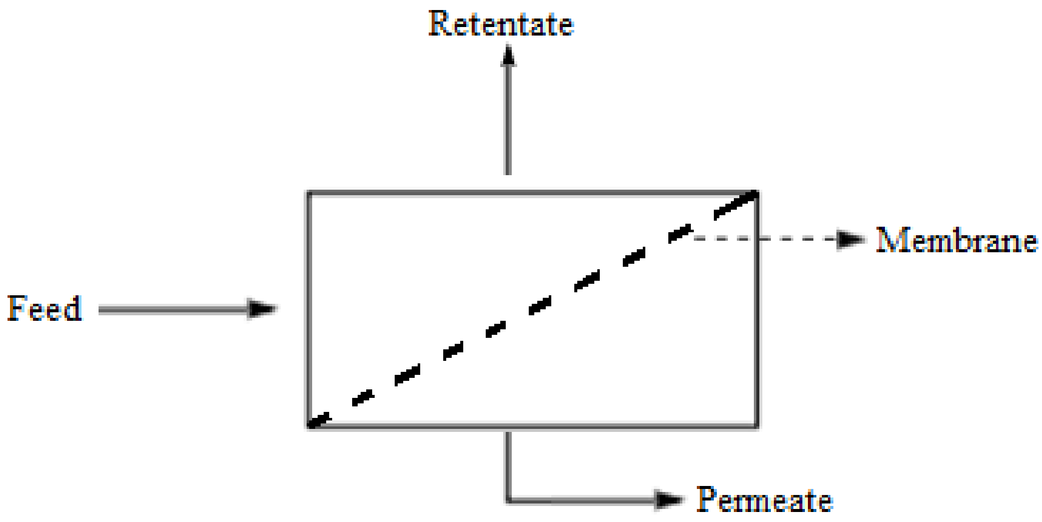


Figure 1.1.1. Typical membrane filtration processes' flow diagram.

Two transport models are used to describe the permeation of compounds from the membrane. These are the pore-flow model and the solution-diffusion model. Among them in the pore-flow model, with the pressure-driven convective flow, compounds are transferred through pores. Size and the charge exclusion is the main reason for the separation to take place. On the other hand, in the solution-diffusion model, during separation, compounds firstly dissolve in the membrane. Then, down a concentration gradient, they diffuse through the membrane. The reasons for separation are in the membrane solubilities of compounds, and their diffusion rates variation (Baker, 2004).

Driving force for the membrane separation can be partial pressure, pressure, concentration and electrical potential gradients.

According to the size of species rejected, membranes can be divided mainly into four groups for pressure driven processes. These are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO) membranes (Figure 1.1.2.). Among these membranes both MF and UF membranes use the pore-flow model for the separation.

From these membranes, UF membranes are preferred for the separation of water and microsolutes from compounds that has a size between 1 to 100 nm such as macromolecules, proteins, viruses, and colloids. On the other hand, MF membranes are used for the separation of suspended particles that has a diameter of larger than 100nm such as blood cells and bacteria. RO membranes have dense polymer layer structures. Separation in these membranes is explained with the solution diffusion model. These membranes are generally used in monovalent ions removal and water desalination processes. While rejecting salt by letting the passage of water from the membrane, they separate the salt from water. The final group of the membranes according to size are NF membranes. Transport in these membranes is intermediate, between solution diffusion and pore flow. They are usually preferred for small organic compounds, which have a size of few nanometers, and multivalent ions removal.

At the membrane filtration, as cross-flow filtration and dead-end filtration, two operation modes are applicable (Figure 1.1.3.). Among them in dead-end filtration feed flow is perpendicular to the membrane. Feed is forced towards the membrane, and passage of selected compounds to the permeate side is achieved. On the other hand, in cross-flow filtration, feed flow is tangential to the membrane. During this parallel flow, separation is achieved.

Concentration polarization is the situation where the concentration of rejected materials by the membrane is higher on the membrane surface than the bulk solution concentration. If the substance concentration on the membrane surface exceeds a certain value, as a result of concentration polarization, it causes a cake or gel layer formation, in other words, membrane fouling. The concentration polarization, which is observed up to a certain extent in every membrane filtration, results in a decrease in the rejection of the membrane. At the same time, since it increases the resistance of the membrane against filtration, in constant pressure filtrations, decreases in the flow rates are inevitable (Baker, 2004).

In the cross-flow filtrations, only concentration polarization or concentration polarization together with gel or cake layer formation can occur over time. However, due to the parallel flow, accumulated compounds on the membranes are swept. So that, fouling can be kept at a certain level and permeate flow is maintained. But, in the dead-end filtrations, gel or cake layer formation is inevitable over time due to perpendicular flow. In lab-scale dead-end systems experiments, a stirrer is usually used to reduce accumulation on the membrane surfaces.

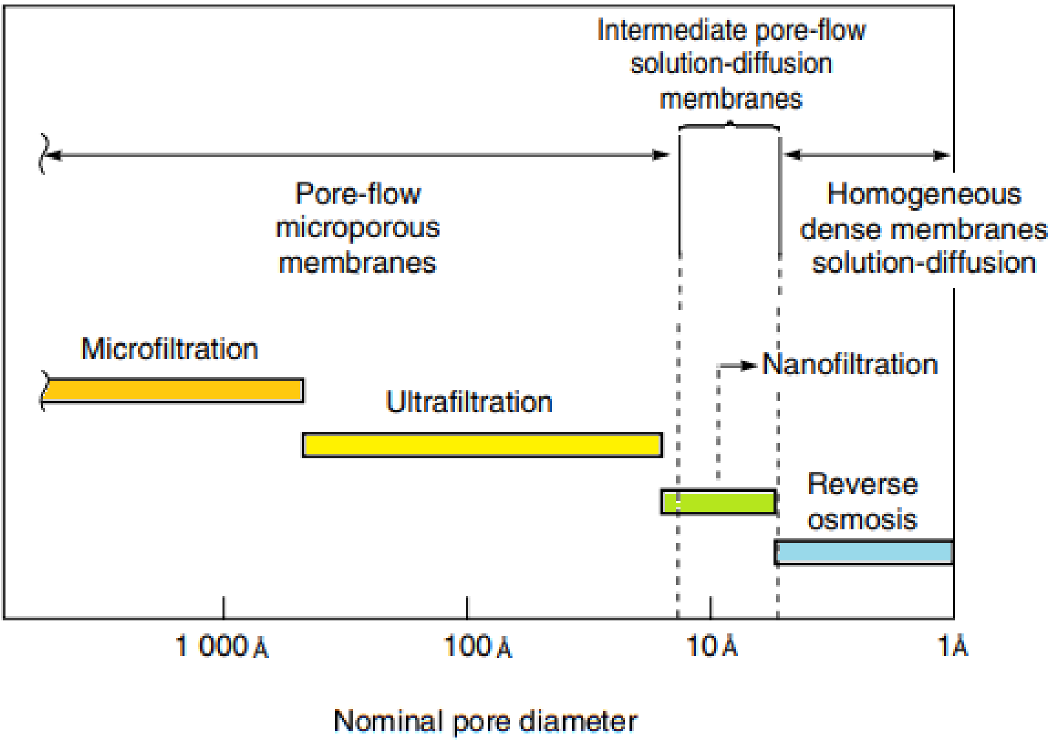


Figure 1.1.2. According to the size type of the membranes, and their transport models (Baker, 2004).

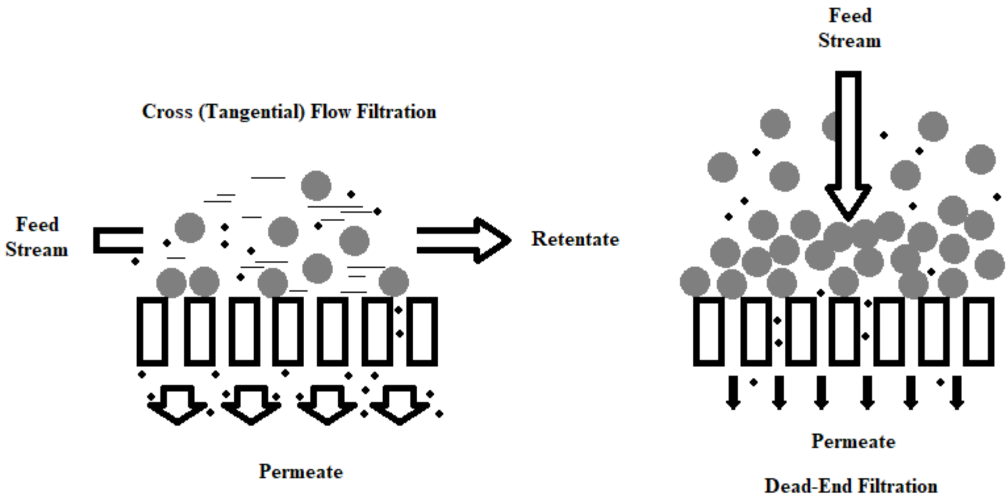


Figure 1.1.3. Cross (Tangential) flow and dead-end operation modes of membrane filtrations.

Fouling, which can be seen in either porous or dense membranes, is the main drawback in membrane separation operations. According to the IUPAC, this fouling in membrane processes is defined as "*Process resulting in loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores*". The main reasons for the fouling are adsorption, pore blockage, cake or gel formation, and biofouling (Baker, 2004; Ning, 2011). When there is fouling on membranes, there is an increase in resistance against the flow. Due to this increase, decrement in the flux or increase in pressure necessary to sustain a given flux, decrease in the membrane performance, membrane operational life, and product quality, and increment in the energy consumption is observed (Baker, 2004; Ning, 2011). To overcome these problems controlling the membrane fouling carries big importance. Feed pre-treatments, operational conditions selections, and membrane cleanings are the way of controlling fouling. Among these methodologies, feed pre-treatment and operational conditions only help to avoid or reduce fouling. However, to defeat reversible fouling, periodic membrane cleaning must be performed (Ning, 2011). Here, as physical, and chemical cleaning, two methods are applicable.

In physical cleaning methods such as forward and reverse flushing, backwashing, or air flushing conventional cleaning methods are used (Lin et al., 2010; Ning, 2011).

At the point where these methods are not sufficient for membrane cleaning, chemical cleaning methods such as acid, base, hypochlorite, or enzyme cleaning are applied (Lin et al., 2010; Ning, 2011). The main problem with using chemical cleaning for membranes is that repetition of chemical cleaning reduces the lifetime of the membrane.

In the interpretation of membranes fouling, commonly Darcy's Law (equation 1) is used. That is the equation that combines the transmembrane pressure, permeate viscosity, and flux with the resistance, to explain, in the porous media, pressure-driven convective flow.

$$R = \frac{TMP}{J\eta} \tag{1}$$

In this equation, while TMP (Pa) represents the transmembrane pressure difference, η (Pa.s^{-1}) is the permeate viscosity, J (m^{3}.m^{-2}.s^{-1}) is the permeate flux and R (m^{-1}) is the resistance of the membrane against the flow.

This resistance from the resistance-in-series model is defined as the summation of membrane resistance and fouling resistance (equation2) which involves both reversible and irreversible fouling (equation 3).

$$R_{filtration} = R_{membrane} + R_{fouling} \tag{2}$$

$$R_{fouling} = R_{reversible\ fouling} + R_{irreversible\ fouling} \tag{3}$$

For the permeate flux equation, in calculations, the formulation in equation 4 is used. Here, V(m^3) is symbolizing the permeate volume, A_{mem} (m^2) is the active membrane area and t(s) is the time.

$$J = \frac{V}{A_{mem}t} \tag{4}$$

Rejection and selectivity calculation of species are the two other calculated parameters. For the rejection calculation of species i in the feed, equation 5 is used. For the selectivity calculations of compound i over compound j, equation 6 and equation 7 is used.

$$\mathbb{R}_i\% = \left(1 - \frac{C_{P,i}}{C_{F,i}}\right) \times 100 \tag{5}$$

In equation 5, $C_{i,p}$ is the i concentration in the permeate side, and $C_{i,f}$ is i concentration in the feed (or retentate) side.

$$a_{ij} = \left(\frac{K_j}{K_i}\right) \tag{6}$$

$$K_{i\ (or\ j)} = \frac{Permeate\ concentration\ of\ i\ (or\ j)}{Retentate\ concentration\ of\ i\ (or\ j)} \tag{7}$$

1.2 MEUF

Micellar enhanced ultrafiltration, shortly MEUF, is a membrane-based separation technology that allows the separation of relatively small sized organic or inorganic compounds from water-based solutions by using ultrafiltration membranes due to the entrapment of these compounds inside or around micelles formed from anionic, cationic, zwitterionic or nonionic surfactants (Mungray et al., 2012; Schwarze, 2017; Yaqub & Lee, 2018). In this separation technique, surfactants are added to the aqueous solution, and their concentrations are increased above the critical micelle concentration (CMC). This is the necessary minimum concentration for micelle formation at a specific temperature. After the micelle formation, solutes attach to the micelles, and are rejected by UF membranes inside the micelles which are larger than the UF membranes' pores.

In the literature, it is seen that MEUF is used in various processes such as heavy metal removal from different wastewater (Mungray et al., 2012), removal of phenol from the fermentation medium (Heerema et al., 2010b), and cleaning of wastewater of different industrial processes mainly for olive processing (El-Abbassi et al., 2011), oil extraction (Aoudia et al., 2003) and textile (Aryanti et al., 2018).

This process's main advantage is that it can separate the very small molecules, for UF membranes, even at lower concentrations by combining high flux of UF membranes with high rejection of NF/RO membranes. The performance of the MEUF process can be changed depending on the different parameters. These are surfactant type, membrane, and operating conditions as shown in Figure 1.2.1. Although many types of research are conducted about the effect of these parameters on MEUF processes, no universal experimental conditions are set for the best MEUF performance. Hence, in each experiment, the system's own experimental parameters should be specified.

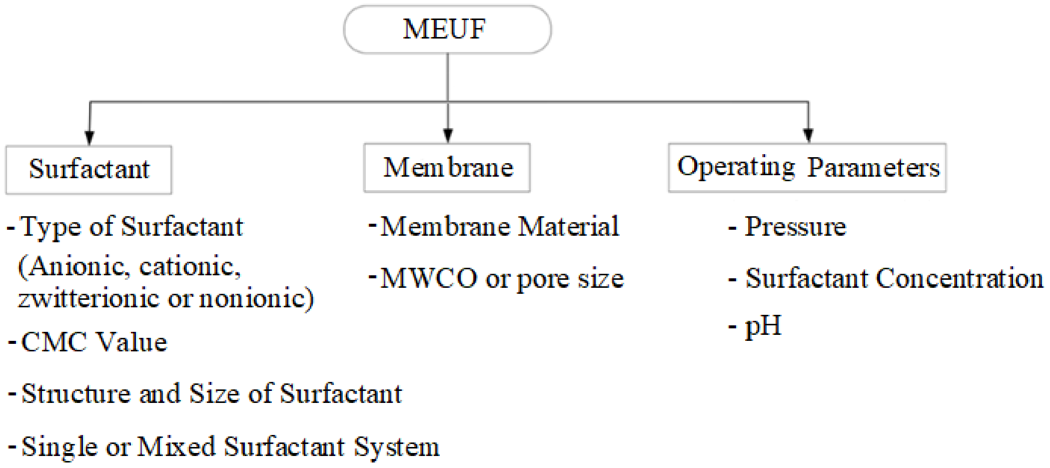


Figure 1.2.1. MEUF Operating parameters block diagram

1.2.1 Surfactant Selection

Surfactants are surface-active agents that have amphiphilic nature with their hydrophobic and hydrophilic parts. Their hydrophobic part, which is the tail of the surfactants, doesn’t show affinity to water. This part of the surfactants is named as hydrophobic part, in the water-based systems, and in the lipid systems, is named the lipophilic part. On the other hand, the head of the surfactants shows an affinity to water and is named the hydrophilic part.

Depending on their affinities, during the micelle formation, the hydrophobic tails of surfactants look at each other and create the core of the micelles. Besides, the hydrophilic heads of the surfactants by looking at the outside of the core contact with water and create the shell of the micelle. If surfactants are solved in apolar media, the orientation of surfactant molecules is reversed (Figure 1.2.1.1.) (Rosen, 2004).

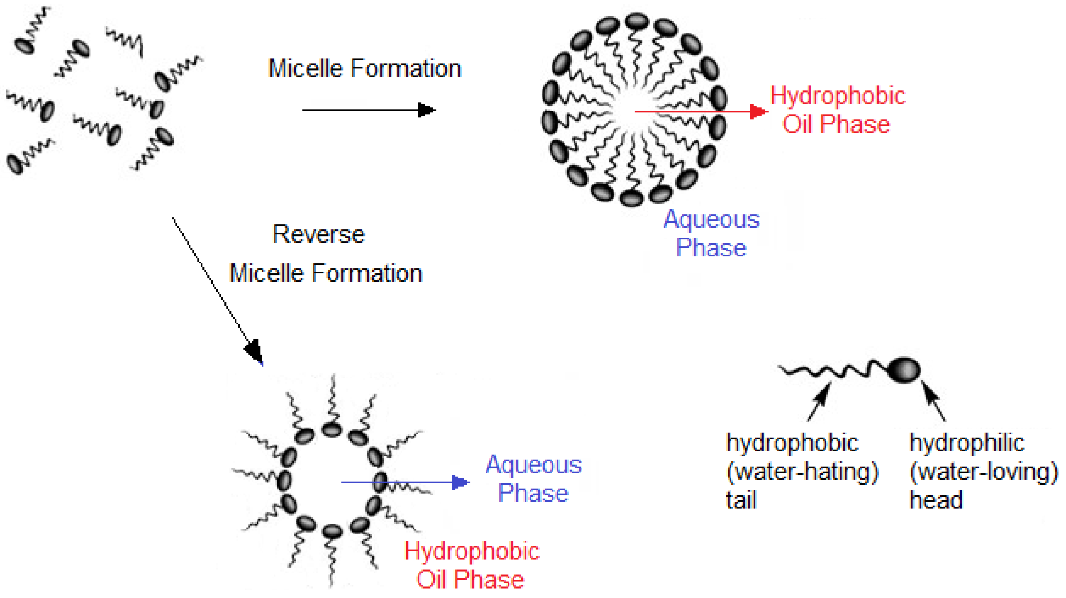


Figure 1.2.1.1. Formation of micelle and reverse micelle

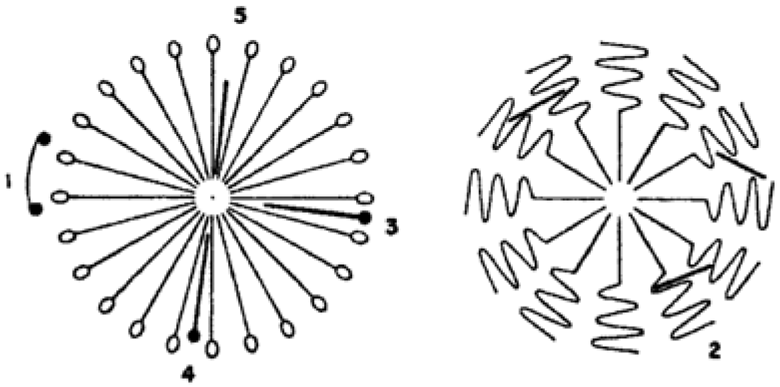
Depending on their head groups, surfactants are mainly classified as ionic and non-ionic surfactants. Furthermore, ionic surfactants are divided into 3 subgroups as anionic, cationic, and zwitterionic surfactants. Hydrophobic groups of surfactants, which are an alkyl chain with 8-22 carbons, are similar both in ionic and nonionic surfactants. However, the hydrophilic part varies. For ionic surfactants, this group is usually carboxylate (-COO), sulfate ($-OSO_3^-$), sulfonate ($-SO_3^-$), carboxy betaine ($-NR_2CH_2COO^-$), sulfobetaine ($-N(CH_3)_2\ C_3H_6SO_3^-$), and quaternary ammonium ($-R_4N^+$). For nonionic surfactants, this group is commonly a polyoxyethylene group (Nakama, 2017). There are also nonionic surfactants seen with glycerol or sorbitol groups. Depending on the application area, the selection of hydrophilic groups should be carried out.

Anionic surfactants are the type of surfactants that produce a negatively charged surface-active group (De & Mondal, 2012; Yuan et al., 2014). During micellization, for substrate binding, they create different regions, which are negatively charged surface and hydrophobic core regions.

Therefore, they can be used in the removal of both ionic and organic compounds (Das et al., 2008; Dunn et al., 1989; Misra et al., 2009; Witek et al., 2006). Cationic surfactants are the other type of surfactants, which produce a positive charged surface-active group (De & Mondal, 2012; Yuan et al., 2014). Similar to anionic surfactants, during micellization, they can create different regions and can be used in the removal of both ionic and organic compounds (Baek & Yang, 2004). Zwitterionic surfactants are another member of surfactants that include both anionic and cationic groups. These surfactants show different properties depending on the pH of the solution. At acidic solutions (pH <7), while they act as a cationic surfactant, at basic solutions (pH> 7) they act as an anionic surfactant. There also exists a specific pH value for zwitterionic surfactants where molecules have equally negative and positive groups. This pH value is called the isoelectric point. At this point, the zwitterionic surfactants represent the characteristic properties of the nonionic surfactants. They are generally used with nonionic or anionic surfactants to modify these surfactants' properties (De & Mondal, 2012). Nonionic surfactants are the final member of surfactants. These surfactants are electrically neutral. Therefore, the usage of nonionic surfactants alone is only possible for the removal of organic contaminants by Van der Waals force (De & Mondal, 2012).

When surfactants are added to the solutions, they can make slightly soluble or insoluble compounds soluble by binding solute with the surfactant micelles (Puasa et al., 2011; Qureshi &Blaschek, 1999). This phenomenon is named as solubilization and takes place with the micelle formation. Depending on types of compounds, materials binding with the surfactant micelles differs (Figure 1.2.1.2.) (Puasa et al., 2011; Rosen, 2004). For example, if compounds are ions, they bond with the surface of the head part of the ionic micelles with the help of electrostatic interaction (Puasa et al., 2011).

If compounds are large polar molecules, for example, polar dyestuffs or long-chain alcohols, it is believed that they are soluble in the palisade layer, which is the layer mainly between the micelle surfactants' hydrophilic group and their hydrophobic group's first few atoms closed to the hydrophilic group, because of the H-bond or dipole-dipole attraction between the solute's and the surfactant's polar groups. On the other hand, if compounds are hydrocarbons or longer-chain and less polar ones, they interact with core parts of the micelles by Van der Waals force and solubilize in the deep in the palisade layer or interior of the micelles (Puasa et al., 2011).



1. Surface of the micelle (micelle - surface interface)
2. Between the hydrophilic head groups
3. Palisade layer of micelle
4. Deeper part of the palisade layer
5. Inner core of micelle

Figure 1.2.1.2. Places of materials binding with the surfactant micelles (Rosen, 2004).

To obtain high separation in MEUF processes, selecting the correct type of surfactant is very important, because solubilization of compounds with micelles, and surfactants solubilization potential highly depends on surfactant type. For compounds, which are solubilized in the interior of the micelle or deep in the palisade layer, an increase in the size of the micelles has a positive contribution to their solubilization capacity (Rosen, 2004).

That is why any factor, which contributes to an increase in the micelle diameter or aggregation number, may causes the increase of solubilization of these types of compounds.

One of these factors is surfactants hydrophobic chain length. When the hydrophobic chain length of the surfactant is increased, there is an increase in solubilization of organic compounds in aqueous media. The reason of this phenomenon can be explained by the increase of the degree of dissimilarity between solvent and surfactant, which causes an increase in the aggregation number (De & Mondal, 2012). Examples of this factor can clearly be seen in literature (Kim et al., 2003; Luo et al., 2010; Zaghbani et al., 2009). Another factor that affects the aggregation number of micelles is the type of surfactants. Non-ionic surfactants tend to create larger micelles with approximately at the range of 20 to 16600 surfactant molecules (Rosen, 2004). On the other hand, for ionic surfactants, these clusters are created with about 15-130 surfactant molecules (Rosen, 2004) because the charge of the head groups tends to break the particles' unity by electrostatic repulsion (Baeurle & Kroener, 2004; Misra et al., 2009). That is why the non-ionic surfactants form larger micelles than their ionic counterparts.

As it is mentioned; above specific surfactant concentrations called critical micelle concentration, surface-active agents manage to increase the solubilization of poorly water-soluble substances by creating micelles. Thus, critical micelle concentration is the concentration where insoluble molecules start to solubilize. In addition to their high aggregation numbers, nonionic surfactants, also have lower CMC values than their ionic counterparts with the same hydrocarbon chain (De & Mondal, 2012). Thus, they can form micelles more easily with a greater size at lower concentrations. Hence, in very dilute solutions, they are better solubilizing agents compare to their ionic counterparts (De & Mondal, 2012; Rosen, 2004).

In general, among the different surfactants with the same hydrophobic chain length, the solubilization capacity of surfactants for hydrocarbons and polar compounds at micelles core is observed to be higher for nonionic surfactants.

After nonionic surfactants, this solubilization power is followed by cationic and then anionic surfactants (De & Mondal, 2012; Rosen, 2004).

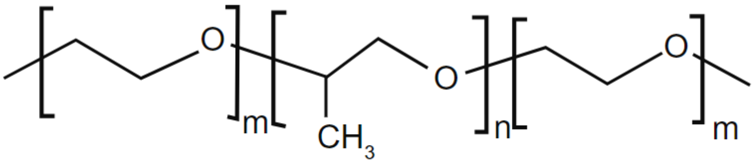
During surfactant selection, another factor that has big impact for MEUF performance is the surfactant characteristic for solubilization. Surfactants can also be classified according to their solubilities in water and lipids. If surfactants are soluble in water, they are named as hydrophilic, if they are soluble in lipids, they are named as hydrophobic or lipophilic surfactants. Although most of the ionic surfactants show hydrophilic property nonionic surfactants can show an either hydrophilic, or lipophilic property. This solubility property of them varies depending on the balance between their hydrophilic and hydrophobic groups and HLB (hydrophilic-lipophilic balance) is used as an indicator of this balance (Nakama, 2017). Depending on balance, higher HLB values indicate that surfactants have an affinity to the water phase. These surfactants create micelles solubilized in water and encapsulate the oily phase (Cheng & Sabatini, 2007). On the other hand, lower HLB values indicate that surfactants have an affinity to the oil phase. These surfactants tend to create reverse micelles to solubilized in oil and encapsulate the water phase (Cheng & Sabatini, 2007). Since, HLB shows the solubility property of nonionic surfactants, it is usually used for the selection of surfactants for different applications (Nakama, 2017).

In addition to HLB, the cloud point is the other important term that is used to describe nonionic surfactants' solubility characteristics. The cloud point is known as the specific temperature above which added surfactants cannot be solubilized in the water anymore. When polyoxyethylene nonionic surfactants are examined, that is seen; if the temperature is increased towards to cloud point hydrophilic group starts to lose their hydrophilic property and gain hydrophobic ability. This property transfer causes the shape of micelles to transform into a coil-shape meander structure. That results with raise up the molecular aggregation number and size enlargement of the micelle.

However, if temperature increase continues, when it reaches to cloud point surfactant loses its hydrophilic property and starts to show the lipophilic property. So that phase separation takes place and surfactant henceforth cannot be solved in water (Nakama, 2017).

In this study, among the surfactants, because of their mentioned advantages over ionic ones and separation potential for organic compounds, nonionic surfactants were used. Among nonionic surfactants, in the same molecular structure, but in different molecular weight and HLB ratio Pluronics (Alexandridis et al., 1994; Batrakova et al., 1999), which are the triblock copolymers of poly(ethylene oxide) (PEO)-poly(propylene oxide) (PPO)-poly(ethylene oxide) (PEO) (Figure 1.2.1.3.) were selected to be used in the experiments.

These surfactants, even in their non-micelle-formed state, can be highly retained by UF membranes. This reduces the loss of surfactants to the permeate (Choi et al., 1998; Heerema et al., 2010a; Heerema et al., 2010b). In other words, due to their high molecular weight, Pluronics can minimize the surfactant loss (Choi et al., 1998; Heerema et al., 2010a; Heerema et al., 2010b), which is the main disadvantage of the MEUF process. This became the basis affecting the selection of Pluronics as a nonionic surfactant.



PEO-PPO-PEO

Figure 1.2.1.3. Molecular structure of preferred nonionic surfactant.

In the literature, different MEUF studies exist which uses these surfactants.

Choi et al. (1998) used the PEO-PPO-PEO block copolymers with the MEUF method to study the separation of 1-naphthol and phenol compounds from the aqueous wastewater. In the study, which was done with the dialysis system, by using polysulfone (PS) Membrane at 3500 Dalton MWCO value and Pluronic P85, P103, and F108 surfactants, with the highest hydrophobicity value (PPO / PEO Ratio = 1.79) Pluronic P103 had shown the best 1-naphthol and phenol separation performance. In the experiments, which were done by using 125 ppm 1-naphthol and phenol at 25°C, when there was no Pluronic P103, there was approximately 2.5% 1-naphthol and phenol rejection observed. On the other hand, when there was Pluronic P103 at its CMC (0.08wt.%), this rejection value had reached 72% for phenol and 85% for 1-naphthol. Moreover, in the case of P103 concentration at the solution was doubled, 1-naphthol and phenol rejection had reached 90% and 75%, respectively. When there is a temperature increase had taken place, a slight increase in the rejections was seen.

Richardson et al. (1999) with MEUF method, by using Pluronic F127 in the PEO-PPO-PEO Block Copolymer structure, N-octylamide-substituted poly (sodium maleate-alt-ethyl vinyl ether) (C8-MA-EVE), and Bovine Serum Albumin (BSA) polymers, aimed to separate p-creasol from the aqueous wastewater. In this separation, with the regenerated cellulose (RC) membrane at 6000 Dalton MWCO values, and the dialysis system studies had been conducted. As a result of the first filtration, which was conducted at 25°C with the 0.8 g/dL concentration of Pluronic F127 that has a CMC value of 0.6 g/dL, 22% p-cresol rejection had been obtained. However, a cascade of series connected UF membranes were used, it was observed that the removal rate of p-creasol from the water was increased. This rejection ratio had reached the 65% due to the filtration of the same sample 5 times.

Aoudia et al. (2003) performed ultrafiltration experiments using Triton X-100, which has a short PEO chain as hydrophilic side, and Tergitol DX surfactants, which is an alkyl EO/PO copolymer, to purify the petroleum emulsion in water from the wastewater of the oil extraction process. In Dead-end filtration experiments performed at room temperature using RC membrane with 3000 Dalton MWCO value, 38% oil rejection was obtained when there was no surfactant in the environment. When 1CMC and 2 CMC concentrations of Tergitol DX was added, it was observed that the obtained rejection rate was over 99.5%. Researchers also observed similar high oil retention rates in filtrations with 0.7CMC concentration of Tergitol DX surfactant. The reason for the high retention value seen in this concentration, which is not expected to form micelle under normal conditions, is attributed to the concentration polarization formed during filtration. In other words, it is thought that high rejection is obtained due to the increased concentrations on the membrane surface leading to micelle formation.

Heerema et al. (2010a, 2010b) conducted a study in which they aimed to remove phenol from the fermentation medium by using Pluronic group surfactants. Phenol formed during fermentation in the bioreactor operated at 30°C was trapped inside the Pluronic micelles. These micelles containing phenol were retained in the membrane unit in the reactor and low phenol concentration water was fed back to the reactor. Experimental results showed that solutions containing 2.5% Pluronic and 3.5 mM phenol concentration by weight at fermentation temperature (30°C) have phenol solubility ratios ranging from 0.58 to 1.75. In other words, in the stripping phase, it was observed that the phenol concentration was 0.58 to 1.75 times higher than the phenol concentration in the aqueous phase.

When the studies are examined, it is obvious that Pluronics make an important contribution to the separation of organic materials.

During MEUF processes, surfactant selection is important in terms of separation performance and permeability of solutes. However, surfactant recovery also carries big importance after each process.

The high cost of surfactants composes the large part of the operating cost of this separation process. In case surfactants are not recovered, each time new surfactants should be added to the system. That means extra cost to operation. Moreover, even though PEO-PPO-PEO block copolymers are environmentally safe and mild as biosurfactants, they should not be discarded to the environment.

For surfactants recovery, in literature application of different methods are seen. However, the performance of each method is not the same in terms of the high surfactant recovery rate and reuse after recovery. Among these methods, for ionic surfactants mainly three methods are preferred for recovery after MEUF processes (Huang et al., 2017; Tortora et al., 2018). These are acidification followed by ultrafiltration (Anthati & Marathe, 2010; Huang et al., 2017; Kim et al., 2006; Li et al., 2009; Tortora et al., 2018), the chelating agent followed by ultrafiltration (Anthati & Marathe, 2010; Kim et al., 2006; Li et al., 2009), and precipitation (Kim et al., 2006). On the other hand, in the literature it is seen; after the MEUF process for the recovery of nonionic surfactants which are in the form of the PEO-PPO-PEO block the temperature effect is used. Temperature-dependent micellization and gel formation are two of the most characteristic properties of aqueous PEO-PPO-PEO block copolymer solutions (Alexandridis et al., 1994). PEO-PPO-PEO block copolymers can be self-assembled into the various structures in aqueous solutions due to the concentration and temperature changes. At the low temperature and low concentration, they exist in the form of unimers. However, due to the temperature or concentration increases after passing the certain temperature (CMT) or concentration (CMC) barrier, they form micelles. Also, further increase in the temperature or the concentration causes the increment in the solution viscosity and ends up with gel formation. For the gel formation, while the concentration value that has to be overcome is named critical gel concentration (CGC), the temperature value exceeds the name critical gel temperature (CGT) (Figure 1.2.1.4.) (Cho, 2009). Therefore, in addition to the concentration, to create micelles they should also satisfy the specific temperature, which is called critical micelle temperature (CMT).

After the usage of surfactants which are in the form of the PEO-PPO-PEO block, decreasing solution temperature below CMT results with the breakdown of micelles and the release of encapsulated solutes. Hence, by simple filtration surfactants and solutes can be separated from each other (Choi et al., 1998; Heerema et al., 2010a).

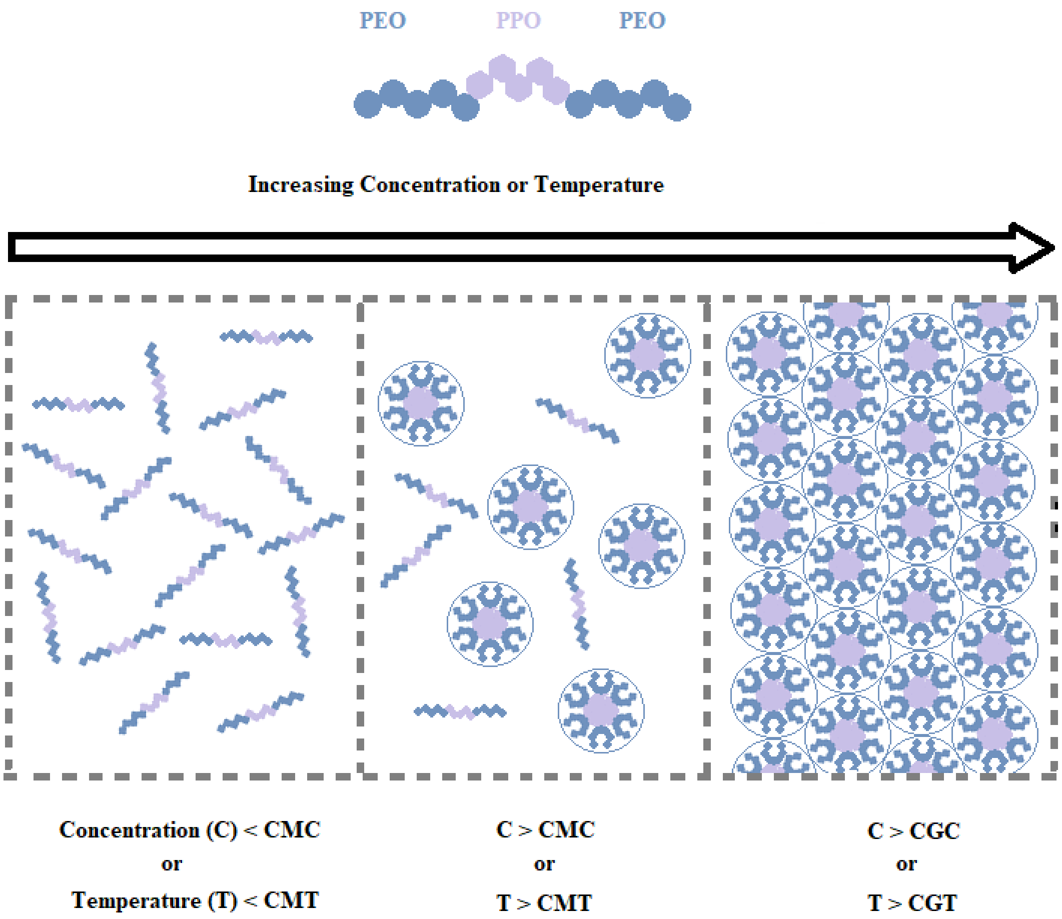


Figure 1.2.1.4. Due to the increasing concentration and temperature surfactants firstly micelle and then gel formation (Cho, 2009).

1.2.2 Mixed Surfactant Systems

During MEUF processes, although the separation processes can be performed by single surfactant solutions, by preparing mixed surfactant solutions performance of separation processes may be improved. In the literature, there are different studies in which mixed surfactant systems are used. As an example, mixtures of anionic and nonionic surfactants can be given. The anionic surfactants are often used in MEUF experiments to separate charged particles from solutions. In cases where these surfactants are mixed with nonionic surfactants, it is seen that the CMC values decrease, the amount of anionic surfactant lost to the permeate side decreases, and the mixed system contributes positively to the rejection of ionic materials that are solubilized in micelles. Therefore, the anionic-nonionic mixed surfactant system is an example of a mixed surfactant system frequently encountered in the literature. (Yenphan et al., 2010). Also, anionic-cationic surfactant mixtures used to separate both anionic and cationic materials from solutions can be given as another example of mixed surfactant systems (Das et al., 2008).

In the mixed surfactant systems, for nonionic-nonionic surfactant systems, nonionic surfactants can be adjusted to the desired properties. HLB values and water solubility of surfactants can be given as an example in this case. For instance, when two nonionic surfactants with a higher and lower HLB value than X are mixed, a water-soluble surfactant with an HLB value of X can be obtained (Rosen, 2004; Williams,2007). So that, instead of one surfactant with an HLB value of X but which cannot be used because of its insoluble in water, two surfactant mixtures can be preferred. The formulation used for HLB value analysis is as follows.

$$\begin{aligned} \text{HLB Desired} &= (\text{wt.\% of Surfactant 1}) \times (\text{HLB value of Surfactant 1}) \\ &\quad + (\text{wt.\% of Surfactant 2}) \times (\text{HLB value of Surfactant 2}) \end{aligned}$$

1.2.3 Membrane Selection

Choosing a suitable membrane is as important as choosing a suitable surfactant for a successful separation process. For MEUF experiments, membrane material, surface properties, and MWCO/pore size are the three basic properties that should be considered during membrane selection.

During the experiments, the membrane material selection should be made by considering the operating conditions such as pressure, temperature, and pH value of the filtered solution. In the experiments, generally, polymeric membranes such as polytetrafluoroethylene (PFTE), regenerated cellulose (RC), polyvinylidene difluoride (PVDF), cellulose acetate (CA), polyacrylonitrile (PAN), polysulfone (PS), polyamide (PA), and polyethersulfone (PES) are used (Schwarze, 2017; Yaqub & Lee, 2018). However, there are also experiments using ceramic membranes in different studies (Aoudia et al., 2003; Fernández et al., 2005; Gadelle et al., 1996).

Another basic membrane property to be considered during membrane selection is the surface properties of the membranes. These properties affect the adsorption of surfactants or dissolved substances in solution by the membrane and the permeate flow rate. The concentration polarization and surfactant adsorption are two main problems that affect the membrane performance during the filtration processes. Between them, the adsorption of surfactants on the membrane is a serious disadvantage as it has a negative effect on both flow rate and rejection of surfactants (Byhlin & Jönsson, 2003; Schwarze et al., 2009). In different studies conducted by using TritonX-100 nonionic surfactant which has an HLB value of 13.5 and hydrophobic PES and hydrophilic RC membranes with the same MWCO value, it was observed that TritonX-100 adsorption was stronger on the hydrophobic surface. This adsorption caused by hydrophobic interaction substantially decreases the permeate flux in PES membranes compared to pure water flux (Byhlin & Jönsson, 2003; Schwarze et al., 2009).

On the other hand, it is seen in literature studies that the adsorption of surfactant to the membrane material change depending not only on the type of surfactant but also on the hydrophilic-lipophilic balance (HLB) of surfactants from the same group (Kim et al., 1998; Schwarze et al., 2009). Another study aimed to use the MEUF procedure to separate phenol and o-cresol from an aqueous solution at room temperature. However, as a result of the filtration of the solution with PES membrane before the surfactant was added, 24% phenol and 41% o-cresol rejection were observed. Due to their size, these materials cannot be rejected by ultrafiltration membranes. However, due to their structural similarities with the membrane material, the hydrophobic interaction between them caused them to be adsorbed by the membrane (Chaudhari & Marathe, 2010).

MWCO is a characterization method used for defining solute rejection capabilities and pore size distribution of filtration membranes among a mixture of probe solutes of varying MW. It indicates the molecular weight of the solute, which is %90 rejected by the membrane. During membrane selection, it should be taken into consideration that the micelles that will form should be larger than MWCO value. As the MWCO value of the selected membranes increases, the flow rate of pure solvent increases. With the increase in the MWCO value, there is also an increase in the permeate flux of the MEUF solutions. However, this increase in MWCO may also cause internal fouling on the membrane pores (Baker, 2004; Schwarze, 2017; Yaqub & Lee, 2018).

1.2.4 Pressure

Pressure is the driving force of the separation in the MEUF process. Its increase positively affects the pure water flux. However, the pressure increase in the presence of surfactant or solute increases the permeate flux only up to a certain point (Figure 1.2.4.1.).

During the filtration processes, under the effect of pressure, both solvent and macromolecules are transported towards the membrane surface. As a result of this transport, while small-sized materials pass from the membrane to the permeate side, macromolecules are rejected. Since the return of rejected materials from the membrane surface to the bulk solution takes place relatively slowly, concentration polarization is observed on the membrane surface. At that point, a rise in the applied pressure increases the permeate flux. However, as the amount of rejected materials carried towards the surface rises with the increment of flux, an increase in concentration polarization is observed. Further increase of the pressure results in gel layer formation on the membrane surface. This pressure at the point of gel layer formation is named plateau pressure and flux as limiting flux. The pressure increase made after this point only increases the thickness of the gel layer and does not cause a change in the flow rate. For this reason, for the best filtration performance in the long term, experiments should be done at the point where the limiting flux is reached or slightly below that point (Baker, 2004).

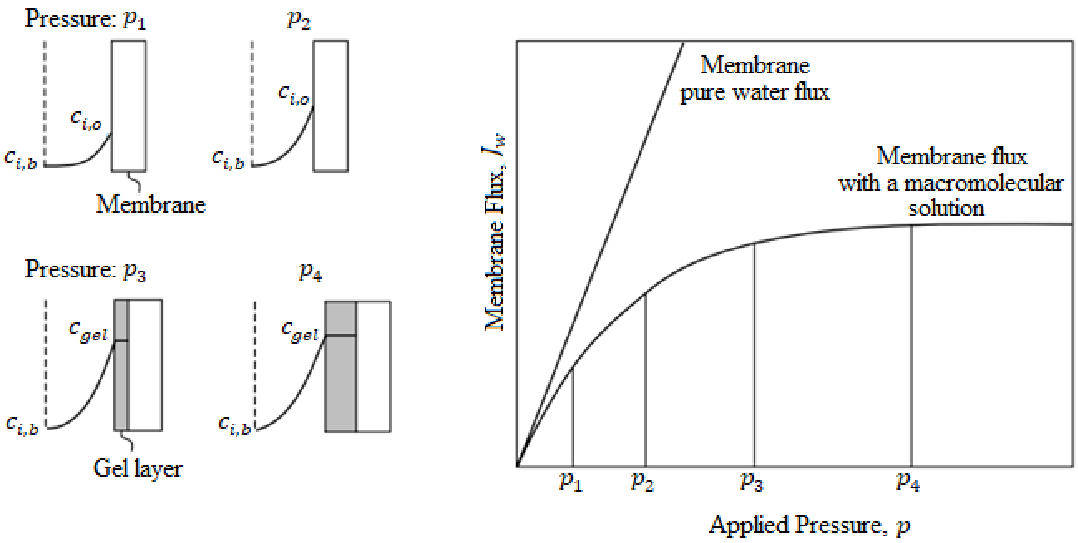


Figure 1.2.4.1. Gel layer formation and the change of membrane flux with applied pressure (Baker, 2004).

1.2.5 Surfactant Concentration

As mentioned earlier, surfactants are one of the main costs of the MEUF process. That is why, to reduce the cost, the surfactant concentration should be kept as low as possible and should not be lost during the process. However, the efficiency of the process is also directly related to the amount of surfactant in the solutions.

In different studies conducted using anionic, cationic, and nonionic surfactants with phenolic or phenolic derivatives, an increase in the separation efficiency of solutes (phenolic or phenolic derivatives) was observed with increasing surfactant concentration (Huang et al., 2015; Purkait et al., 2005a; Purkait et al., 2005b; Zhang et al., 2012). Also, the experiments had shown an increase in distribution coefficient, which is the solute concentration's ratio in the retentate and permeate stream. So that, more surfactant molecules had found in the micellar phase and by binding more solute increased their rejection (Huang et al., 2015; Zhang et al., 2012). On the other hand, as a result of the increase in the amount of solute in the solutions, a decrease in solute rejection was observed. While the concentration and that is why the solubilizing capacity of micelles was constant, the amount of solute concentration ascends had been interpreted as the reason for this decrement. Because, due to this increase and constant surfactant concentration, the concentration of insolubilized solute in the solution had increased. So that, the solute concentration in the permeate had raised, and the rejection had decreased (Zhang et al., 2012; Purkait et al., 2005a; Purkait et al., 2005b).

Based on these studies, working with a high surfactant concentration is beneficial for better separation performance. However, with increasing surfactant concentration, the number of micelles also increases, and this increase brings about the increase in the amount of fouling formed is another result of the increase in surfactant (Huang et al., 2015; Purkait et al., 2005a; Purkait et al., 2005b). With the increase in the number of micelles in the solution, after a certain point, the micelles, depending on their shapes, start to pack in different geometric patterns.

These different ordered arrangements of molecules cause an increase in viscosity in the solution (Rosen, 2004). Due to this increase in the concentration of surfactants, the formation of thermoreversible gels in the progressive stages with increasing viscosity values of the solutions is the other result of surfactant's concentration increase (Rosen, 2004; Wanka et al., 1990). That is why gelation and fouling should be taken into consideration as well as the separation efficiency while determining the surfactant concentration to be used.

In the literature, it has been seen that both micelle and gel formation is affected by different factors such as the different materials in the feed solution and temperature (Alexandridis & Alan Hatton, 1995; Rosen, 2004). For example, alcohol, urea, and sodium dodecyl sulfate in the solutions caused a decrease in CGT value, while the presence of $NaSO_4$, KCl, and NaCl had the opposite effect (Alexandridis & Alan Hatton, 1995). In addition, with increasing concentration, the CGT moves towards lower values, while with increasing temperature the CGC moves to lower values. In other words, concentration and temperature values are inversely proportional to each other (Wanka et al., 1990).

1.2.6 Temperature

Temperature is an operating parameter that has many effects on the performance of the experiments. Starting from surfactants' solubility, it is effective on many factors such as CMC values of surfactants, the viscosity of solutions, and micelle properties. One of the important points to be considered about the solubility of nonionic surfactants is the cloud points of surfactants. The cloud point is the point where above, nonionic surfactants are separated into the surfactant-rich, and the water-rich phases in their aqueous solutions. After the phase separation occurs, surfactants cannot be dissolved in water (Rosen, 2004). Structural changes which are seen in surfactants cause changes in cloud point values of surfactants (Rosen, 2004).

For example, it is seen that cloud point values increase with the increase of hydrophilic character of surfactants, which is one of these structural differences (Alexandridis & Alan Hatton, 1995; Dhamole et al., 2015; Rosen, 2004).

At the same time, similar to the formation of micelle and gel, there may be a change in cloud point value in the presence of solutes (Alexandridis & Alan Hatton, 1995; Rosen, 2004). The main advantage of the increase in temperature is that the size of the formed micelle increases as the temperature increases and approaches the cloud point (Alexandridis & Alan Hatton, 1995; Qureshi & Blaschek, 1999; Rosen, 2004). In this way, for nonionic PEO surfactants, non-polar materials such as aliphatic hydrocarbons and alkyl halides dissolved in the inner core of the micelle show increasing solubility as the temperature rises, and the increase becomes much faster as the cloud point of the surfactant approaches (Rosen, 2004).

In addition to temperature effects on gel formation, the temperature is another factor that causes the CMC values of surfactants to change. There is a decrease in CMC values in nonionic surfactants depending on the temperature increase (Alexandridis et al., 1994). So that, more micelles are present in the solution at higher temperatures with the same surfactant concentration.

1.3 Acetone-Butanol-Ethanol (ABE) Fermentation

Butanol that has the molecular formula of C_4H_9OH is a multifunctional alcohol. It is extensively used in the production and synthesis of other chemicals such as butyl acetate, acrylate, methacrylate esters, glycol ethers, and many other compounds used in electronics, paints, plastics, detergents, drugs, cosmetics, hormones, textile products, vitamins, and antibiotics. However, the realization that it can be used as an alternative fuel recently has increased the interest in butanol (Dürre, 2007; Gottumukkala et al., 2019; Lee et al., 2008; Ni & Sun, 2009).

The main reason for this interest is that at certain points, it has more advantageous features compared to ethanol and methanol, which are other alternative fuels. For instance, butanol is a more effective energy source compared to ethanol and methanol, because the released energy as a result of its combustion is closer to the energy released from gasoline combustion. While the energy density of gasoline as a result of combustion is 32MJ/L, the energy density of butanol, ethanol, and methanol is 29.2 MJ/L, 19.6 MJ/L, and 16 MJ/L, respectively (Gottumukkala et al., 2019; Lee et al., 2008). In addition to that, compared to other alcohols, butanol is not completely soluble in water and not hygroscopic. Therefore, when it is mixed with gasoline, the water absorption rate is less than the ethanol-gasoline mixture. Since water can dissolve acids and ions, water in the fuel transfer lines creates a corrosive effect. Compounds with a high water absorption rate will increase the water absorption of fuel, in other words, they increase the water rate in the fuel transfer lines, and gain corrosive features (Matějovský et al., 2017). Hence, butanol is less corrosive compared to ethanol. Thanks to this feature, contrary to ethanol, it does not need to be mixed with gasoline just before use. It can be found in storage and distribution areas mixed with gasoline and can be used in all infrastructure of the refinery such as tanks, pumps, pipelines. Also, in case of any spillage, due to its partially miscible feature, it prevents groundwater pollution (Abdehagh et al., 2014; Dürre, 2007). Moreover, ethanol can only be blended with gasoline up to specific ratios. On the other hand, butanol can directly replaces gasoline or mixed with gasoline in any proportion without needing any modification in automobile engines (Abdehagh et al., 2014; Dürre, 200; Ni & Sun, 20097). Also, Butanol's lower volatility, lower vapor pressure properties make it safer to handle.

Among the production ways of butanol, whose size is estimated to be 3.1 billion USD for the global market in 2020 and which is expected to increase gradually (n-butanol Market, 2021), there is fermentation in addition to a few chemical synthesis methods which are Oxo process, Reppe process, Guerbet reaction, and crotonaldehyde hydrogenation (Lee et al., 2008; Patil et al., 2019).

In butanol production, for the fermentation process, different bacteria and substrates can be used (Li et al., 2019; Patil et al., 2019; Zhao et al., 2019). The selection of the used bacteria depends on different factors such as production conditions and locally available raw materials (Ni & Sun, 2009). Among these bacteria, because of their relatively high yields under favorable fermentation conditions, mainly four different *Clostridium* strains are preferred. These are *C. acetobutylicum, C. beijerinckii, C. saccharoperbutylacetonicum,* and *C. saccharobutylicum* (Li et al., 2019, Ni & Sun, 2009).

As a result of fermentation, not only butanol but also ethanol and acetone are obtained as products in aqueous media. This produced mixture is called the ABE mixture. The amounts of acetone, butanol and ethanol obtained in this mixture can vary depending on various factors such as the used substrates and strains (Ni & Sun, 2009). In different studies, it has been reported that 1 - 9 g / L acetone, 1 - 10 g / L ethanol, and 6 - 25 g / L butanol are present in the solutions obtained by the following ABE fermentation (Abdehagh et al., 2014; Lee et al., 2008; Lépiz-Aguilar et al., 2013; Lodi et al., 2016).

There are several methods in the literature for product recovery from ABE mixture, including pervaporation, gas stripping, liquid-liquid extraction, pertraction (membrane extraction), distillation, membrane distillation, adsorption, and reverse osmosis (Abdehagh et al., 2014; Kraemer et al., 2011; Kujawska et al., 2015; Liu et al., 2005; Liu et al., 2011; Lu et al., 2012; Qureshi & Blaschek, 1999; Qureshi et al., 2001; Qureshi et al., 2005). Among these methods, pervaporation, gas stripping, distillation, adsorption, and liquid-liquid extraction are widely used.

Distillation is one of the separation technique used for the recovery of ABE mixture compounds in the industry. Nowadays, in different processes frequently used this traditional ABE separation technique uses the boiling point differences of the compounds in the mixture. However, high energy consumption and low selectivity in the butanol recovery make the technique disadvantageous (Outshoorn et al., 2009).

In adsorption, butanol is separated from the ABE mixture using a suitable adsorbent. Later on, it is desorbed from the adsorbent, and concentrate butanol solution is produced. As a result of different studies, this separation technique has been one of the most energy-efficient techniques among the other butanol separation methods is observed (Abdehagh et al., 2014; Outshoorn et al., 2009). Moreover, used adsorbents have a higher selectivity to butanol over water is the other advantage of this separation technique. However, besides these advantages, there are also different problems in the recovery of butanol via desorption of adsorbed butanol from the adsorbent surface (Kujawska et al., 2015; Sarchami et al., 2016). Furthermore, in *in-situ* butanol recovery systems, bacteria can adhere to the adsorbent, and specifically in the recycle of adsorbent to the system its adsorption efficiency can be decreased (Kujawska et al., 2015).

Gas stripping process, which is used in ABE separation due to the compounds' volatility properties, is advantageous because of the low operating cost and simplicity of the system. Moreover, since the process, which can be operated under the fermentation temperature, removes only volatile compounds from the fermentation broth, almost all reaction intermediates can be converted to the ABE. Additionally, in separation, the usability of fermentation produced CO_2 and H_2 gases is another advantage of the process (Abdehagh et al., 2014;Kujawska et al., 2015; Sarchami et al., 2016). However, gas stripping has low butanol selectivity and low efficiency make the process disadvantageous (Outshoorn et al., 2009; Sarchami et al., 2016). Also, to prevent excessive foam formation created because of tiny bubbles during gas stripping used antifoam agent may be toxic to the bacteria (Kujawska et al., 2015).

Liquid-liquid extraction (LLE) is another technique used to separate butanol from fermentation broths. Extractants' high butanol capturing capacity (Kujawska et al., 2015) and high selectivity of butanol over water are the main advantages of the LLE method compared to the other techniques (Outshoorn et al., 2009; Kujawska et al., 2015). Also, for extraction, low energy demand is another advantage of the method (Abdehagh et al., 2014; Friedl, 2016).

On the other hand, in the direct contact of extractants with fermentation broth, fouling of the extractants (Kujawska et al., 2015) and emulsion formation (Abdehagh et al., 2014; Friedl, 2016; Kujawska et al., 2015; Sarchami et al., 2016) are the main drawbacks of the method.

Pervaporation which is generally used for separation processes in binary or multi-component liquid mixtures is the other ABE separation method. The method which uses the difference in solubility/sorption and diffusivity of components is advantageous in terms of usability in the separation of azeotropic mixtures near the boiling point (Abdehagh et al., 2014). On the other hand, it is an advantageous method for the separation of butanol in terms of having high selectivity, low operating temperature, being an energy-efficient method, and having no effect on microorganisms and nutrients (Abdehagh et al., 2014; Outshoorn et al., 2009; Sarchami et al., 2016). However, because pervaporation is a rate-controlled process, the permeate flux through the membrane is generally low and a large membrane surface area is required. The factors including membrane swelling, low fluxes, and concentration polarization are the mains drawbacks of the method (Abdehagh et al., 2014; Sarchami et al., 2016).

As it is seen, although each process has its own benefits, some disadvantages must be eliminated for better separation performance. Therefore, improvements in the product recovery methods, and new product recovery techniques from the ABE mixture are under investigation.

In the butanol separation process, most of the methods have focused on separating the butanol from the ABE after it has formed. However, in biobutanol production, the amount of butanol being more than certain values, depending on the used strain, has a toxic effect on microorganisms during fermentation. That inhibits the cell growth, so the butanol production. Thus, to increase the produced butanol concentration, separating butanol from the fermentation broth, instead of separating it from ABE, is another aspect of the studies.

For this purpose, Dhamole et al. (2012, 2015) conducted studies on extractive fermentation of butanol using the nonionic surfactants for the first time. Afterward, Singh et al. (2017) continued the research by using a strain producing a relatively high amount of butanol.

Dhamole et al. (2012) aimed to increase butanol amount produced as a result of fermentation by overcoming the problem of the end product (butanol) toxicity with the help of nonionic surfactants. For this purpose, by using *Clostridium pasteurianum* (NRRL B-598) as an acetone-butanol (AB) production strain and Triton X 114, Pluronic L61, L62, L62LF, and L64 as nonionic surfactants experiments were conducted. At first, it was aimed to find the butanol capturing capacity (BCC) of the selected nonionic surfactants with the dialysis cell method at 30°C. As a result of the experiments, it was seen that; while Triton X 114 had the highest BCC rate with 0.6kg/kg, the BCC of Pluronic L62LF, L62, L64 were 0.52, 0.32, 0.06 kg/kg, respectively. On the other hand, since L61 is insoluble in water, its BCC value could not be found. Moreover, when the surfactants were added to the fermentation broth, while Triton X 114 was totally inhibiting AB production, L64 was reducing the rate of produced acetone and butanol by approximately 50%, and L61 and L62LF were producing nearly the same amount of butanol as the control. Contrary to all, it had been seen that the fermentation with L62 enhanced the AB fermentation. The addition of 3% L62 increased the acetone as well as butanol production by 70%. In the experiments with L62, also, acetone and butanol production increased by 25% with the increase of the added surfactant concentration to 6% had seen. But the subsequent pluronic additions did not cause any enhancement in the production. At the end of the experiments, the solutions were divided into surfactant-rich and aqueous phases by increasing the temperature above the cloud point. To separate butanol and water from the surfactant-rich phase, the surfactant phase was heated to 120-130°C, and the butanol and ethanol were first evaporated and then condensed with a water trap. In this way, while 95% of butanol was recovered from the surfactant-rich phase, it was observed that it worked with the same efficiency in the reuse of the recovered Pluronic.

In the study of Dhamole et al. (2015), the previous study carried on a wider Pluronic scope. In this study, as a continuation of the previous one, Dhamole et al. (2015) were aimed to find a nonionic surfactant with the highest BCC in fermentation broth by working on a wider Pluronic scope. At the same time, separation of the surfactant from butanol at a temperature close to room temperature, and not extracting it with any intermediate or substrate such as glucose were other studies within the scope of the study. During experiments, while as a surfactant Pluronic L31, L61, L62D, L62LF, L62, L64, P65, L81, P84, L92, L101, P104, P105, L121 were used, as a strain *Clostridium acetobutylicum* ATCC No. 824 (NCIM No. 2337) was preferred.

As a result of experiments conducted by adding 1% v/v into the model fermentation medium system, used L62D both had maximum butanol capturing capacity (0.68 g/g of butanol) and was biocompatible had been observed. Also, when L62D concentration in the fermentation medium was raised to 3% v/v, butanol production enhanced by %148 compared to the surfactant-free system. In addition to these, in the presence of 1-5% L62D, 60g/L glucose, 3g/L acetic acid, and butyric acid in the medium, total loss of glucose, acetic acid, and butyric acid was less than 4% had been observed.

So, L62D can be used for extractive fermentation as it not only enhances butanol fermentation but also results in negligible loss of intermediates and glucose.

1.4 The Aim of the Study

In this study, as an alternative to the other separation methodologies, developing a procedure using the micellar enhanced ultrafiltration (MEUF) method to separate butanol from the aqueous acetone-butanol-ethanol mixture that formed as a result of fermentation is aimed.

All of the MEUF applications focus on the removal of minor contaminants for environmental and/or water reuse purposes, and the product is mainly permeate. In this study, a MEUF process is tried to be developed to selectively obtain a major component from the fermentation broth, and the main product is the retentate. No similar application exists in the literature.

It is known that, in the aqueous environment, surfactants at specified concentration (CMC) and temperature values (CMT) create micelles whose inner core is hydrophobic, and the outer shell is hydrophilic. Also, while ethanol and acetone show the totally miscible property in the water environment, butanol is partially miscible in water. Therefore, in the MEUF procedure which planned to be developed, when dissolved acetone, butanol, and ethanol in water exist in the same environment with the formed micelles, butanol is expected to be selectively encapsulated in the micelles. In this way, at low-pressure, it will be possible to reject butanol by ultrafiltration (UF) membranes which has much larger pores than the organic substances to be retained. In this study, nonionic polymeric surfactants, Pluronics are used.

The important feature of these surfactants for the MEUF process is their high molecular weight. Hence, when large-pore and high permeability UF membranes are used, they will not be lost by passing to the permeate side. Also, the change in the CMC for micelle formation of these surfactants with temperature is the other reason for their preference. Thanks to this feature of Pluronics, after the separation process is completed by decreasing the temperature under the certain value (CMT) necessary for micelle formation, micelles can be broken up. After that point, with a conducted filtration, the surfactants can be separated from butanol and fed back to the process. Moreover, if the butanol solubility limit in water is passed in the permeate side obtained concentrated mixture, butanol and water can be separated from each other easily.

Starting from the used nonionic surfactant type, many factors such as the surfactant concentration, mixed or single surfactant system, temperature, and pressure affect both the butanol rejection and the filtration flux of the experiments. For this reason, determining the optimum conditions and surfactant or surfactant mixtures with the best butanol separation performance for experiments has been the primary goal of the study. Then, it became the aim of the second stage to complete the ABE filtration and to observe the separation performance with the selected surfactant or surfactant pair under specified conditions.

CHAPTER 2

EXPERIMENTAL PROCEDURE

2.1 Materials

In the study, as nonionic surfactants Pluronic F127, L61, L64, L101 and P123 were used. Important properties of these surfactants can be seen in Table 2.1.1. Also, as membranes EMD Millipore hydrophilic regenerated cellulose ultrafiltration membranes with 1 kDa (PLAC07610) and 5 kDa (PLCC07610) MWCO values were used. These membranes are suitable to use a maximum of under 50°C temperature and 4.8 bar pressure. Moreover, they are suitable in pH range of 3–13 (Merck, 2019). In later stages, experiments continued with DOW hydrophilic NF90 nanofiltration membranes, which are thin-film composite (TFC) polyamide membranes. Different from RC membranes, they are resistant up to 45°C temperature and 41 bar pressures. Also, their operable pH interval is 2–11 (DUPONT, 2020).

Table 2.1.1. Properties of selected Pluronics (Alexandridis et al., 1994; Batrakova et al., 1999).

Pluronic	**Molecular Weight**	**Average Number of PPO Units**	**Average Number of PEO Units**	**HLB**	**CMC**
F127	12600	65.2	200.4	22	5.55×10^{-4}
L64	2900	30	26.4	15	4.8×10^{-4}
L61	2000	31	4.5	3	1.1×10^{-4}
L101	3800	58.9	8.6	1	2.1×10^{-6}
P123	5750	69.4	39.2	8	5.2×10^{-5}

Butanol (98%), ethanol (99.5%), acetone (99.5%), Pluronic F127, and Pluronic P123 were purchased from Sigma-Aldrich. Pluronic L61 and Pluronic L101 were supplied by BASF. Commercial NF90 nanofiltration membrane from DOW and 1kDa and 5kDa regenerated cellulose ultrafiltration membranes from Millipore were purchased.

While preparing feed solutions for filtration experiments and at physical membrane cleaning procedures ultrapure water (UP) was used.

2.2 Solution Preparation

During experiments, different solutions were prepared. While preparing these solutions, for the ones included butanol, ethanol, acetone, and ABE initially solutions without surfactants were prepared in the aqueous environment. For the solutions only including Pluronic or Pluronic mixture directly UP was used.

Simulated synthetic ABE mixture used in this study contains 5g/L acetone, 20g/L butanol, and 5g/L ethanol. From prepared butanol or ABE aqueous solutions, part of the solutions was separated as a feed solution for GC analyses. Remaining was mixed with the specified amount of surfactants. In the mixtures which include two different surfactants, firstly one surfactant and prepared aqueous solutions were mixed, and a homogeneous mixture was obtained. Afterward, the obtained solution was mixed with the other surfactant. The surfactant, which was solubilized at the first step, was chosen as the one which has higher water solubility. Depending on their solubility at room temperature, for some of these solutions stirring procedure was conducted in a water bath. One of the solution calculations and preparation were demonstrated in Appendix A, to show how much compound was added to prepare the solutions, which were at specified concentrations.

Mainly solutions that included butanol were aimed to be used for filtration experiments which was conducted for butanol separation. However, before filtrations depending on their solubility, turbidity, micelle size, and gel formation, they were also examined for either they could be used as feed at the filtrations or not. Among the solutions, there were ones that containing only surfactants. From them, Pluronic L61 and Pluronic L101 solutions were prepared to test the solubility amount of these two surfactants in aqueous media. On the other hand, Pluronic F127 and Pluronic P123 solutions had been prepared for surface tension analysis. Also, Pluronic F127, L64, L101, and P123 included solutions were prepared for the membrane suitability detection for the filtration. The solutions that were including the ABE mixture were prepared to mimic the fermentation product.

2.3 Filtration and Cleaning Procedures

Solutions were stored in the refrigerator until the time they were filtered. When they were taken out from the refrigerator, initially they were brought to room temperature. Later, they were poured into the dead-end filtration module and without applying any pressure they were stirred 60 minutes in a water bath. There were mainly two reasons for mixing and heating the solutions before the filtration. Firstly, heating the solutions to the filtering temperature, which was 26°C for some mixtures and 37°C for the others, was necessary. Also, for homogenizing the solution temperature, a stirrer was used. Secondly, it was wanted the guarantee the micelle formation and butanol encapsulation. During filtrations by using 400 ml Amicon Cell, at 150-200 rpm stirring value, and at 3 bar TMP experiments were conducted. Only at the experiments, which were done for limiting flux detection, with the same cell at the same stirring value, at the 0.5, 1, 3, and 4 bar pressures filtrations were performed. For all filtrations, the used flat sheet membranes' effective areas were 41.8 cm^2.

Temperature is one of the key parameters in terms of micelle formation and surfactant solubilization. Therefore, throughout the filtrations, cells were held in the water bath and the temperature had been stabilized. Picture of the filtration setup and elements of it can be seen from Figure 2.3.1.

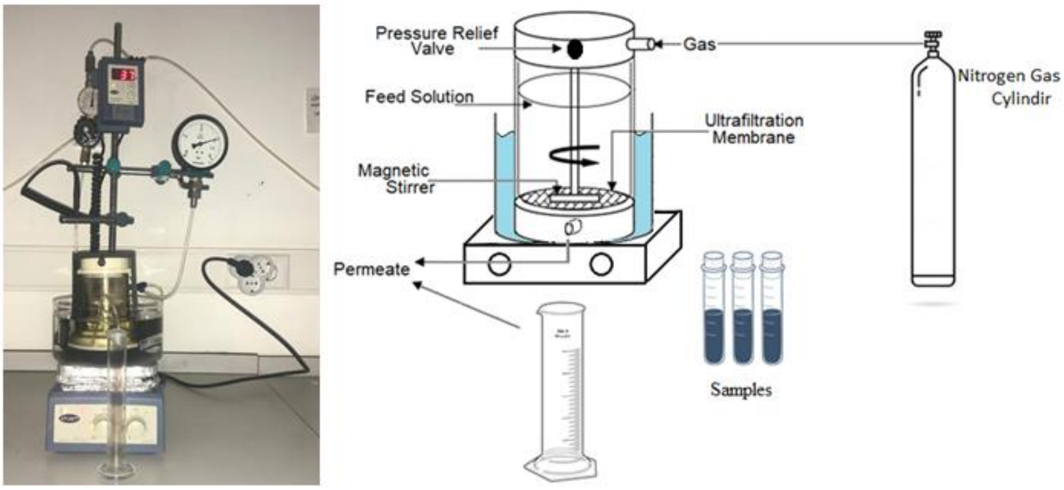


Figure 2.3.1. Filtration experiments setup with 400ml Amicon stirred cell.

At the start-up of the filtration, 85 ml feed was used. In the beginning, while 40 ml of the feed was collected as a filtration permeate. Based on analysis results and used surfactants this amount was later increased to 70 ml. Afterwards, for the gas chromatography collected permeates, and prepared feed solutions, for total organic carbon analysis collected permeates, retentates, and prepared feed solutions were stored. In addition to these, during filtration recorded time and collected permeates' volume, later, utilized in fouling calculations. After each filtration, the remaining sample was collected as retentate, and the membrane was physically cleaned by water. For this cleaning after the cell was emptied, approximately half of the cell filled with up and stirred at 150 - 200 rpm for 30 minutes. Before each filtration and after each cleaning procedure pure water permeances were measured, at filtration conditions.

Thus, it was checked whether there is a decline in performance due to lack of cleaning or not. After each filtration and cleaning step obtained feed, permeate, and retentate samples' vials lids were sealed with parafilm. All samples were kept in refrigerator at +4 degrees until the analysis. On the other hand, used membranes were stored at room temperature in %20 ethanol + 80% UP solution. All filtration experiments performed at least twice.

2.4 Gas Chromatography (GC) Analysis

In gas chromatography experiments, acetone, butanol, and ethanol concentration of both feed and permeate solutions of filtration experiments were analyzed. For these analyzes, primarily samples that were stored at +4 degrees were heated up to room temperatures. Then they were analyzed by making 3 to 5 repetitions for each. Repetition number was changed depending on the precision of the results. Results of GC analyses then were used to determine the rejection of acetone, butanol, and ethanol as a result of filtration.

Throughout all samples' analyses, Agilent Technologies - 6850 Network GC System which has an HP-Plot/Q capillary column was used. In analyses liquid samples, which are injected into the device, are carried by helium gasses into the column. Depending on the interaction of samples with the column, samples are separated there. Separated components move towards to end of the column and they reach the detector at different times. Used TCD (thermal conductivity detector), by using thermal conductivity differences of samples and carrier gas, conducts the area, height, and other measurements. During all these procedures temperature is the main factor that achieves the separation. Therefore, the column is kept in a temperature-controlled oven, and inlet and detector part temperatures are fixed at a certain temperature. Depending on the analyzed components, temperature, pressure, and other parameters were regulated and the method for analysis was created.

In this method, parameters had been adjusted as it had been seen in Table 2.4.1.

Table 2.4.1. Operating parameters of gas chromatography method.

Oven Temperature	170 °C
Front Inlet Temperature	180 °C
Front Detector Temperature	200 °C
Column Flow	12 ml/min
Front Detector Flow	12 ml/min
Front Inlet Total Flow	134 ml/min
Front Inlet Pressure	19.63 psi

Following this method, acetone retention time, butanol retention time, and ethanol retention time was detected. Afterwards, for butanol in the 0 - 40 g/L concentration range, for ethanol and acetone in the 0 - 10 g/L concentration range calibration curves were obtained. Retention times, used calibration curves and how they were drawn were given in Appendix B.

2.5 Total Organic Carbon (TOC) Analysis

Total Organic Carbon analysis were performed at the METU- Environmental Engineering laboratories. For these analyses, the Shimadzu 5000A model TOC device was used, and "the 680°C combustion catalytic oxidation method" was applied. As the column catalyst platinum catalyst was used.

In the device, during Total Carbon (TC) analyses samples drawn into the syringe come to the column. Samples that come to the column are combusted under 680°C temperature and manifested CO_2 are detected in the infrared gas analyzer.

On the other hand, through Inorganic Carbon (IC) analyses samples drawn into the syringe firstly are treated by acid in the device, and digestion of the organic compounds are carried out.

Then, formed CO_2 is detected in the infrared gas analyzer. By subtracting obtained IC values from TC values, TOC values are figured out. By this methodology, filtrated surfactant solutions' feed, permeate and retentate part TOC analyses were conducted.

2.6 Dynamic Light Scattering (DLS) Analysis

In DLS experiments, micelle sizes of the feed solutions which were used in the filtrations had been aimed to be analyzed. For these purposes, targeted solutions were prepared, and they were heated up to their filtration experiment temperatures in a water bath by mixing. Approximately 1 ml of these solutions were transferred to the DLS cells and placed into a zeta-sizer device. To prevent cooling of the analysis samples, device temperature was set to the targeted analyze temperature. In case of any cooling during transfer, samples ware waited in a heated device reservoir for nearly 30 minutes. Then they were analyzed. Moreover, seeing the effect of temperature on micelle size was another aspect of the research. For this purpose, the prepared solution was placed into the zeta-sizer and starting from 26˚C at 30˚C, 37˚C, 40˚C, 45˚C, 50˚C, 55˚C, 60˚C, and 65˚C sample size measurements were conducted. During these analyses from first to the last at every temperature value, about 30 minutes had been waited in the device for sample heat up. In all these analyses, MALVERN-Zetasizer Ultra-Pro was used, and each analysis was repeated between 3 - 6 times. For these analyses, instead of making measurements at one angle, by selecting the MDLS option, which covers backscattering (173^o), forward scattering (13^o), and side scattering (90^o), in all three angle measurements were conducted.

2.7 Turbidity Measurements

In turbidity analysis, Hanna Instruments HI 88703 turbidimeter was used. These analyses mainly was performed for controlling the turbidity of the prepared surfactant solutions. The analyzer does not have a temperature controller mechanism. However, the turbidity of surfactant solutions is temperature dependent. Therefore, before analysis, solutions heated up to the targeted temperature in a water bath. Starting from the moment when samples were placed into the device, throughout ten minutes period continuously turbidity analyses were conducted. Results were calculated by taking the average of these ten minutes measurements. In the beginning, at the end, and in the middle of each analysis temperature measurements were done by the thermometer. Due to these three measurements, temperature drop was detected as approximately 3°C.

2.8 Surface Tension Measurements

Surface tension analyses were performed in METU Central Laboratory (Attention Theta). Prepared Pluronic F127 and Pluronic P123 solutions were analyzed at room temperature. For each solution for 5 minutes, approximately 15 measurements were conducted. Average of these measurements were used as sample surface tension value.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Membrane Selection and CMC Determination of Surfactants

Membrane selection was carried out by assessing the membranes’ surfactant retention. Surfactants are the most significant operating cost item of this separation process. However, because they allow low TMP operation and can be regained and reused via a temperature switch, the MEUF process is considered economically viable. Also, the purity of the products is very important. Therefore, not losing surfactants in experiments carries big importance. For this purpose, by preparing 6.21 wt.% Pluronic F127 solutions, filtration experiments with 1 and 5 kDa membranes were conducted. As a result of these experiments, obtained permeate, retentate, and prepared feed solutions surfactant concentrations were detected by using the TOC analyzer. With these analyses, it was seen that both for 1 and 5 kDa membranes the surfactant rejections were around 97%. Previously, our group reported that; when 10 and 100kDa membranes were used, Pluronic F127 rejection was about 90% and 77%, respectively (Fıçıcı, 2017). Hence, by considering the surfactant loss (Table 3.1.1.), it was decided that it would be more appropriate to continue the experiments with 1kDa and 5kDa membranes.

In addition to these, also in TOC analyses of the experiments conducted by using 1 kDa membrane with smaller size surfactants or surfactant couples, high surfactant rejection values were obtained (Table 3.1.1.). From these experiments, at the filtrations of 6.21 wt.% Pluronic L64 and Pluronic P123 included solutions %99 surfactant rejection were obtained. Moreover, in the filtration of 1wt.% Pluronic P123 + 1wt.% Pluronic L101 solution surfactant rejection was %98. Hence, 1kDa membrane was also suitable for smaller-sized Pluronics.

Table 3.1.1. % Rejection of the surfactants and surfactants mixture as a result of the filtrations and the TOC analyses of these filtrations.

Surfactant Type	**Surfactant wt.%**	**Co-surfactant Type**	**Co-surfactant wt.%**	**Used Membrane**	**Surfactants Rejection %**
Pluronic F127	6.21	-	-	1 kDa	97.6±1.8
Pluronic F127	6.21	-	-	5 kDa	97.8±0.5
Pluronic F127	6.21	-	-	10 kDa	90
Pluronic F127	6.21	-	-	100 kDa	77
Pluronic L64	6.21	-	-	1 kDa	99.1±0.2
Pluronic P123	6.21	-	-	1 kDa	99.3±0.3
Pluronic P123	1	Pluronic L101	1	1 kDa	98.3±0.4

In the literature CMC values of Pluronic F127 are reported as 4.31×10^{-4} mol/L (Ding et al., 2003) by diffusion coefficient measurements method, 2.88×10^{-4} mol/L (Wanka et al., 1990) by surface tension measurements method, and $5.55\ \times10^{-4}$ mol/L (Alexandridis et al., 1994) by dye solubilization analysis. These are 5.43 g/L, 3.63g/L, and 6.93g/L, respectively. The main reason for the diversity of CMC values is the different methods preferred in the CMC analysis.

When surface tension experiments of Pluronic F127 solutions were conducted, it was seen that the CMC value of Pluronic F127 is approximately 3 g/L at 25°C (Figure 3.1.1.). That is consistent with these data (Wanka et al., 1990), when the concentration after which the surface tension is constant marks the CMC.

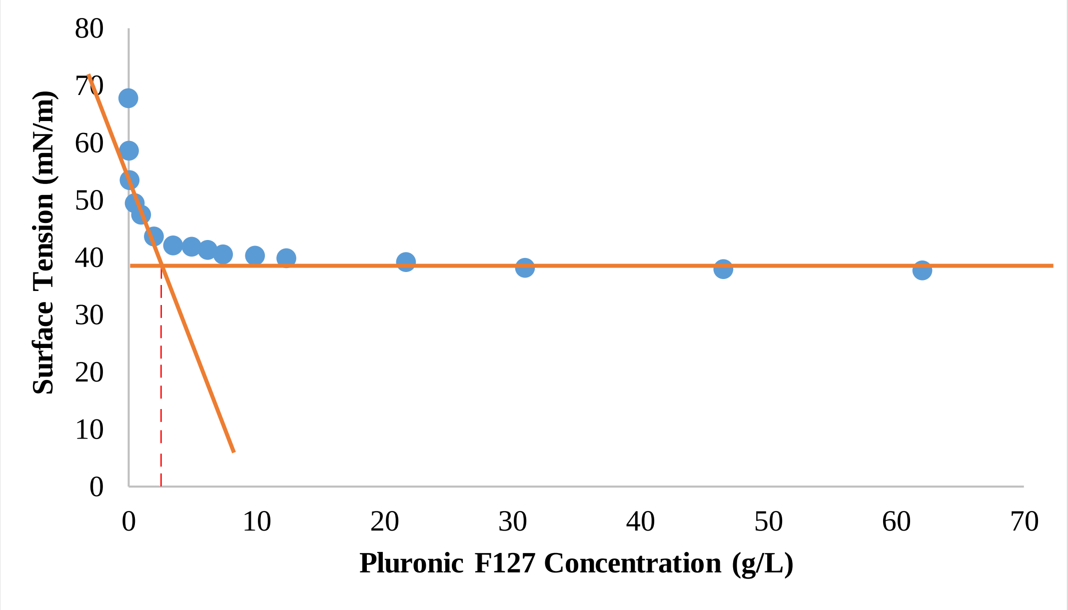


Figure 3.1.1. Surface tension change with respect to Pluronic F127 concentration.

It can be claimed that; it is beneficial to use surfactant amounts as high as possible since the amount of the micelles in the solution would increase, and the amount of encapsulated and rejected butanol concentration could be higher. This concentration raise could be performed up to the surfactants gel formation. Otherwise, filtration of the prepared solutions becomes impossible. According to Parekh et al., 2014, it was seen the necessary concentration for Pluronic F127 gel formation is approximately 15wt.% at 30°C. Moreover, decrement of the necessary amount for gel formation down to 9wt.% at 25vol% n-butanol existence was another result of this study. In the study of Dumortier et al., 2006, at 25°C the necessary concentration for the gel formation was reported as around 18wt.%.

Also, due to the temperature rise, there was a decrease in the necessary surfactant concentration for the gel formation. Therefore, considering that the filtrations would be conducted by collecting about half of the feed solutions as permeate, and in the future experiments temperature change might be the case, for filtrations usage of 6.21 wt.% (almost 10 times of surfactants CMC when Ding et al., 2003 and Alexandridis et al., 1994 study taken into consideration) of Pluronic F127 was decided.

Pluronic P123 was another surfactant that was used for experiments. In the literature CMC value of Pluronic P123 was reported as 0.0299 g/L (Alexandridis et al., 1994). When the CMC value of Pluronic P123 surfactant was measured (Figure 3.1.2.), as a result, 0.02g/L - 0.04g/L Pluronic P123 concentration was detected as its CMC value. That is in harmony with the literature value.

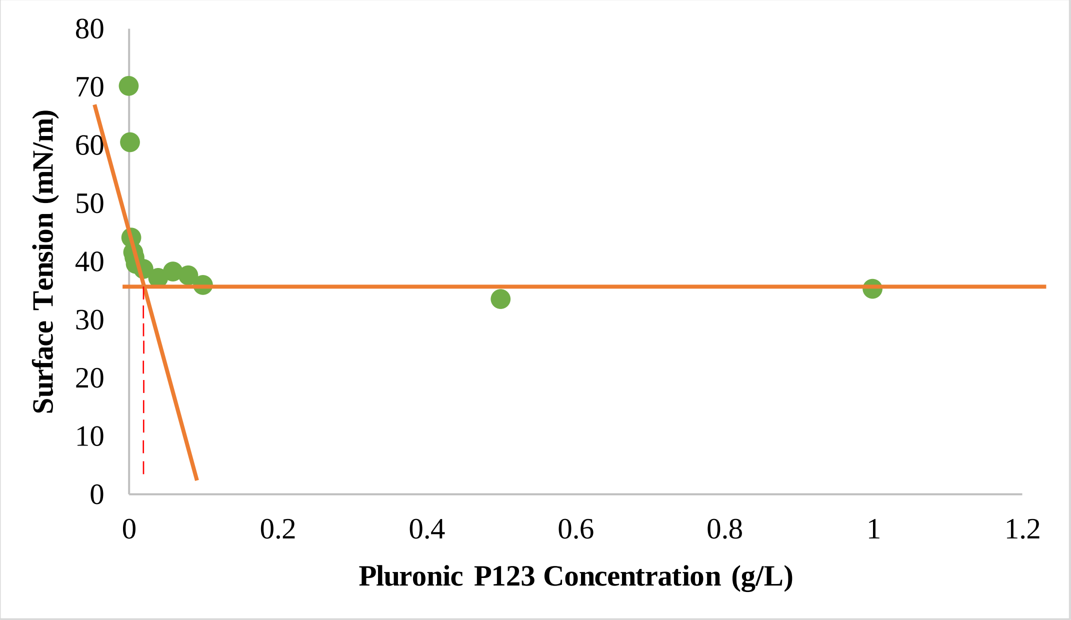


Figure 3.1.2. Surface tension change with respect to Pluronic P123 concentration.

Surface tension against the logarithm of the Pluronic concentration is also plotted and given in Appendix C. The concentration where the rate of change in surface tension changes dramatically agrees well with the CMC values reported in the literature.

3.2 Membrane Permeance During MEUF Process

In addition to the separation of target compounds effectively from solution, achieving this separation with high permeance is important, since this directly affects the membrane area needed for the desired separation. Therefore, permeate flux as a function of TMP was measured during MEUF with 20g/L butanol and 6.21 wt.% Pluronic F127 solutions, with 1 and 5 kDa membranes. The average flux observed between 28-30 ml permeate volume was plotted as a function of TMP in Figure 3.2.1. One example for the calculation methodology of average permeates flux values and raw data of flux and time was shown in Appendix D. As a result, average permeate flux values of 1 kDa membrane at 1, 3, and 4 bar pressures were detected as 1,03 ± 0,09, 2,98 ± 0,1, and 3 ± 0,09 L/hm^2, respectively. On the other hand, values were detected as 0,91 ± 0,17, 1,52 ± 0,06, and 2,3 ± 0,37 L/hm^2, for 5 kDa membrane at 0.5, 1, and 3 bar pressures, respectively (Figure 3.2.1.).

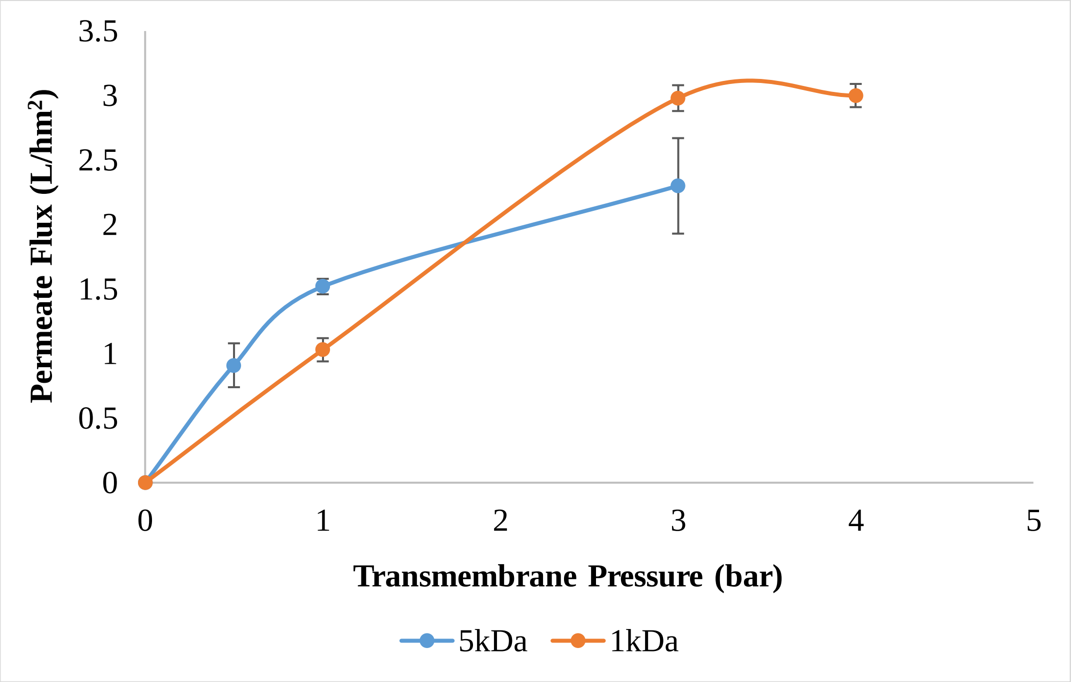


Figure 3.2.1: Graph of change of permeate flux depending on pressure change at 1 and 5 kDa membranes.

Hence, it was seen that 1 kDa membrane was reaching the limiting flux after 3 bar, and limiting flux was about 3 L/hm^2. On the other hand, 5 kDa membrane was reaching the limiting flux around 1 bar pressure and probable limiting flux was about 2 L/hm^2. The flux of the 5kDa membrane was higher at low pressures, as expected. While upon reaching the limiting flux, where the permeate flux no longer changes linearly with increasing TMP, the flux becomes smaller than the 1kDa membrane. This is attributed to internal fouling in the 5kDa membrane with larger pores which is not desired. Therefore, it was decided to carry out the MEUF experiments with the 1 kDa MWCO membrane.

3.3 Butanol Separation from Aqueous Butanol and Surfactant Solutions

After choosing the suitable membrane, and working pressure, at only butanol and surfactant presence filtration experiments were carried out. In these experiments, volume concentration factor (VCF), which is the ratio of the initial feed volume to the retentate volume, was kept at 1.9.

3.3.1 Effect of Surfactant Type and Concentration

Four different solutions containing, 6.21 wt.% of Pluronic F127 and 20, 10, 5, and 1g/L butanol concentration respectively were prepared and filtered by using 1 kDa MWCO membrane. GC analysis showed that; the solutions containing 20, 10, and 5g/L butanol, butanol rejections were 28.7 ± 2.5%, 19.6 ± 2.5, and %20.3 ± 0.8, respectively (Figure 3.3.1.1.). On the other hand, when 1g/L butanol solution is used as feed, permeate butanol concentrations cannot be measured, because of the detection limit of the GC method.

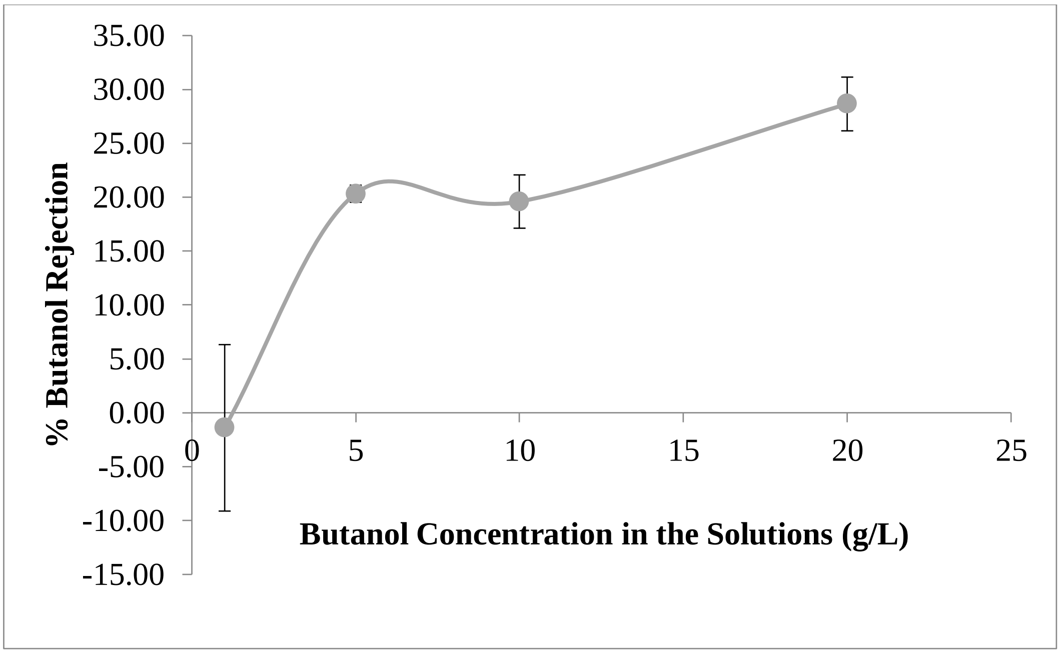


Figure 3.3.1.1. Graph of butanol rejection values which were obtained as a result of filtration of solutions, which contained 20, 10, 5, and 1g/L butanol and 6.21wt.% of Pluronic F127.

When butanol rejection values were taken into consideration, that was seen, under these experimental parameters and with the used amount of surfactant, performing the desired separation with Pluronic F127 could not be possible. The reason for that was thought to be the low butanol affinity of this surfactant.

The HLB value of Pluronic F127, which was used in the experiments, is 22 (Batrakova et al., 1999). Dhamole et al., 2015 observed that Butanol capturing capacity (BCC), which is the ratio of the amount of butanol captured by the surfactant to the amount of surfactant used in the experiments, depends on the HLB value of surfactants. In this study, it was seen that while the BCC was 0.4–0.7 g/g of surfactant for HLB in the range of 1–7, BCC was 0.3– 0.4 g/g of surfactant when HLB in the range of 12-18. This situation was explained by the fact that surfactants with a low HLB value have a lower amount of hydrophilic PEO and therefore retain more butanol than surfactants with a high HLB value.

Surface-active agents with higher HLB values have an affinity for the water phase, while ones with lower HLB values have an affinity for non-polar organic solvents (Cheng et al., 2007; Rosen, 2004). Therefore, to increase the affinity of surfactants to butanol, it was decided to continue the experiments with a surfactant that has a lower HLB ratio. Hence, Pluronic P123 with a HLB value of 8 (Batrakova et al., 1999) was selected as the second nonionic surfactant.

Solutions, which included 1, 2.56, and 6.21wt.% Pluronic P123 and 5, 10, and 20g/L butanol were prepared. By means of experiments with these solutions, it would be possible both to observe the change in butanol rejection when HLB decreased and to understand how the increase or decrease in the surfactant concentration affected the butanol rejection. As a result of the filtrations and GC analysis, butanol rejections of solutions that contained 20g/L butanol and 1wt.%, 2.56wt.%, and 6.21wt.% Pluronic P123 were %14.4 ± 1.1, %24.3 ± 2.4, %28.4 ± 3.6, respectively. In other words, there was an increment in butanol rejection with the increase in the amount of Pluronic (Figure 3.3.1.2.).

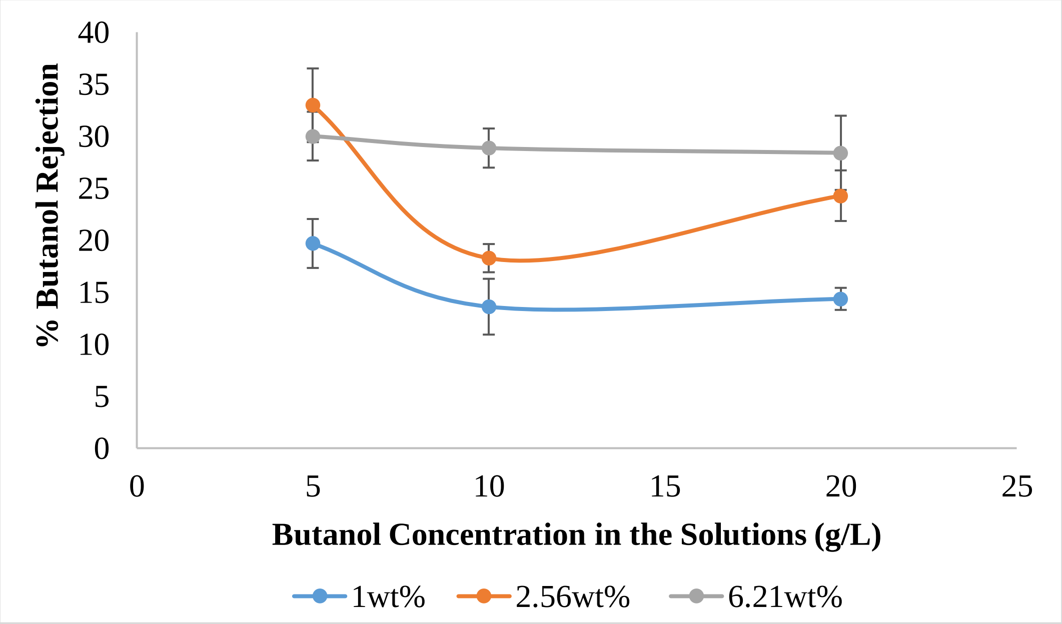


Figure 3.3.1.2. Graph of butanol rejection values which were obtained as a result of filtration of solutions, which contained 20, 10, and 5g/L butanol and 1, 2.56, and 6.21wt.% Pluronic P123.

When the HLB value of surfactants decreases, there becomes a reduction in their CMC values which are required to form micelles at the same temperature (Alexandridis et al., 1994). Therefore, if the experiments were planned with 10 times the CMC value of Pluronic P123, as in the case with Pluronic F127, the amount of Pluronic P123 to be used would be approximately 0.3 wt.%. However, as it can be understood from the results shown in Figure 3.3.1.2, in this case, the butanol rejection would be lower than the rejections of experiments that were done by 6.21 wt.% Pluronic F127 presence. Therefore, adding the surfactants at the same wt. % rather than the same multiple of the Pluronic CMC ratios was considered to be more effective to see the HLB effect. This situation is also clearly seen in another study in the literature. Kim et al. (2003) aimed to obtain pure water from aqueous solutions containing small amounts of toxic organics such as phenol and benzene using the MEUF method. During these experiments, polyoxyethylene glycol alkyl ether, which is briefly expressed as C_nE_m with different methylene groups and oxyethylene groups, was used as a nonionic surfactant. Within the scope of that study, as a result of conducted filtrations with Cellulose Acetate membranes in the presence of 1mM (100 times CMC) $C_{16}E_8$ and 0.2mM benzene and 0.2mM phenol, approximately 90% benzene and 40% phenol rejection were obtained. In the continuation of the study, to examine the effect of alkyl chain length and concentration of a surfactant on the separation performance, the experiments were continued with 100 times CMC of $C_{12}E_8$ instead of $C_{16}E_8$. While the decrease in the number (n) of methylene groups increases the CMC value, it causes a decrease in the size of the micelle. In other words, compared to $C_{12}E_8$, $C_{16}E_8$ can easily form larger micelles at lower surfactant concentrations. Therefore, $C_{16}E_8$ was expected to be more effective than $C_{12}E_8$ in the MEUF process in the study. However, contrary to expectations, it was observed that $C_{12}E_8$ was more effective than $C_{16}E_8$ in removing phenol and benzene at 100 times the concentration of its CMC.

The reason for this was thought to be the difference in the absolute concentrations of the surfactants because the absolute concentration of $C_{12}E_8$ at its 100 times CMC value is about 70 times higher than the absolute concentration of $C_{16}E_8$ at its 100 times CMC value. To understand whether this theory was correct, the experiments were repeated by keeping the amount of surfactant at 1.0 mM. As a result, when added at the same concentration, $C_{16}E_8$ was found to be more effective than $C_{12}E_8$.

Although it was expected that there would be an increase in the butanol affinity of surfactants due to the low HLB value surfactant and, as a result, an increase in butanol rejection of the experiments, there was no significant change, which might be due to the insufficient decrease in HLB value. Therefore, continuing the experiments, with Pluronic with lower HLB values, were decided. In this context, preparing solutions and conducting experiments with Pluronic L61, which has HLB value 3 (Batrakova et al., 1999), and Pluronic L101, which has HLB value 1 (Batrakova et al., 1999) became the next target. However, these surfactants are not soluble in water at room temperatures (BASF, 2002a; BASF, 2002b). On the other hand, in the literature, these surfactants had been used at 37˚C and their CMC values were available (Batrakova et al., 1999). Therefore, it was decided to continue the experiments at 37℃.

To make a healthier comparison among used surfactants, experiments, which were performed at 26˚C using Pluronic F127 and Pluronic P123, were repeated at 37˚C. In these repetition experiments, only solutions, in addition to butanol, containing 6.21 wt.% Pluronic P123, and Pluronic F127 were prepared. In solutions containing Pluronic P123, in the presence of 20, 10 and 5g/L butanol, 25.2 ± 0.8%, 26.7 ± 0.4% and 30 ± 0.3% butanol rejections were achieved, respectively. In solutions containing Pluronic F127, 20.4 ± 2.3%, 24.7 ± 1.1% and 24.2 ± 0.7% butanol rejection was achieved in the presence of 20, 10 and 5g/L butanol, respectively (Figure 3.3.1.3.). Compared to experiments at 26℃, it was clear that there was no significant change in butanol rejection rates with the increase of temperature.

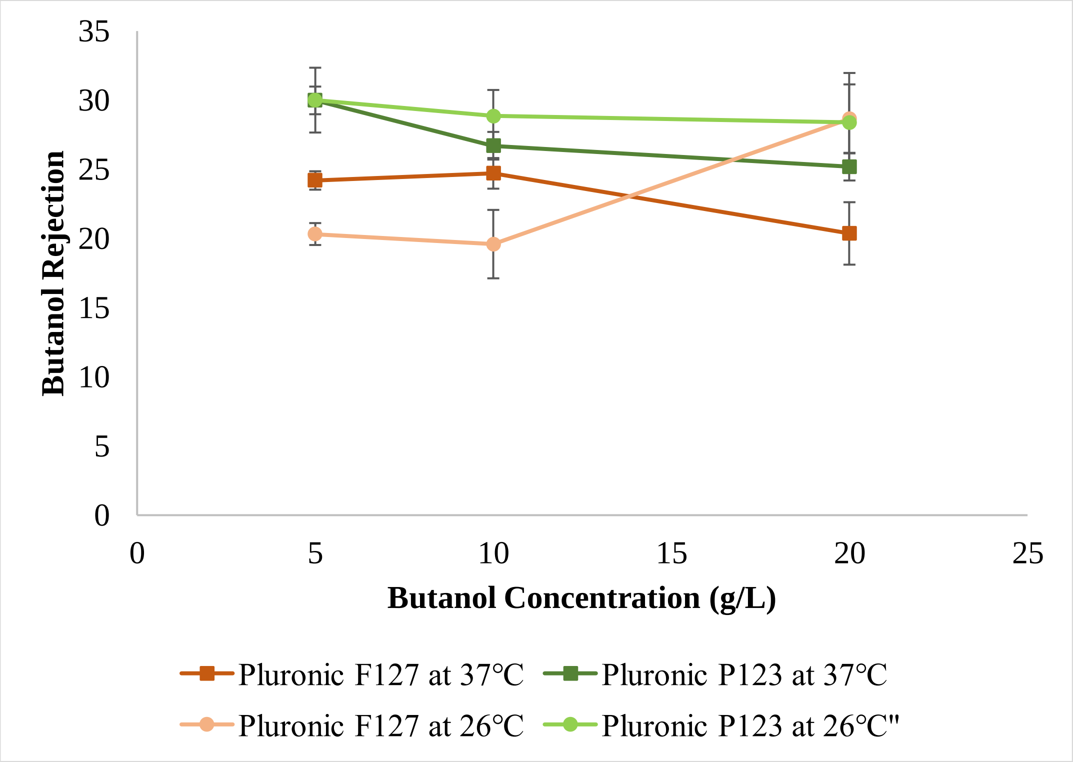


Figure 3.3.1.3 Butanol rejection values which were obtained as a result of filtration of solutions at 37°C, that contained 6.21wt.% Pluronic P123 or Pluronic F127.

Another result reached based on the experiments was the relationship between the butanol content of the solutions and the obtained butanol rejections after the filtrations. When the experiments were examined, it was observed that, as the amount of butanol in the prepared feed solutions reduced, butanol rejection slowly increased. The reason for this increase was thought to be due to the concentration of butanol which remained in the solution out of the micelles.

Before starting the experiments planned with Pluronic L101 and Pluronic L61, initially, water solubilities of these materials were examined by using solutions containing 0.22, 0.18, 0.11, 0.066, and 0.022 wt.% of Pluronic L61 and 0.0080, 0.0064, 0.0040, 0.0024, and 0.0016wt.% of Pluronic L101. The concentrations of the prepared solutions were at the CMC value of 10, 8, 5, 3, and 2 times that of Pluronic L101, and 10, 8, 5, 3, and 1 time of the CMC value of Pluronic L61.

For these prepared solutions, both the turbidity values were measured, and with naked eye control of sedimentation of particles were observed. In the solutions prepared with Pluronic L61, no particle sedimentation was observed. However, there was a visible increase in turbidity due to the increasing Pluronic L61 concentration (Figure 3.3.1.4.). Also, this increase was clearly seen by measurements made with the turbidimeter (Figure 3.3.1.5.).

Figure 3.3.1.4 Turbidity variations of the solutions prepared by adding from left to right 0.22, 0.18, 0.11, 0.066, and 0.022wt.% Pluronic L61.

According to De & Mondal, 2012, the reason for this increment is in the concentration of larger aggregate species. Moreover, the temperature was the other factor that affects the turbidity of the solution. In Rosen, 2004, it is mentioned that when the temperature is elevated, observed dehydration in the PEO chains of surfactants is the reason for the turbidity increase.

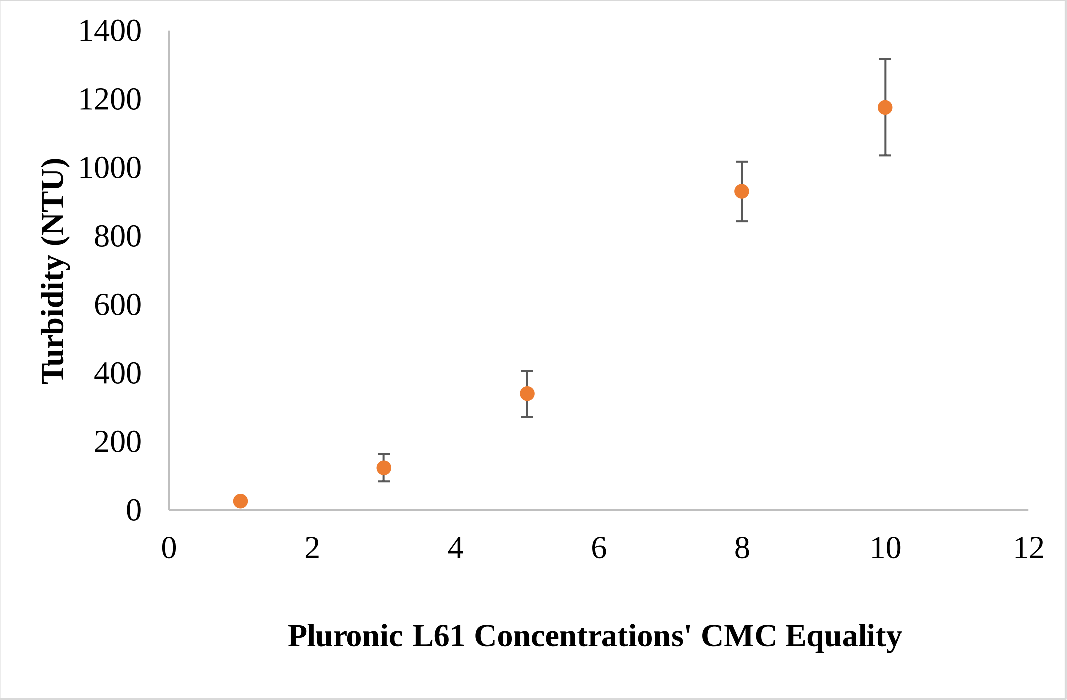


Figure 3.3.1.5 Turbidity values of solutions prepared by addition of different Pluronic L61 concentrations to the water.

Solutions prepared at the specified concentrations with Pluronic L101 doesn’t have high turbidity values (Figure 3.3.1.6.). However, it was observed that a part of the surfactant didn’t solubilize and precipitated.

Since there was no precipitation in the solutions with 10 times the CMC value of Pluronic L61, solutions containing 20g/L butanol and 0.22wt% of Pluronic L61, filtrations were performed, and 12.9 ± 1.3% butanol rejection was obtained. It was thought that the reason for the low rejection value might be because of very low Pluronic L61amounts. Therefore, instead of solving the Pluronic L61 in water by itself, it was decided to dissolve it together with a Pluronic which was known to dissolve alone in the water. In this way, the aim was to increase both the solubility and the concentration of Pluronic L61 in the solutions. On the other hand, due to the observed precipitations, it was clearly understood that Pluronic L101 was not soluble in the water, alone.

Hence, also dissolving Pluronic L101 in water at the existence of another Pluronic was decided. Consequently, all of the above-mentioned Pluronic L61 and L101 solutions prepared only in the presence of water were prepared one more time at the 6.21wt.% Pluronic P123 presence. While preparing these solutions, the reason for preferring the Pluronic P123 rather than the Pluronic F127 was that the P123 had a lower HLB value. Due to the mixing of it with a smaller HLB value surfactant, a solution with a lower HLB value than Pluronic P123 solutions would be obtained. In this way, an increment in the affinity of butanol to micelles might be achieved.

After preparing the solutions, which were containing L61 or L101 at the presence of P123, due to the concentration increase of L61 and L101, no visible turbidity increase of the solutions was observed. Also, according to turbidimeter measurements, it was seen that the turbidity values were close to solutions containing only 6.21wt.% Pluronic P123 (Figure 3.3.1.6.). On the other hand, when the precipitation situations were examined, no particle sedimentation was observed in the prepared L101 solutions. However, undissolved particles in the each L61 solutions were clearly visible.

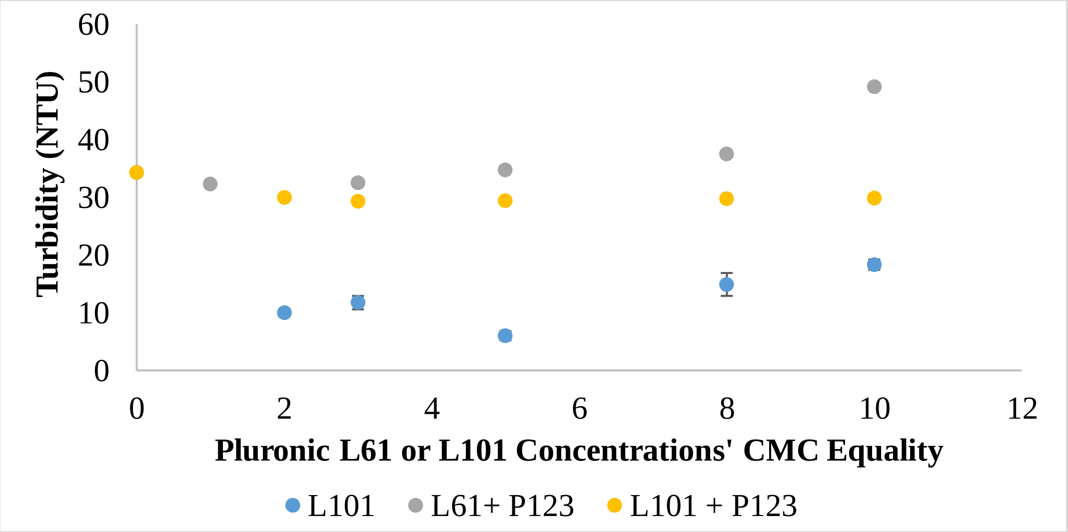


Figure 3.3.1.6 Turbidity values of solutions prepared by addition of different Pluronic L101 concentrations to the water.

To determine the amount of precipitated substance in the L61 and P123 solution, and even though there was precipitation, to see the performance of the surfactant couple, solutions of 20g/L butanol + L61 wt % : P123 wt.% = 0.22:6.21 were prepared for the filtration. In the beginning, these solutions were filtered with a filter paper, without applying any pressure, to calculate the amount of precipitation. As a result, from 100 ml solution containing 0.22wt.% L61 and 6.21wt.% P123, 0.11g (0.11wt.%) compound precipitated. Due to Pluronic L61 concentration increase, precipitation was observed might be thought. However, since the precipitation was observed in all Pluronic P123 and L61 solutions, precipitated surfactants might not only be the L61.

Filtration experiments were completed by using the supernatant. In the post-filtration GC analyses, 30.7 ± 0.3% butanol rejection was detected. By considering filtration of solutions containing only 20g/L butanol and 6.21wt.% Pluronic P123 under the same conditions had approximately 25.2% butanol rejection, there was minor improvement in butanol rejection. Similar to the L61, solutions of 20g/L butanol + L101wt.% : P123wt.% = 0.008:6.21 were prepared for the filtration. Distinctly from the filtration of previous surfactant couple's solutions, no filter paper filtration was conducted, because there was no precipitation was observed at Pluronic L101 solutions. As a result of the GC analysis of these experiments, butanol rejection was observed at a value of 30.9 ± 0.1%. The increase in the butanol rejection was analogous to the increment at L61 and P123 couples' experiments. Afterwards, by keeping the P123 concentration constant at 6.21wt.% and by increasing the Pluronic L101 concentration gradually, solutions were prepared.

For aimed filtrations, at the presence of 6.21 wt.% Pluronic P123 + 20g/L butanol; 0.08 ,0.5, and 1 wt.% Pluronic L101 including solutions (solution 1, 2, and 3, respectively) were prepared. Among these, as a result of the first two solution filtration, butanol rejection was obtained as 31.4 ± 0.9% and 34.1 ± 0.1%, respectively (Figure 3.3.1.7). On the other hand, in the third solution gel formation took place.

Hence, Pluronic L101 concentration was kept constant at 1 wt.% and at different Pluronic P123 concentrations, P123, L101, and butanol solutions were prepared.

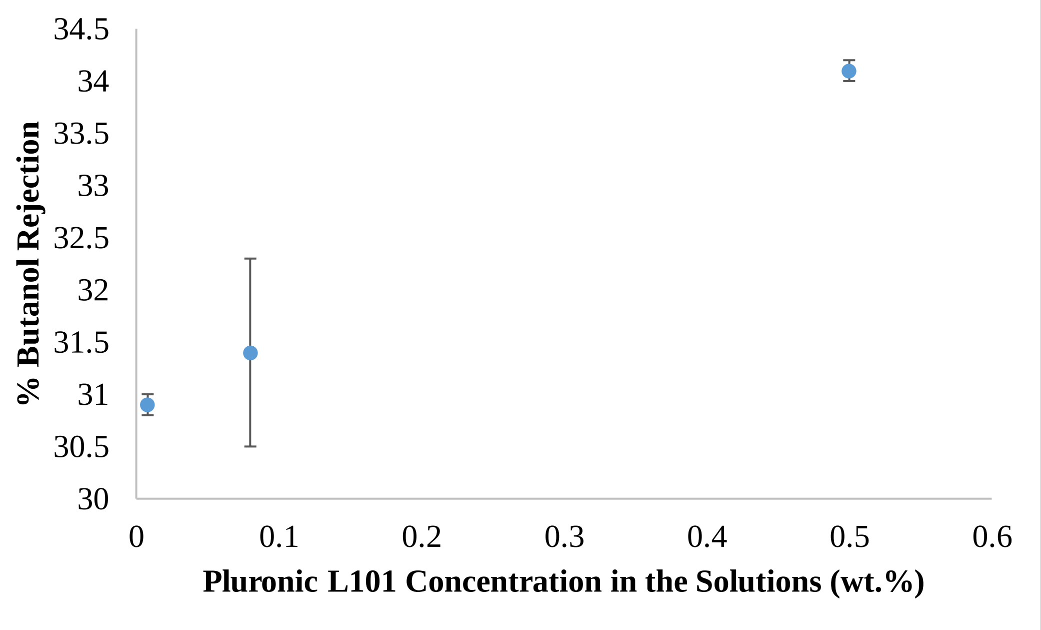


Figure 3.3.1.7. As a result of at the presence of 6.21 wt.% Pluronic P123 + 20g/L butanol; 0.08, 0.5, and 1 wt.% Pluronic L101 including solutions filtrations and analysis, observed increment in the % butanol rejection with respect to L101 increase.

As seen in Table 3.3.1.1., very high turbidity values were observed in almost all of the prepared solutions when P123 content was between 1-3wt.%, and L101 content was 1-2wt.%. Moreover, turbidity values of some solutions were even above the range that the device can measure. All of the solutions were filtered with filter paper and then, one more time, subjected to turbidity measurements. In these measurements, a slight decrease in the turbidity of solutions was seen. This decrease might be due to the separation of the precipitated substances with filter paper. However, despite the precipitation, solutions still were containing enough surfactant to form micelles.

Table 3.3.1.1. Turbidity analysis results of solutions containing different concentrations of Pluronic P123, L101 and 20g/L Butanol.

Pluronic P123 wt.%	Pluronic L101 wt.%	Turbidity (NTU) (Before Filtration)	Turbidity (NTU) (After Filtration)
1	1	2906.8 ± 67.4	2480.8 ± 29
1	2	Out of Range!	Out of Range!
2	-	79.2 ± 1.8	-
2	1	1412.2 ± 16	1190.4 ± 14.6
2	2	Out of Range!	3295.5 ± 24
3	-	84.3 ± 1.8	-
3	1	1189.4 ± 33.7	705.3 ± 12.6
3	2	2275 ± 42.1	2140.1 ± 29.1

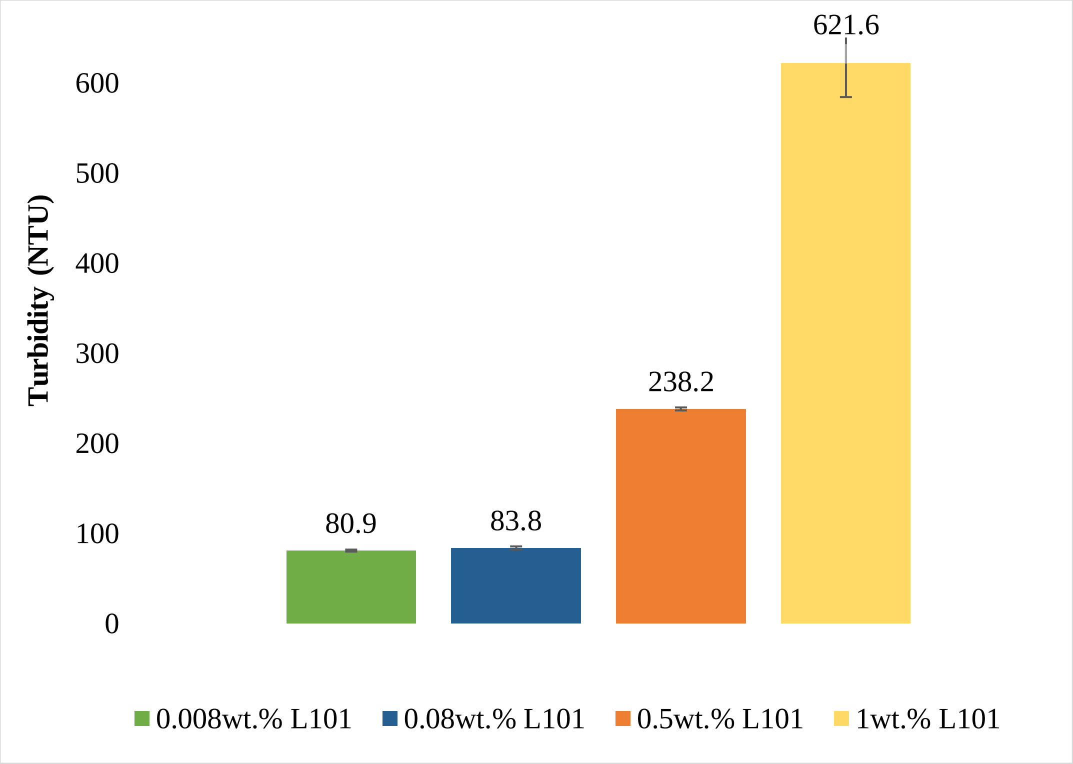


Figure 3.3.1.8. Turbidity analysis results of solutions containing 6.21wt.% Pluronic P123 + 20g/L Butanol and different concentrations of Pluronic L101.

The turbidity values of the solutions where the Pluronic P123 concentration was kept constant as 6.21wt.%, and the Pluronic L101 concentration was increased gradually, were added with Figure 3.3.1.8 to show how high the turbidity values of the new solutions were.

Among the prepared solutions, at the presence of 20g/L butanol + 1 wt.% Pluronic L101; 1 wt.% and 3 wt.% Pluronic P123 included solutions were selected. With these solutions' filtrations, it was aimed to examine the effect of changes in Pluronic concentrations on butanol rejection. During the filtration of solutions, some of the feed solutions passage directly into the permeate side was observed (Figure 3.3.1.9.). To understand at what point the transition would stop, at 5 ml amount permeate samples were collected. When there was no visible turbidity, the permeates were started to be collected in the same container. In addition to them, the presence of visible turbidity on the permeate side was interpreted as an indication that the surfactants passed to the permeate side enough to form a micelle.

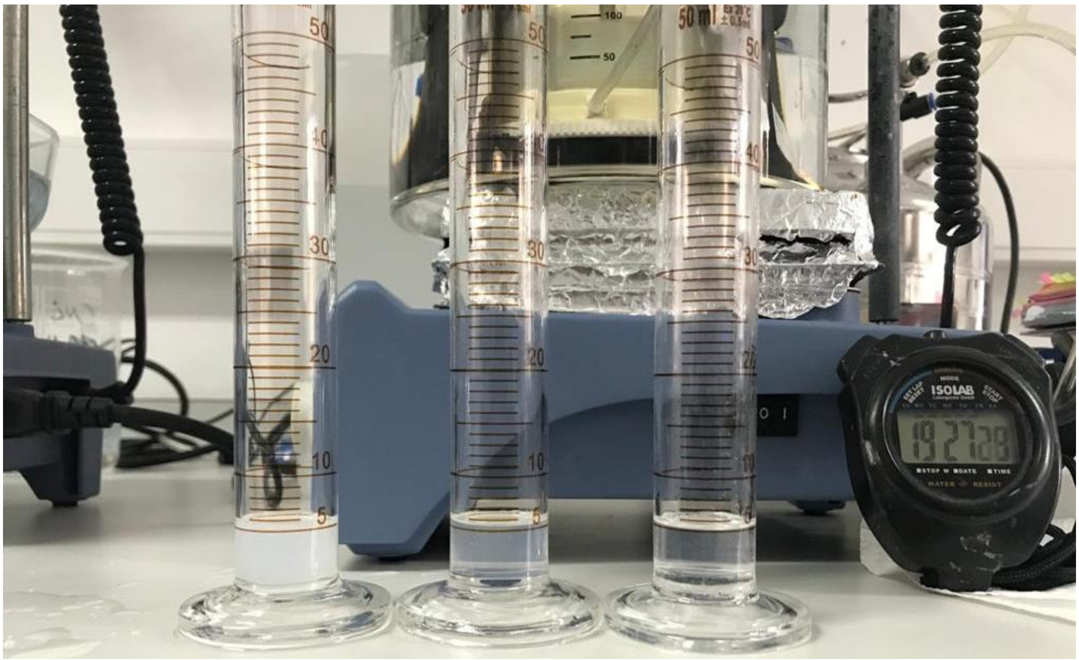


Figure 3.3.1.9. The permeates collected during the filtration experiment of 1wt.% Pluronic P123 + 1wt.% Pluronic L101 + 20g/L Butanol solution.

20g/L butanol + L101wt.% : P123 wt.% = 1:1, and 1:3 experiments yielded 20.7 ± 1%, 27.1 ± 1.4% butanol rejection, respectively.

Although the amount of Pluronic L101 was increased, it was thought that there might be two reasons for the observed reduction in the rejection values. Firstly, the solubility of Pluronic L101 might be decreasing at low Pluronic P123 concentrations. Due to that, the rejection values might be getting closer to the rejections, which might be obtained by filtration using only 1 and 3 wt.% P123. In previous experiments, at 26˚C performed 20g/L butanol + 1wt.% Pluronic P123 experiments yielded approximately 14.4% butanol rejection. On the other hand, at the same temperature, in the studies of 20g/L butanol + 2.56wt.% Pluronic P123, this ratio was approximately 24.3%. Secondly, there was a possibility that the amount of surfactant transferred to the permeate side might be decreasing the butanol rejection.

In the further experiments, to control whether the passage of surfactants to the permeate side could be prevented by increasing the amount of added Pluronic P123 to the solutions and whether the rejection could be increased or not had become the next goal. Since the in 20g/L butanol + L101 wt.% : P123 wt.% = 1:6.21 solutions gel formation was observed, keeping the P123 concentration less than 6.21 wt.% had been decided. For this purpose, 20g/L butanol + L101 wt.% : P123 wt.% = 1:4, and 1:5 solutions were prepared. During the experiments with 20g/L butanol + L101 wt.% : P123 wt.% = 1:5 solutions, after VCF reaching 1.14, rapid increase in the viscosity on the feed side was observed. Therefore, filtrations were terminated after VCF reach to the 1.4. In GC analyses with these permeates rejection was found to be 26 ± 0.9%.

In the experiments with 20g/L butanol + L101 wt.% : P123 wt.% =1:4 solutions, such an increase in viscosity was not encountered. But the turbidity of the permeate obtained from the first filtration was measured as 57.3 ± 2.4 NTU. Also, the turbidity of the permeate obtained from the second experiment was 33.3 ± 0.6 NTU. The butanol rejection obtained as a result of the experiments had a value of 28 ± 0.3%.

However, since there was surfactant transition to the filter side again; it was not possible to understand whether the passage of surfactants to the permeate side could be prevented by increasing the amount of added Pluronic P123 to the solutions and whether the rejection could be increased or not.

Test results of the solutions prepared by mixing of Pluronic P123 and L61, or Pluronic P123 and L101 at the existence of 20g/L Butanol gathered at Table 3.3.1.2.

Table 3.3.1.2. Butanol rejection results of filtrated solutions prepared by mixing Pluronic L101 or Pluronic L61 with Pluronic P123 + 20g/L Butanol solution and prepared by mixing Pluronic L61 with Pluronic P123 + 20g/L Butanol solution.

Co-surfactant Type	**Co-surfactant wt.%**	**Co-surfactant Conc. Co-surfactant CMC Equality**	**Pluronic P123 wt.%**	**% Butanol Rejection**
Pluronic L61	0.22	10	-	12,9 ± 1,3
Pluronic L61	0.22	10	6.21	30,7 ± 0,3
Pluronic L101	0.008	10	6.21	30,9 ± 0,1
Pluronic L101	0.08	100	6.21	31,4 ± 0,9
Pluronic L101	0.5	625	6.21	34,1 ± 0,1
Pluronic L101	1	1250	5	26 ± 0,9
Pluronic L101	1	1	4	28 ± 0,3
Pluronic L101	1	1	3	27,1 ± 1,4
Pluronic L101	1	1	1	20,7 ± 1

Since during all conducted experiments in addition to the obtained butanol, acetone and ethanol rejection, observed permeate flux values are as important as the rejection values, obtained permeate flux data of all experiment were shown at Appendix E. Moreover, in order to examine the factors causing fouling, conducted fouling analyses were placed into the Appendix F.

3.3.2 Nanofiltration Experiments and Results of GC Analyses

Filtration experiments of solutions containing 1 and 3 wt.% Pluronic P123 + 20g/L butanol + 1wt.% Pluronic L101 with 1 kDa ultrafiltration membranes and following GC analyses, resulted in low butanol rejection. As was mentioned in the previous part, the low rejection value in these experiments might have two reasons. Firstly, the decrement of solubility of Pluronic L101 at low Pluronic P123 concentrations might be the case. Secondly, it dwelled on the possibility that the surfactants passing to the permeate side might be decreasing the butanol rejection. To understand the affected factor, filtering the solutions with a nanofiltration membrane under the same conditions was decided. Because of smaller pore size of nanofiltration membranes, surfactants passage to the permeate side would not be allowed. As a result of these experiments, if low rejection would be obtained, the notion that decreasing Pluronic P123 concentrations reduce the solubility of Pluronic L101 would be supported. On the other hand, if relatively high rejection was achieved, it would be understood that; while increasing the Pluronic L101 concentration, decreasing the Pluronic P123 concentration became beneficial in increasing the affinity of the butanol molecules to the micelles. Moreover, it would be revealed that this effect could not be seen in UF membranes because of the permeation of surfactants to the permeate side.

As a result of nanofiltration experiments which using 20g/L butanol + L101 wt.% : P123 wt.% = 1:1 solution, 39.9 ± 0.5% butanol rejection was obtained.

This showed, by increasing the amount of Pluronic L101 and decreasing Pluronic P123, micelle affinity to butanol increased. The probable reason for it was the decrement of the HLB value of surfactant with ascending of the Pluronic L101 wt.% increase in the solution. The lower rejection with the UF membrane was attributed to the surfactant loss to the permeate.

As described in the experimental procedure, in the beginning, VCF for the experiments was 1.9. All rejection values calculated so far were for permeate solutions collected by this VCF value. When the VCF was rise to 5.7, it was seen that butanol rejection had reached 55.6 ± 2.3% in 20g/L butanol + L101 wt.% : P123 wt.% = 1:1 solution filtration. The analysis results of the permeate samples collected at intervals had shown in Figure 3.3.2.1. As the amount of collected permeate increased, improvement in butanol rejection of filtrate solutions was seen.

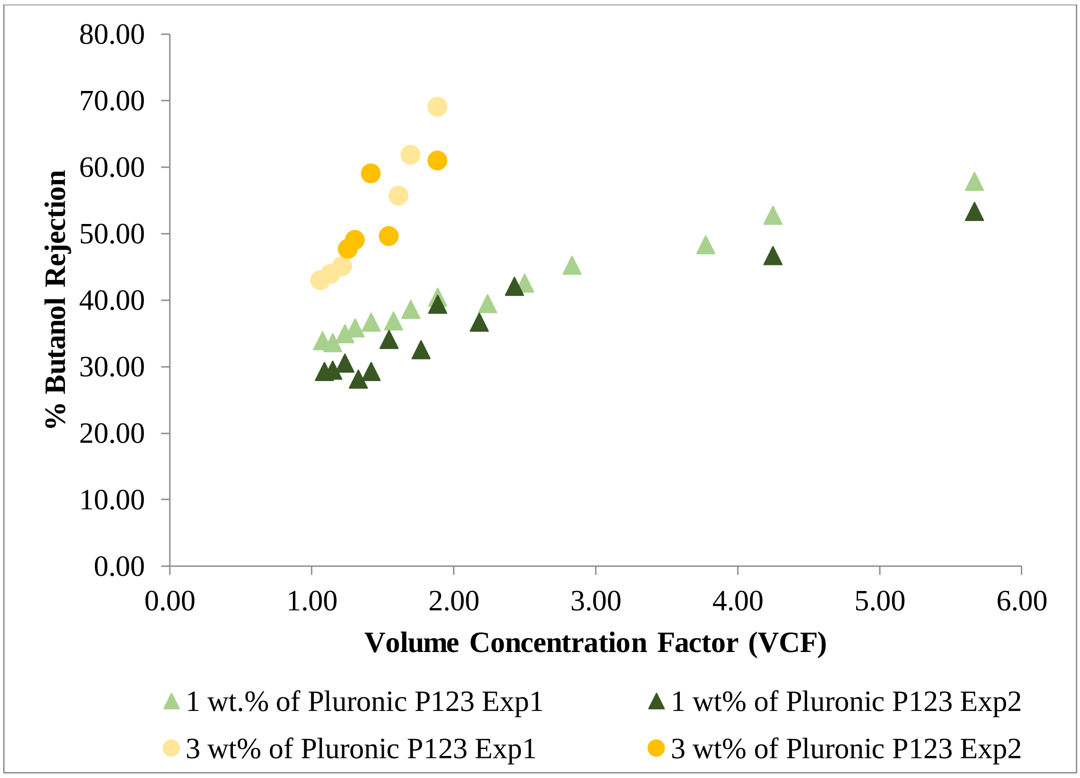


Figure 3.3.2.1 Butanol rejection values of 20g/L butanol + Pluronic L101 wt.% : P123 wt.% = 1:1, and 1:3 solutions filtrations.

As it can be seen from Figure 3.3.2.1, conducted 20 g/L butanol + L101 wt.% : P123 wt.% = 1:3 experiments supported the conclusion that butanol rejection increased as the amount of collected permeate increased. However, in comparison to 20g/L butanol + L101 wt.% : P123 wt.% = 1:1, VCF only was 1.9 in 20g/L butanol + L101 wt.% : P123 wt.% = 1:3 experiments. The reason for this was that; clear gel formation was observed in the solution, even at the beginning of the filtrations, and continuing the filtrations became difficult. Compared to the 20g/L butanol + L101 wt.% : P123 wt.% = 1:1, the amount of fouling in the membrane can be understood clearly from Figure 3.3.2.2. While the butanol rejection obtained, when VCF was 1.9 in conducted 20 g/L butanol + L101 wt.% : P123 wt.% = 1:1 experiment, was 39.9 ± 0.5%, butanol rejection obtained when VCF was 1.9 in conducted 20 g/L butanol + L101 wt.% : P123 wt.% = 1:3 experiments were 65 ± 4%. It was thought that the reason for this increase in rejection might be due to the increase in the amount of surfactant as well as the reversible gel formation on the membrane surface.

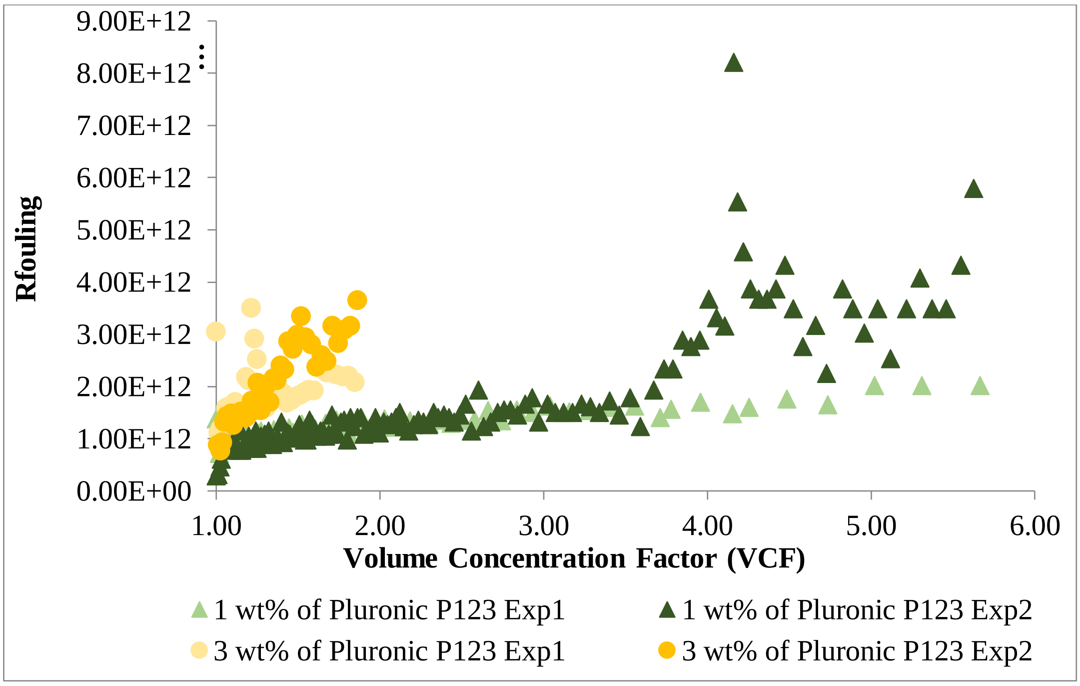


Figure 3.3.2.2 Change of fouling resistance of 20g/L butanol + 1:1 and 1:3wt.% L101:P123 solutions filtrations at 37°C with respect to permeate volume.

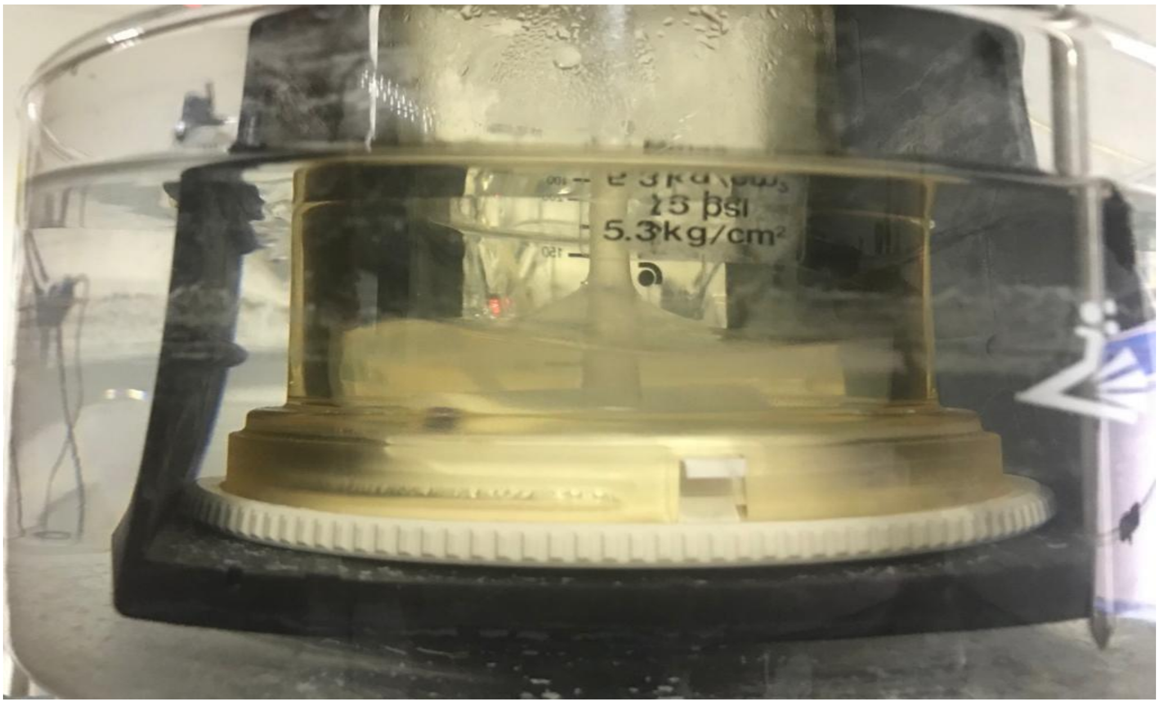


Figure 3.3.2.3 Gel formation in 20g/L butanol + L101 wt.% : P123 wt.% = 1:3 solution.

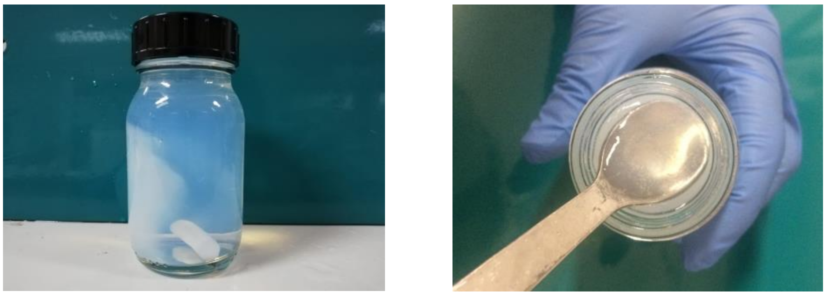
3.4 Surfactant and Micelle Size Analysis of Used Feed Solutions and Effect of Temperature on Solutions and Surfactant and Micelle Sizes

DLS analysis was carried out in the following stages with the solutions used in the experiments. The main reason for these analyzes was to understand whether there was any change in the micelle dimensions formed by surfactants depending on the type and concentration of the changing surfactant. At the same time, it was desired to observe whether there was an increase in the size of the micelles, which also occurs with the increase in the temperature.

In the first part of the experiments, observing whether there was an increase in the size of the micelles due to the rise in the temperature was aimed.

Therefore, it had been planned to make DLS analyzes by using 6.21wt.% Pluronic P123 + 20g/L butanol, and 6.21wt.% Pluronic F127 + 20g/L butanol solutions at gradual temperature increase. However, before starting these analyzes, whether there was any gel formation, turbidity, or precipitation in the solutions or at which temperature gel formation, turbidity, or precipitation would take place wanted to be observed. The main reason why such a situation is expected to occur is the cloud points of the surfactants and the high amount of surfactants concentration in the solutions. Although the cloud point of Pluronic F127 is above 100℃ for 10wt.% aqueous solution (BASF, 2012), for Pluronic P123 this value is about 90℃ for 1wt.% (Sigma, 2021). Considering the increased amount of Pluronic P123 added to the solution will cause a decrease in cloud point (Ricardo et at., 2011), P123 may inevitably rise above the cloud point after a very small increase. In other words, after a small temperature increase, the phase separation might occur, and the surfactant might be insoluble in water. Since the cloud point of 10 wt.% F127 is above 100℃, this risk is not present, but considering the high surfactant concentration, the risk of gelation with an increase in temperature should not be ruled out.

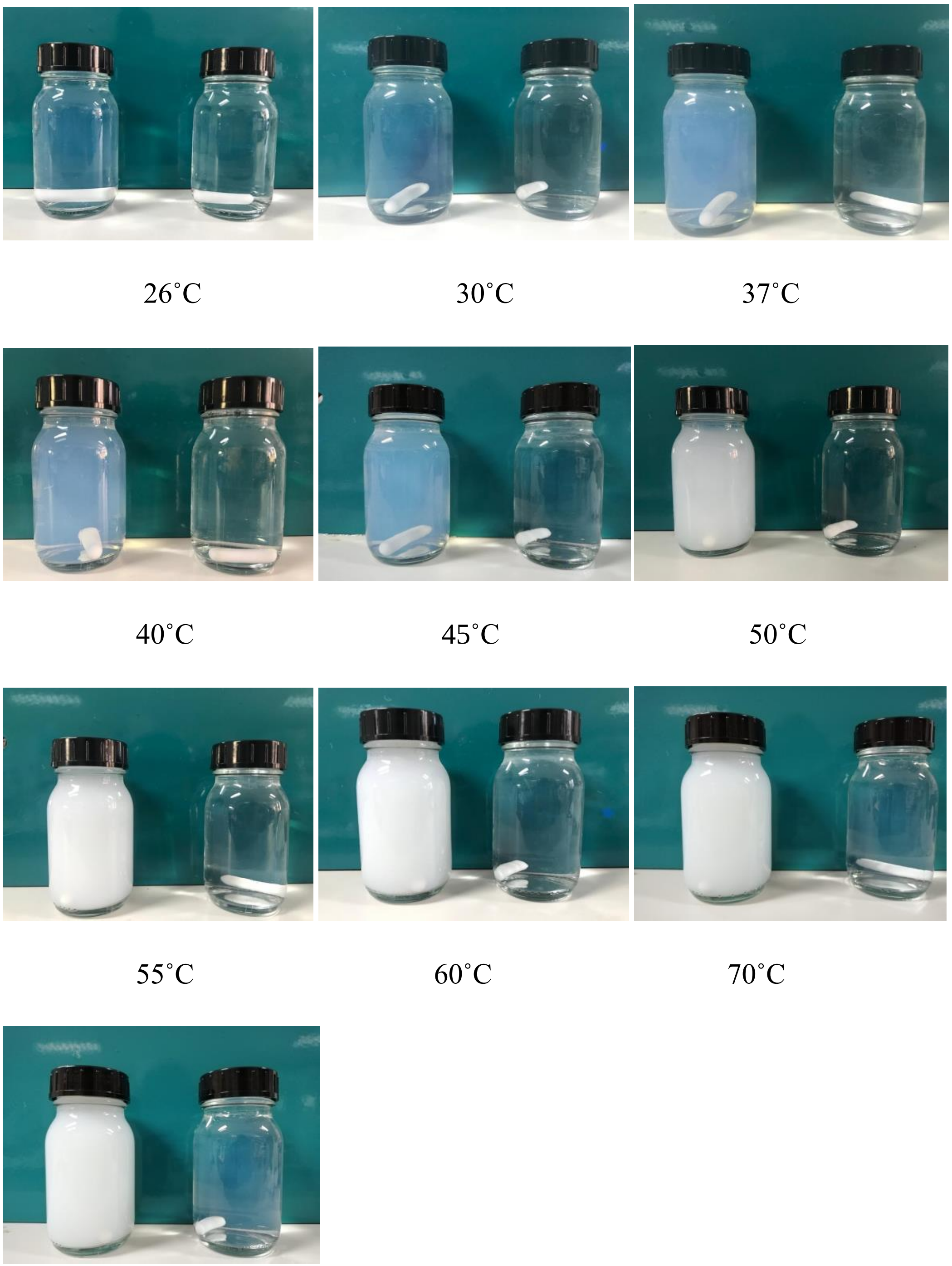
With the bare eye, it was observed whether there was any turbidity or phase change in the solutions during the gradual heating from 26˚C up to 80˚C. Throughout these observations, as could be seen in Figure 3.4.1, it was seen that 20g/L butanol + 6.21wt.% Pluronic P123 solution had increased turbidity while the temperature was around 48˚C. When the same solution was heated to 50˚C, a serious increase in its viscosity was observed. Moreover, the solution became more turbid with the continuation of the temperature increase (Figure 3.4.2.), but there was no more increase in its viscosity was noticed. This result had shown that the maximum temperature that could be studied in experiments with Pluronic P123 at this concentration was around 40˚C.



48˚C 50˚C

Figure 3.4.1. Turbidity and phase change examinations of 20g/L Butanol + 6.21wt.% Pluronic P123 solution at 48˚C and 50˚C.

The main reason for the turbidity formation and increase in its value observed with the increase in temperature is explained as dehydration of the POE chains (Rosen, 2004). On the other hand, no visible turbidity or phase change was seen in 20g/L Butanol + 6.21wt.% Pluronic F127 solution (Figure 3.4.2.).



26°C 30°C 37°C

40°C 45°C 50°C

55°C 60°C 70°C

80°C

Figure 3.4.2. Temperature dependent turbidity examinations of 20g/L Butanol + 6.21wt.% Pluronic F127 solution (on the right side) and 20g/L Butanol + 6.21wt.% Pluronic P123 solution (on the left side).

Since experiments could not be operated by using 20g/L butanol + 6.21wt.% Pluronic P123 solution at temperatures higher than 40˚C, DLS analysis due to temperature change was not performed for this solution. On the other hand, for 20g/L butanol + 6.21wt.% Pluronic F127 solution that had not shown any turbidity and phase change with temperature change, DLS analyses had performed at 26, 30, 37, 40, 45, 50, 55, 60, and 65˚C. As a result of DLS measurements made with Pluronic F127 at 26˚C, two peaks were seen (Table 3.4.1.). One of these peaks was around 5 nm and it was thought that this peak had been indicating the size of the surfactant which did not form a micelle. The second peak had a size around 20nm and this one was probably showing the size of the formed micelle. These observed surfactant and micelle sizes were also in line with the other studies in the literature. In the study of Aw et al., 2011, as a result of DLS measurements average size of formed micelles of Pluronic F127 was observed as 20.0 ± 0.7. In the Valerón Bergh & Tønnesen, 2017 in the obtained biomodal size distribution of Pluronic F127 had average diameter of 5.88 ± 0.22 for unimers and 38.7 ± 1.7 for formed micelles.

One of the factors affecting the size increase of micelles was the temperature. When polyoxyethylene nonionic surfactants were examined; at the temperature rising towards the cloud point, the hydrophilic group began to lose its hydrophilic feature and gained hydrophobic ability (Nakama, 2017). This resulted in an increase in the number of molecular aggregations and the size of the micelles. (Nakama, 2017). This increase in micelle size might increase the butanol holding capacity of micelles, in other words, it might have a positive effect on the butanol rejection rate obtained at the end of filtration. However, as it can be understood from the DLS results in Table 3.4.1, it was observed that the micelle sizes observed when the same solution was measured at different temperature values were between 14-16 nm. In other words, there was no specific raise in the size due to the temperature increase. The main reason of temperature-dependent growth was not observed might be that the cloud point of Pluronic F127 becomes above 100 degrees. So, to see the growth effect of the micelle, it might be necessary that analysis at higher temperatures should be conducted.

In other words, analyzing temperatures that were closer to the cloud point might be necessary. Also, according to Rosen, 2004, below 60°C there is no change in the aggregation numbers of surfactants with cloud points above 100°C is seen. However, increasing the temperature above 60°C means that getting far away from the initial target of the experiments. That is achieving separation around room temperature.

As a result of filtering the prepared 6.21wt.% Pluronic F127 + 20g/L Butanol solution at 26˚C and 37˚C separately; from the analysis results, obtained butanol rejections at both temperatures were almost the same was known. Therefore, it was concluded that experimenting with higher temperatures would not make any critical contribution to the butanol rejection in the range where the temperature examination was made.

Table 3.4.1. Temperature-dependent DLS analysis results of 6.21wt.% Pluronic F127 + 20g/L Butanol solution.

Pluronic F127 Concentration (wt.%)	**Butanol Concentration (g/L)**	**Temperature** (˚C)	**Peak 1 (nm)**	**Peak 2 (nm)**
6.21	20	26	5.03 ± 0.17	20.8 ± 0.7
6.21	20	30	5.52 ± 0.18	16.5 ± 0.57
6.21	20	35	4.13±0.15	14.3± 0.5
6.21	20	37	5.65	14.3 ±0.5
6.21	20	40	-	14±0
6.21	20	45	-	14±0
6.21	20	50	-	14.7±0.5
6.21	20	55	-	15±0
6.21	20	60	-	15±0
6.21	20	65	-	16.1±0

The analysis of 1, 2.56, 6.21wt.% Pluronic P123 + 20 g/L Butanol solutions used for the filtrations, and 0.3wt.% Pluronic P123 + 20g/L Butanol solution analysis was another analysis group performed by DLS. As a consequence of the filtration of the mentioned solutions, due to the increasing Pluronic P123 concentration, there was an increase in butanol rejection.

It had thought that because of the rise in the surfactant concentration, the number of micelles in the solution increased, and this increment in the number of micelles had a positive effect on the separation of butanol. However, possibility of expansion in micelle dimensions due to the increase in surfactants concentration (which may be partially responsible for the improvement in the rejection) also exist.

As a result of the DLS analysis, as can be seen from Table 3.4.2, the sizes of the micelles formed in prepared solutions were in the range of 17-21nm. With rising Pluronic P123 concentration, there was no increase in the size of the formed micelles. In other words, the increase or decrease in the determined Pluronic concentration did not affect the micelle size.

According to the Wu et al., 2014, the sizes of the majority of the P123 micelles were around 20 nm. Hence similar to the F127 measurements, our results were also in line with the literature.

Table 3.4.2. At 26˚C conducted DLS analysis results of solutions prepared using at different concentrations Pluronic P123 + 20g/L Butanol.

Pluronic P123 Concentration (wt.%)	**Peak 1 (nm)**	**Peak 2 (nm)**
0.3	20.8±0.7	431± 0
1	21.4±2.2	431
2.56	18.5±0	-
6.21	17.3 ± 0	-

Another factor affecting the micelle size in the literature was the balance between the hydrophilic-lipophilic groups of surfactants expressed with HLB. As the hydrophobic chain length of a surfactant rises, the degree of difference between solvent and surfactant increases. This increment causes an escalation in the number of surfactants involved in micelle formation, in other words, an increase in the size of the micelles (Kim et al., 2003; Luo et al., 2010; Zaghbani et al., 2009)

When the Pluronic P123 concentration used in the filtrations was kept constant as 6.21wt.%, and the solutions were prepared by adding Pluronic L101 in different proportions, there was an increase in the obtained butanol rejection values in line with the increasing Pluronic L101 amount. Moreover, when DLS analyzes of these prepared solutions had made, it was clearly seen that in all experiments, there was clustering in two different size distributions (Table 3.4.3). This shows that the used mixtures of surfactants, change the micelle structure and this change has a positive effect on the amount of rejected butanol.

Table 3.4.3. At 37˚C conducted DLS analysis results of solutions prepared using at different concentrations Pluronic L101 & L61 + 6.21wt.% P123 + 20g/L Butanol.

Co-surfactant Type	**Co-surfactant wt.%**	**Peak 1 (nm)**	**Peak 2 (nm)**	**Peak 3 (nm)**
Pluronic L61	0.22	22.7±3.9	72.2± 6.3	-
Pluronic L101	0.008	20.4±1.8	65.3±3.8	-
Pluronic L101	0.08	20.4±0.7	68.4±2.3	431± 0
Pluronic L101	0.5	27.6±0.9	86.4±4.9	431 / 929

Additionally, there was also peaks around 431nm. These peaks which were both seen in Table 3.4.2 and Table 3.4.3 and had a small percentage in the analyses were observed probably because of created micelle aggregates in the solutions.

3.5 Acetone, Butanol and Ethanol Separation from Aqueous ABE and Surfactant Solutions

In terms of butanol rejection values, filtration of 20g/L butanol in Pluronic L101 wt.% : P123 wt.% = 1:1, and 1:3 solutions with NF90 membrane, and 20g/L butanol in Pluronic L101 wt.% : P123 wt.% = 0.5:6.21 solution with 1 kDa ultrafiltration membrane yielded the highest rejection result. Additionally, since the rejection values were increasing with collected permeate volume increase, increasing the VCF was also important to obtain higher butanol rejections. Therefore, to separate butanol from ABE, filtering the ABE solution with one of the Pluronic L101 wt.% : P123 wt.% 1:1, 1:3, and 0.5:6.21 surfactant couples continuing the filtration until VCF became 5.7 was the best option. When solutions fouling results and physical behavior of them before and during filtrations were examined, it was seen that 20g/L butanol + Pluronic L101 wt.% : P123 wt.% = 1:3 solution viscosity was getting higher, and gel formation was taking place during filtration. This means, due to the viscosity increment, at the filtrations with this solution permeance would be low, and a larger membrane area would be necessary. For the filtrations, obtaining the high rejection of the target compound alone is not enough. As well as having high rejections, conducting the filtrations as fast and economic as possible is important. Therefore, for the ABE experiments, it was decided to use L101 wt.% : P123 wt.% = 1:1 and 0.5:6.21 surfactant couple. As a result of filtration experiments conducted with L101 wt.% : P123 wt.% = 1:1 surfactant couple and NF90 membrane approximately 1.35% acetone, 68.19% butanol, and 26.87% ethanol rejection were obtained (Figure 3.5.1.). On the other hand, with L101 wt.% : P123 wt.% = 0.5:6.21 surfactant couple and 1kDa UF membrane conducted filtration experiments approximately 23.44% acetone, 66.09% butanol, and 19.97% ethanol rejection were seen (Figure 3.5.2.).

Raw concentration data and calculation methodology are available in Appendix G.

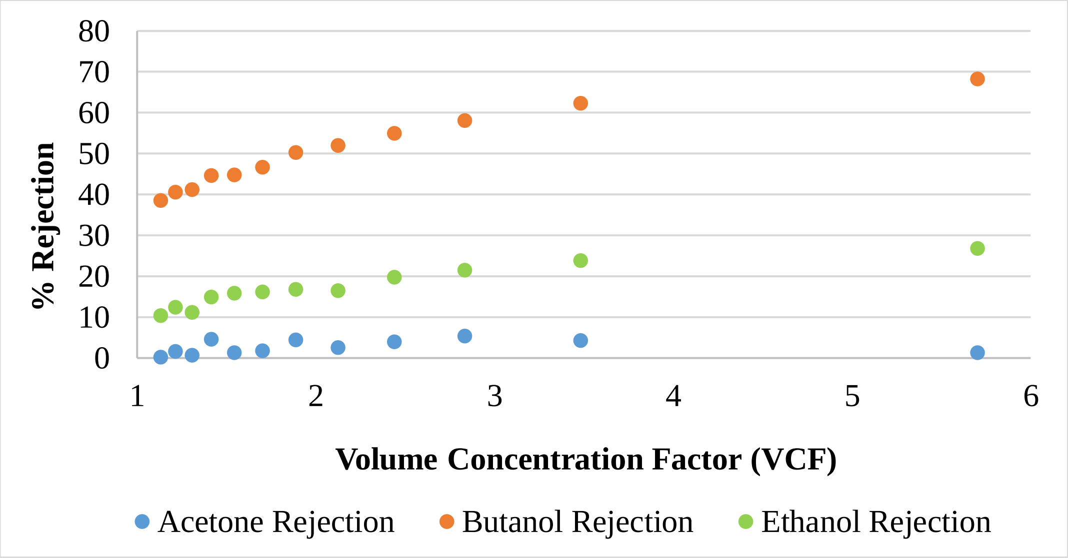


Figure 3.5.1. Rejection values as a result of L101 wt.% : P123 wt.% = 1:1 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with NF90 membrane when we take the average of the permeate concentrations of two experiments.

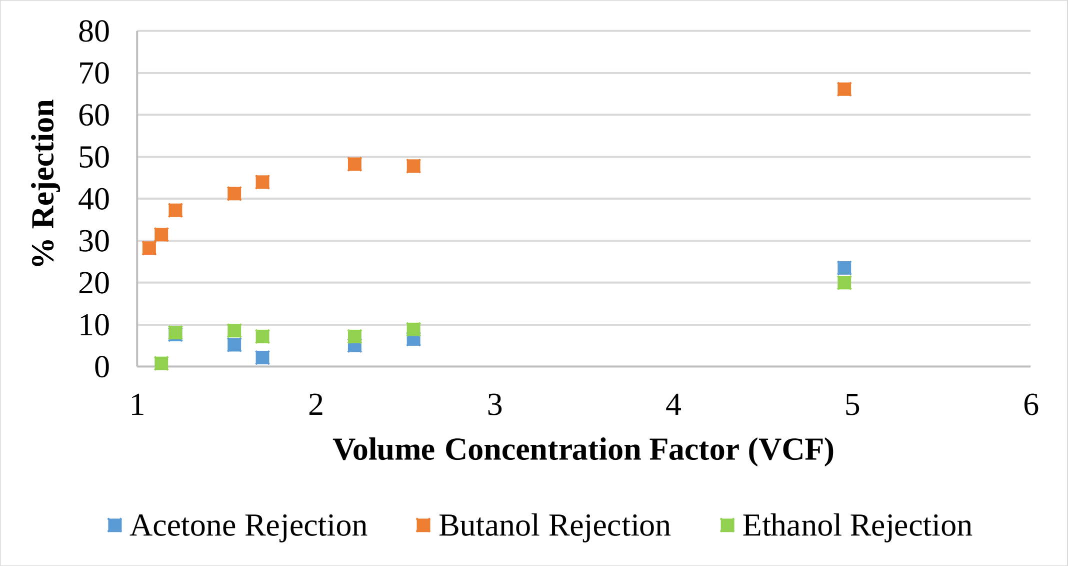


Figure 3.5.2. Rejection values as a result of use L101 wt.% : P123 wt.% = 0.5:6.21 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with 1kDa UF membrane when we take the average of the permeate concentrations of two experiments.

Butanol solubility is 66g/L at 20℃ (Dow, 2012) and approximately 70g/L at 25℃ (Yalkowsky et al., 2010) in water. In other words, it is partially miscible with water. On the other hand, ethanol and acetone are totally miscible in water (ILO, 2018; ILO, 2009). Therefore, it was expected when surfactants were added to the ABE mixture while butanol shows a tendency to surfactants and encapsulates in micelles, ethanol, and acetone remains in the water. So that, as a result of filtration, up to some point, butanol can be separated by remaining on the retentate side from the rest of the mixture. When rejection percentages were considered, results support the main expectation. In both of the experiments, 66-68% of the butanol separation had been achieved. However, at the same time, there was small ethanol and acetone rejection values were obtained.

According to the selectivity calculations, due to the VCF increase, a rise in the butanol selectivity over ethanol and acetone was observed. At the end of the NF experiments, when VCF was 5.7, butanol selectivity over acetone was detected as approximately 3. Moreover, butanol selectivity over ethanol was detected as 2.3 (Figure 3.5.3.). On the other hand, both butanol selectivity over acetone and ethanol was detected as about 3 in UF experiments when VCF was 5 (Figure 3.5.4.).

Normally small-sized compounds removal by ultrafiltration membranes without any surfactant is not possible. However, in some cases, because adsorption of compounds by the membrane, removal of the compounds is seen (Shwarze, 2017). To understand such a situation exists in our process or not, by preparing ABE solutions without any surfactant filtration experiments were conducted. Consequently, in used UF and NF membranes, less than %10 acetone, butanol, and ethanol rejections were obtained.

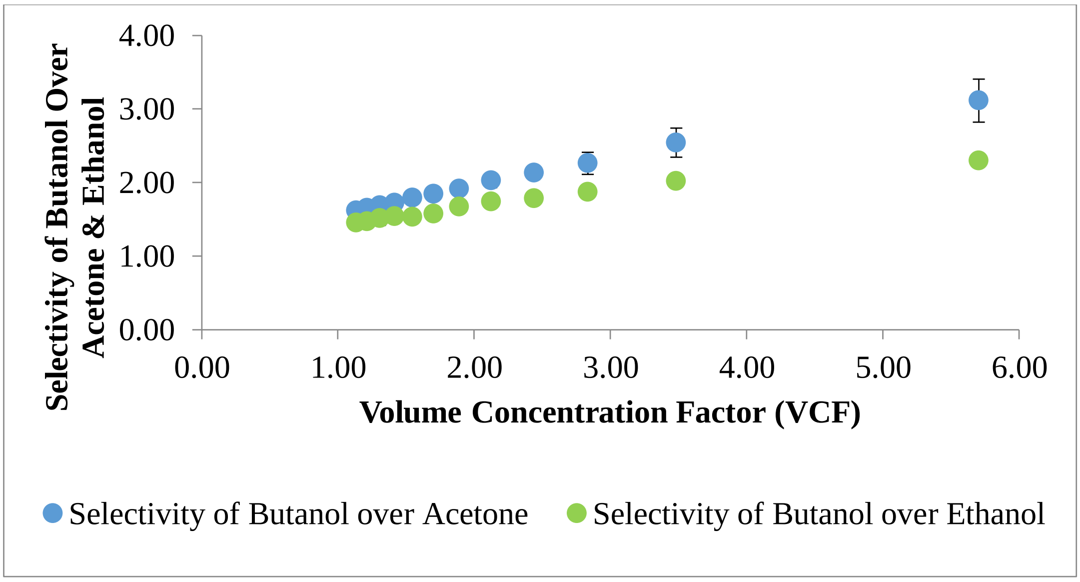


Figure 3.5.3. Selectivity of butanol over acetone & ethanol as a result of L101 wt.% : P123 wt.% = 1:1 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with NF90 membrane.

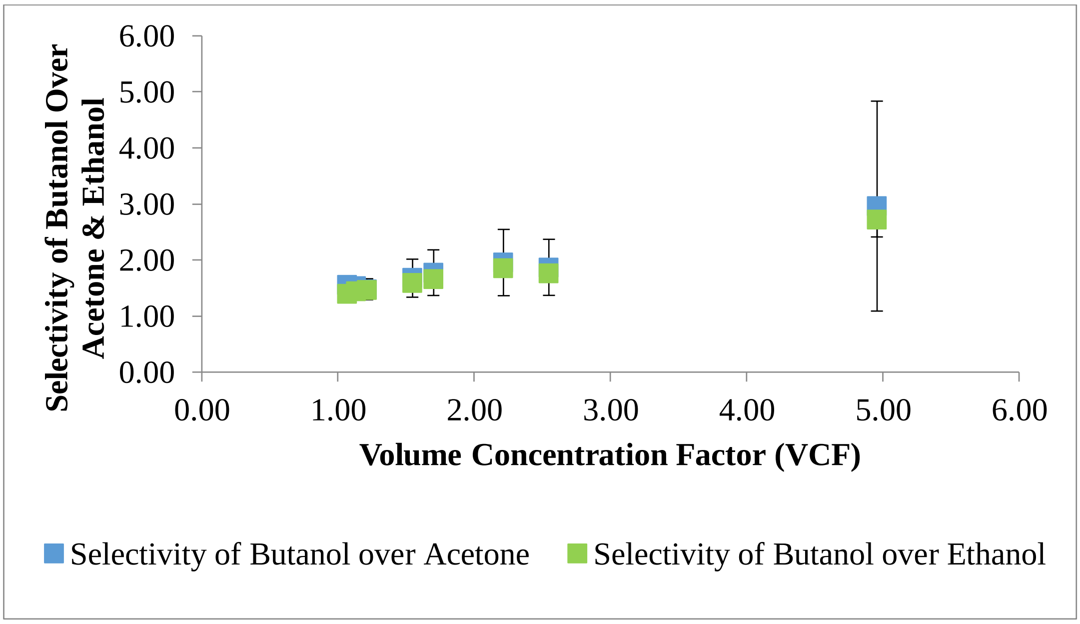


Figure 3.5.4. Selectivity of butanol over acetone & ethanol as a result of L101 wt.% : P123 wt.% = 0.5:6.21 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with 1kDa UF membrane.

In the industry usually rather than a dead-end (DE) filtration system, a cross-flow (CF) system is preferred. Therefore, by considering a CF system with a 1000 kg/h feed flow rate, process calculations were conducted (Figure 3.5.5.a, b, c). In these calculations, when VCF was equal to 5.67 (≅ 5.7), it was seen that the obtained permeate flow rate was becoming equal to 823.6 kg/h, while the retentate flow rate is 176.4 kg/h. In the system where NF90 membrane and Pluronic L101 wt.% : P123 wt.% = 1:1 was used to separate 5, 20, and 5 g/L acetone, butanol, and ethanol, respectively, obtained average acetone rejection was %2.66, average butanol rejection %50.18, and average ethanol rejection %17.16. So that, at the retentate side it was seen that the butanol concentration was reaching 34.1 g/L while acetone and ethanol concentrations were becoming 5.1, 5.8 g/L respectively. Also, since average permeate flux was equal to 0.69 ± 0.0007 L/hm^2, the necessary membrane area for this system was 1193 m^2 for the 1000 kg/h feed. After the first CF separation was achieved, obtained retentate would be subjected to a temperature switch to bring the surfactant concentration below the CMC at the subjected temperature and release the butanol free surfactants would be removed from the ABE mixture via by NF membrane to be rejected to the process and the ABE mixture would be fed to the second MEUF stage with the necessary amount of surfactant only (Pluronic L101 wt.% : P123 wt.% = 1:1 + acetone g/L : butanol g/L : ethanol g/L = 5.1:34.1:5.8). When this new solution was fed to the second CF with a 176.4 kg/h flow rate, at VCF equal to 5.67 (≅ 5.7), permeate flow rate would become equal to 145.3 kg/h, while the retentate flow rate 31.1 kg/h. Moreover, in the system where average acetone butanol and ethanol rejections were %2.66, %50.18, %17.16, the retentate side acetone, butanol, and ethanol concentrations would be 5.2, 58.1, and 6.8 g/L, respectively. Also, the necessary membrane area for this system would be 210.6 m^2.

In the system, when the procedure which was conducted between CF1 and CF2 systems was repeated and prepared Pluronic L101 wt.% : P123 wt.% = 1:1 + acetone g/L : butanol g/L : ethanol g/L = 5.2:58.1:6.8 solution was fed to the third CF system with 31.1 kg/h flow rate, at VCF was 5.67 ($\cong$ 5.7), on the retentate side obtained acetone, butanol, and ethanol concentrations would be 5.3, 99, and 7.9 g/L, respectively. Also, the necessary membrane area for this system would be 37.1 m^2.

In the system where 1kDa UF membrane and Pluronic L101 wt.% : P123 wt.% = 0.5:6.21 was used to separate 5, 20, and 5 g/L acetone, butanol, and ethanol, respectively, obtained average acetone rejection was %6.1, average butanol rejection was %43, and average ethanol rejection was %7.5. So, when the same system was considered with this surfactant couple (Figure 3.5.6.a, b, c) as a result of the first CF system operation, at the retentate side it was seen that the butanol concentration was reaching 31 g/L while acetone and ethanol concentrations were becoming 5.3, 5.3 g/L respectively. Also, since average permeate flux was equal to the 0.31 ± 0.01 L/hm^2, the necessary membrane area for the CF1 system was 2656.8 m^2. At the end of the CF2 system, retentate side butanol concentration would be 47.9 g/L while acetone and ethanol concentrations were 5.6, 5.7 g/L respectively, and the necessary membrane area for the CF2 system was 468.7 m^2. Furthermore, at the end of the CF3 system retentate side butanol concentration would reach to the 74.2 g/L, while acetone and ethanol concentrations were 5.9, 6.1 g/L respectively and, the necessary membrane area for the CF3 system, would be 82.6 m^2.

When two systems were compared with each other, in the used UF system, without membrane used for the surfactant recycle, the overall necessary membrane area was 3208.1 m^2 while in the NF system this area was 1440.7 m^2. Hence, in terms of used membrane area, preferring the NF system was more advantageous. If it was assumed that the UF membrane was rejecting the %98 of used surfactants by looking at Table 3.1.1 and NF membrane was rejecting %100, for recycled surfactant system with 1000 kg/h initial feed, in the UF system used surfactant amount was 67.1 kg/h, in the NF system this amount was 20 kg/h.

Moreover, with this surfactant amount, while concentrating butanol up to 74.2 g/L was possible in the UF system; in the NF system butanol concentration could be raised to 99 g/L. Therefore, in terms of the used surfactant amount and the obtained final butanol concentration, the NF system was more advantageous, too.

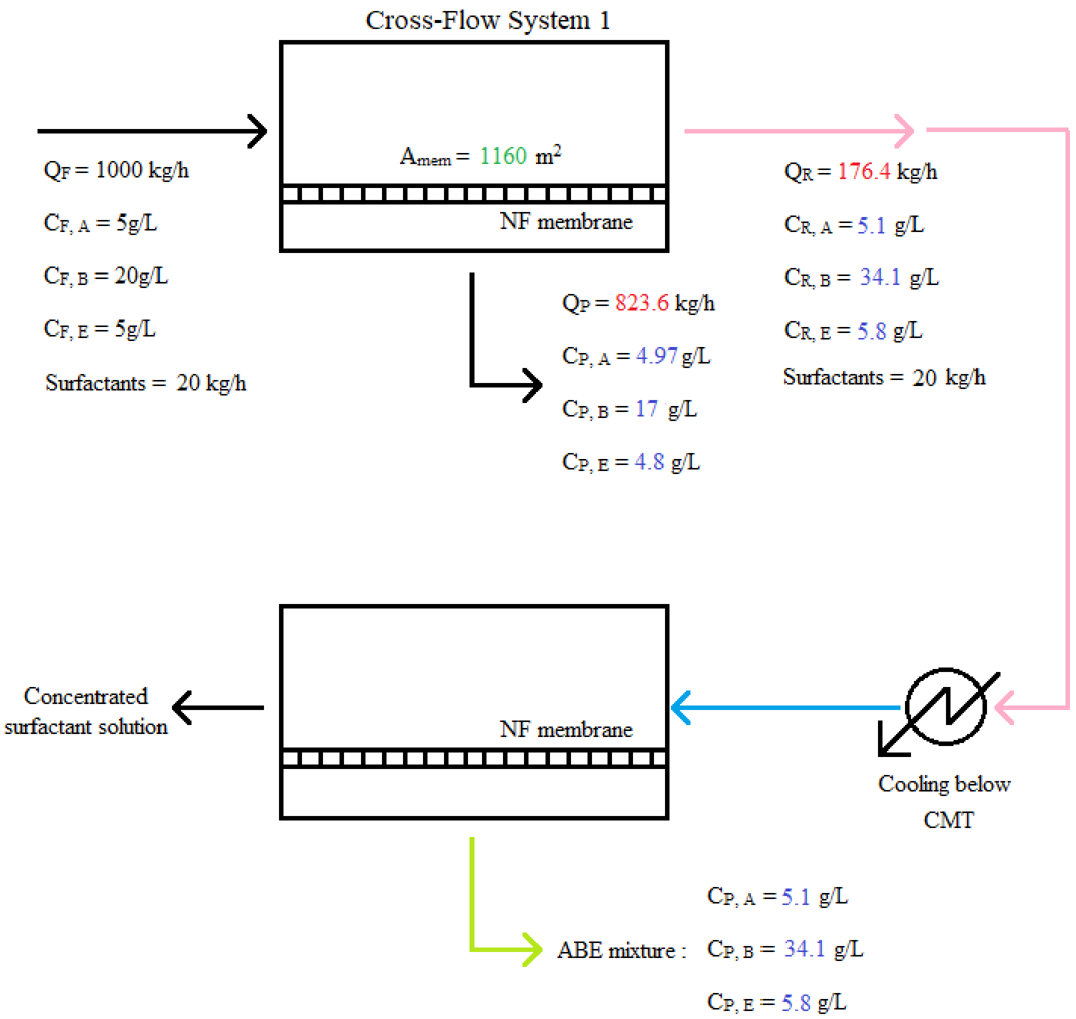


Figure 3.5.5.a. Pluronic L101 wt.% : P123 wt.% = 1:1 + 5, 20, and 5 g/L acetone, butanol, and ethanol feed solution filtration system with NF90 nanofiltration membrane process calculations first cross-flow system.

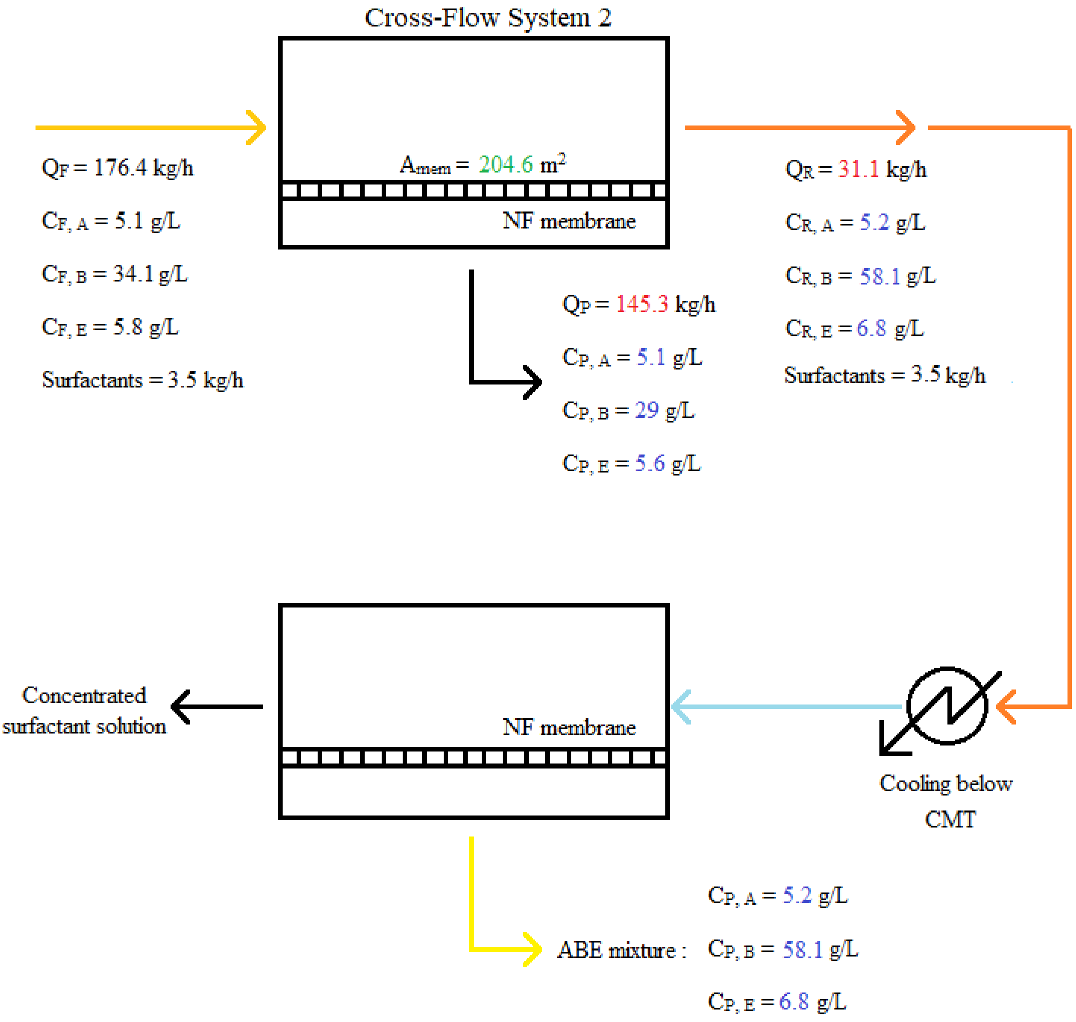


Figure 3.5.5.b. Pluronic L101 wt.% : P123 wt.% = 1:1 + 5, 20, and 5 g/L acetone, butanol, and ethanol feed solution filtration system with NF90 nanofiltration membrane process calculations second cross-flow system.

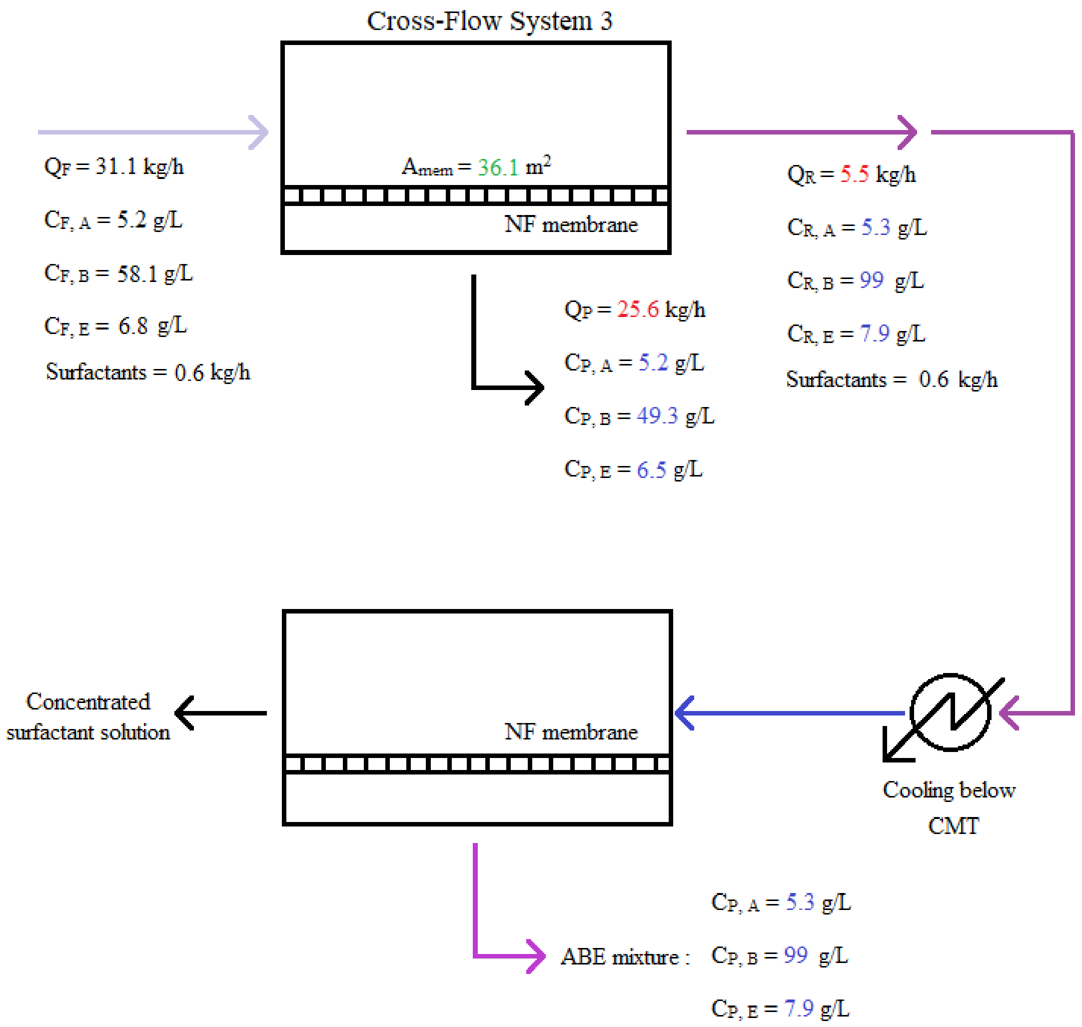


Figure 3.5.5.c. Pluronic L101 wt.% : P123 wt.% = 1:1 + 5, 20, and 5 g/L acetone, butanol, and ethanol feed solution filtration system with NF90 nanofiltration membrane process calculations third cross-flow system.

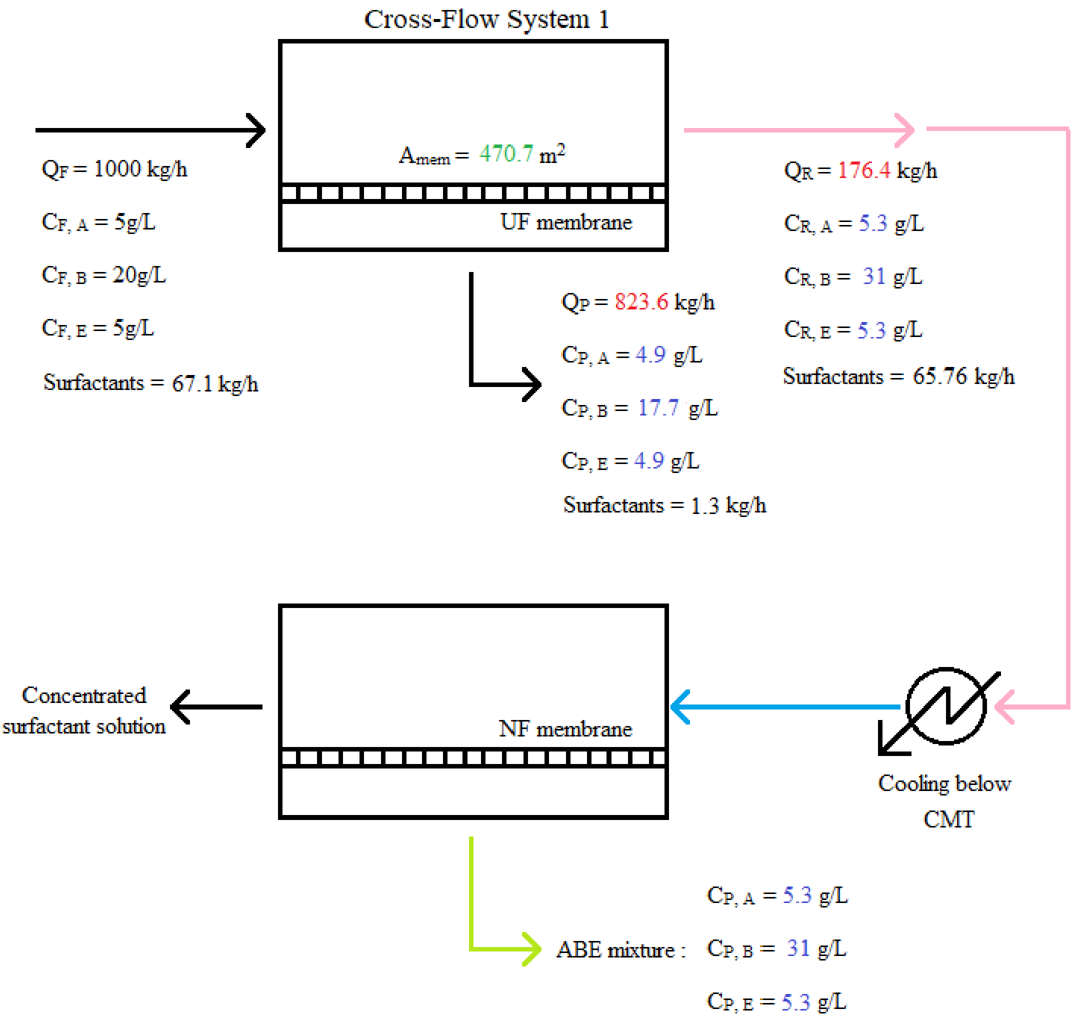


Figure 3.5.6.a. Pluronic L101 wt.% : P123 wt.% = 0.5:6.21 + 5, 20, and 5 g/L acetone, butanol, and ethanol feed solution filtration system with 1kDa ultrafiltration membrane process calculations first cross-flow system.

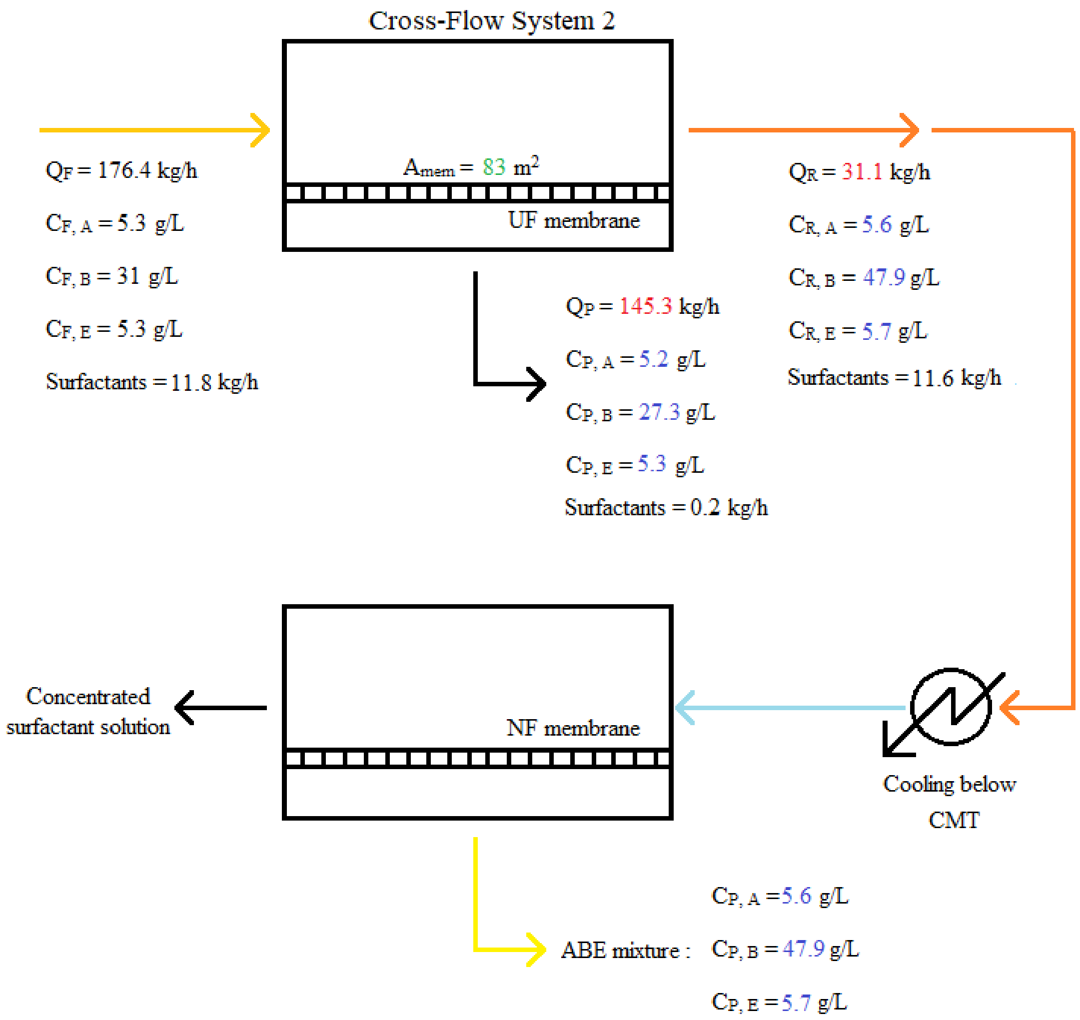


Figure 3.5.6.b. Pluronic L101 wt.% : P123 wt.% = 0.5:6.21 + 5, 20, and 5 g/L acetone, butanol, and ethanol feed solution filtration system with 1kDa ultrafiltration membrane process calculations second cross-flow system.

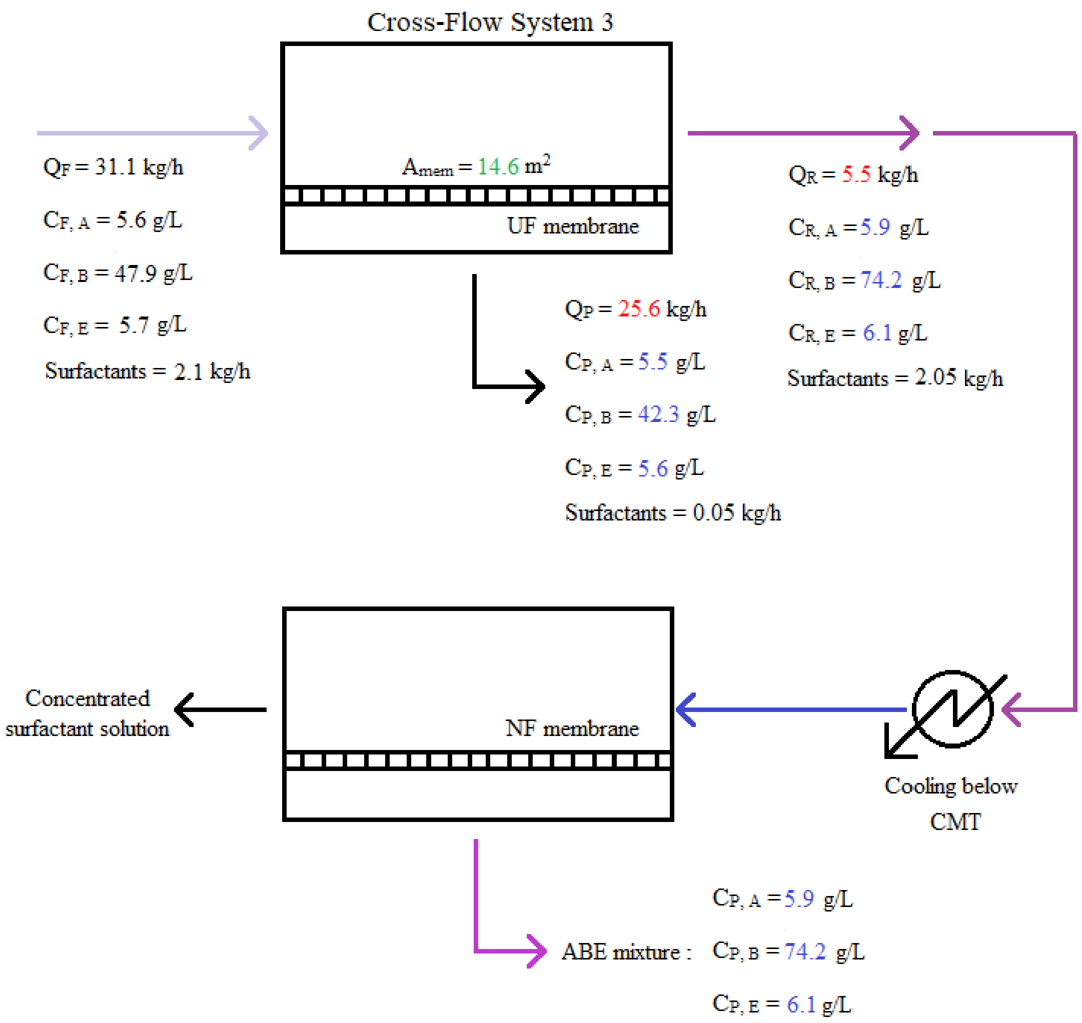


Figure 3.5.6.c. Pluronic L101 wt.% : P123 wt.% = 0.5:6.21 + 5, 20, and 5 g/L acetone, butanol, and ethanol solution filtration system with 1kDa ultrafiltration membrane process calculations third cross-flow system.

After the separation of surfactants in both of the systems, due to exceeding the solubility limit of butanol which is approximately 70 g/L at 25°C (Yalkowsky et al., 2010) in water, phase separation between butanol and water would be seen and butanol would be separated from water easily with the help of decanter. Because of the collected retentate amount, a high amount of butanol would be lost on the permeate side and %2-3 of butanol feed would be recovered here.

Therefore, mixing of the obtained permeates streams and by feeding this mixture back to the other CF systems, repeating same procedure was another step in the considered separation system. Moreover, if obtained average butanol rejection rate is increased to 60, 70, 80, 90 and 95%, % recovery of butanol which can be obtained is given in the Table 3.5.1.

Table 3.5.1. % Recovery of butanol which can be obtained if obtained average butanol rejection rate is increased to 60, 70, 80, 90 and 95%.

$\mathbb{R}_{\boldsymbol{Butanol}}\%$	**VCF**	**Number of Stages**	**Final Retentate Butanol Conc.**	**% Butanol Recovery**
60	5.67	2	78.3	12.2
70	5.67	2	111.5	17.3
80	5.67	2	171.8	26.7
90	5.67	1	77.3	68.2
95	5.67	1	91.9	81.1

CHAPTER 4

CONCLUSION

The main aim of this study was to separate butanol from ABE mixture with the MEUF method at the existence of the nonionic surfactants. For this purpose, the experimental study was separated into two main parts. Firstly, detecting the most suitable operating conditions for aimed experiments and selecting the best surfactant or surfactant couple for the butanol separation in the aqueous environment was aimed. On the other hand, in the second part, the objective was with the selected operating conditions and surfactant or surfactant couple separating butanol from ABE mixture.

Due to the permeate flow rate and the surfactant rejection values, 1kDa UF membrane and NF90 nanofiltration membrane was selected as the membranes and 3 bar pressure as operating pressure of selected membranes.

For selecting the surfactant or surfactant couple, which showed the best butanol separation performance in the aqueous environment, different solutions containing at different rates Pluronic F127, P123, L61, and L101 and butanol solutions were prepared. During experiments, butanol affinity to micelles increased with decreasing surfactants HLB values was observed. When 1kDa membrane was used, the solution of 6.21wt.% P123 + 0.5wt.% L101 exhibited the best butanol separation performance by % 34.1 ± 0.1 butanol rejection at 37°C, and VCF 1.9. When NF90 membrane is used, solutions containing 1wt.% L101 + 3wt.% P123 and 1wt.% L101 + 1wt.% P123 had exhibited the best butanol separation performances by 39.9 ± 0.5%, 65 ± 4% butanol rejection, respectively, at 37°C, and VCF 1.9. Also, it was observed that when the VCF was increased to 5.7, butanol rejection was reaching to 55.6 ± 2.3% in 20g/L butanol + 1wt.% L101 + 1wt.% P123 solution filtrations. Therefore, collecting retentate as much as possible was necessary.

Because of their butanol separation performances, the separation of butanol from ABE mixture was tested with NF90 membrane at the existence of 1wt.% P123 + 1wt.% L101 and at the existence of 6.21wt.% P123 + 0.5wt.% L101 with 1kDa membrane among the best butanol separation performing surfactant couples. As a result, NF90 experiments, when VCF was 5.7, approximately 1.35% acetone, 68.19% butanol, and 26.87% ethanol rejection were obtained. Also, it was seen that; butanol selectivity over acetone was about 3, and butanol selectivity over ethanol was approximately 2.3. Similar to that, when VCF was 5, approximately 23.44% acetone, 66.09% butanol, and 19.97% ethanol rejection was obtained as a result 1kDa membrane experiments. Moreover, butanol selectivity over acetone and ethanol were about 3.

When process calculations were conducted for a three-stage filtration,based on result of the ABE experiments with 1 kDa membrane and Pluronic P123 wt.%: L101 wt.% = 6.21:0.5, at the end of the third stage;acetone, butanol and ethanol concentrations are expected to be 5.9, 74.2, 6.1 g/L, respectively. On the other hand, for the NF90 membrane and Pluronic P123 wt.%: L101 wt.% = 1:1, concentrations of 5.3, 99, 7.9 g/L would be expected, respectively. Thus, it was observed as proof of concept that with the MEUF method it is possible to obtain a major component from the fermentation broth and the main product as retentate.

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APPENDICES

A. Solution Calculation & Preparation Example

As an example solution, let’s think about 5g/L acetone + 20g/L butanol + 5g/L ethanol + 6.21 wt. % Pluronic P123 + 0.5 wt.% Pluronic L101 solution. To prepare this solution, initially necessary calculations for each of the compounds were conducted.

- For the 1 L ABE solution necessary acetone amount was

Target acetone amount (g) × 1/ (acetone density) × necessary unit conversion

= Target acetone amount (L)

$$5\ g\ \mathrm{Acetone}\ \times\ \frac{1}{784}\frac{\mathrm{m}^3}{\mathrm{kg}}\times\frac{1000\ \mathrm{g}}{1\ \mathrm{kg}}\ \times\frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}=0.00638\ \mathrm{L}$$

= 6.38 mL (Calculation 1)

- For the 1 L ABE solution necessary butanol amount was

Target butanol amount (g) × 1/ (butanol density) × necessary unit conversion

= Target butanol amount (L)

$$20\ g\ \mathrm{Butanol}\ \times\ \frac{1}{810}\frac{\mathrm{m}^3}{\mathrm{kg}}\times\frac{1000\ \mathrm{g}}{1\ \mathrm{kg}}\ \times\frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}=0.02469\ \mathrm{L}$$

= 24.69 mL (Calculation 2)

- For the 1 L ABE solution necessary ethanol amount was

Target ethanol amount (g) × 1/ (ethanol density) × necessary unit conversion

= Target ethanol amount (L)

$$5\ g\ \text{Ethanol}\ \times\ \frac{1}{789}\frac{\text{m}^3}{\text{kg}} \times \frac{1000\ \text{g}}{1\ \text{kg}}\ \times \frac{1\ \text{m}^3}{1000\ \text{L}} = 0.00634\ \text{L}$$

= 6.34 mL (Calculation 3)

For targeted ABE solution, by mixing the necessary acetone (6.38 ml, from calculation 1), butanol (24.69ml, from calculation 2), and ethanol (6.34 ml, from calculation 3) amounts with up 1L 5g/L acetone + 20g/L butanol + 5g/L ethanol (ABE) solution were prepared.

This prepared solution 4ml separated as the feed solution for GC analysis. Remaining 996 ml ABE was added on 65.95g Pluronic P123 (from calculation 4) to obtain 5g/L acetone + 20g/L butanol + 5g/L ethanol + 6.21 wt. % Pluronic P123 solution.

- To add 996 ml ABE solution necessary Pluronic P123 amount is

$$\frac{X\ g\ Pluronic\ P123}{X\ g\ Pluronic\ P123 + 996\ g\ ABE\ solution} \times 100 =\ 6.21$$

X g Pluronic P123 = 65.95 g Pluronic P123 (Calculation 4)

Note: During this calculation calculated ABE solution density was accepted as 1g/ml. Also, a similar assumption was made for only butanol included and butanol + Pluronic P123 included solutions.

When Pluronic P123 totally dissolved in the ABE mixture, 1000mL of formed homogeneous ABE + P123 solution was added on 5.03g Pluronic L101 (from calculation 5) to obtain 5g/L acetone + 20g/L butanol + 5g/L ethanol + 6.21 wt. % Pluronic P123 + 0.5 Pluronic L101 solution.

- To add 1000 ml ABE + Pluronic P123 solution necessary Pluronic L101 amount is

$$\frac{X\ g\ Pluronic\ L101}{X\ g\ Pluronic\ L101 + 1000\ g\ (ABE + Pluronic\ P123)\ solution} \times 100 =\ 0.5$$

X g Pluronic L101 = 5.03 g Pluronic L101 (Calculation 5)

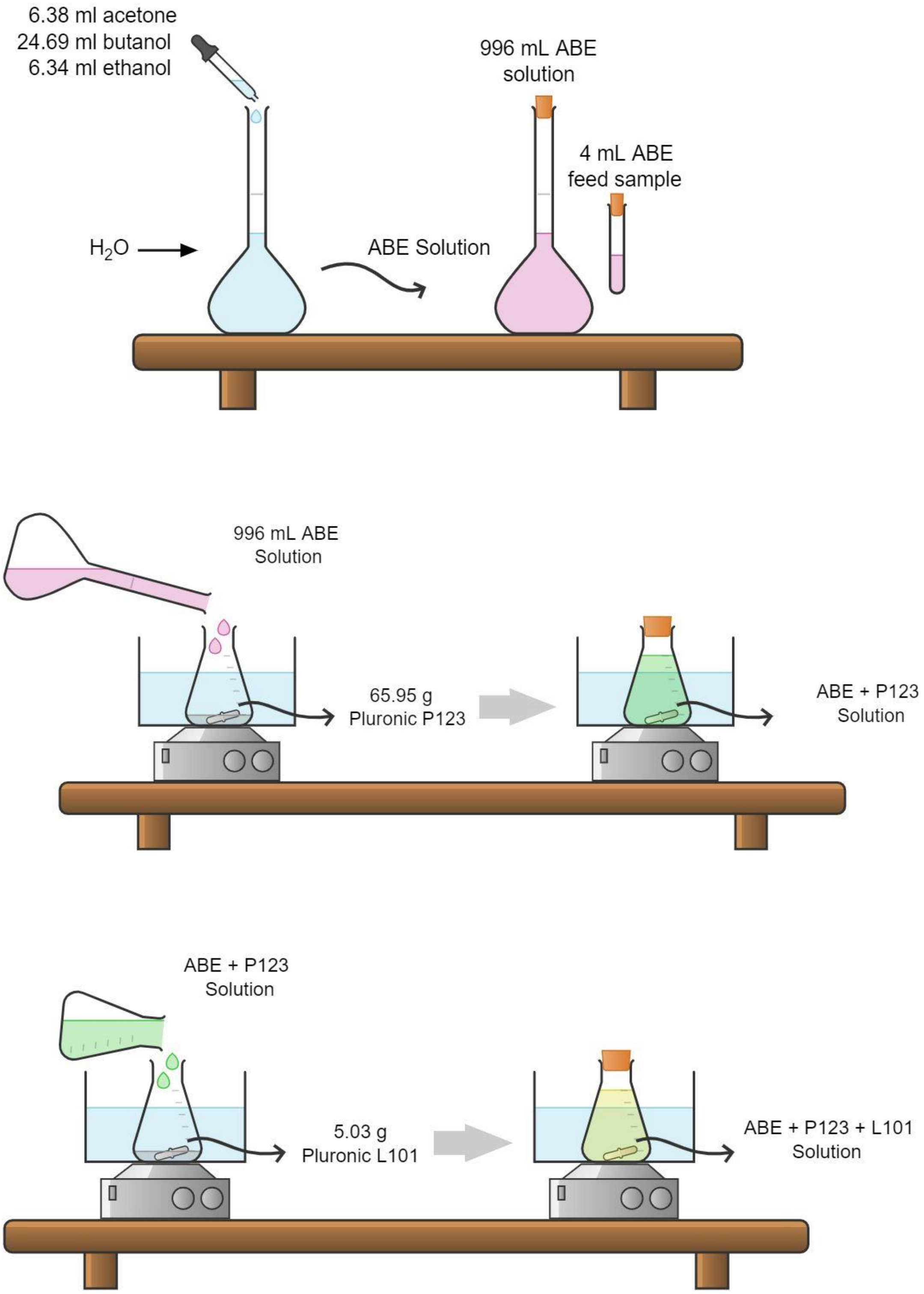

Figure A.1. Sample preparation procedure.

B. Calibration Curves

Acetone Calibration Curve

Retention Time: 2.0 min

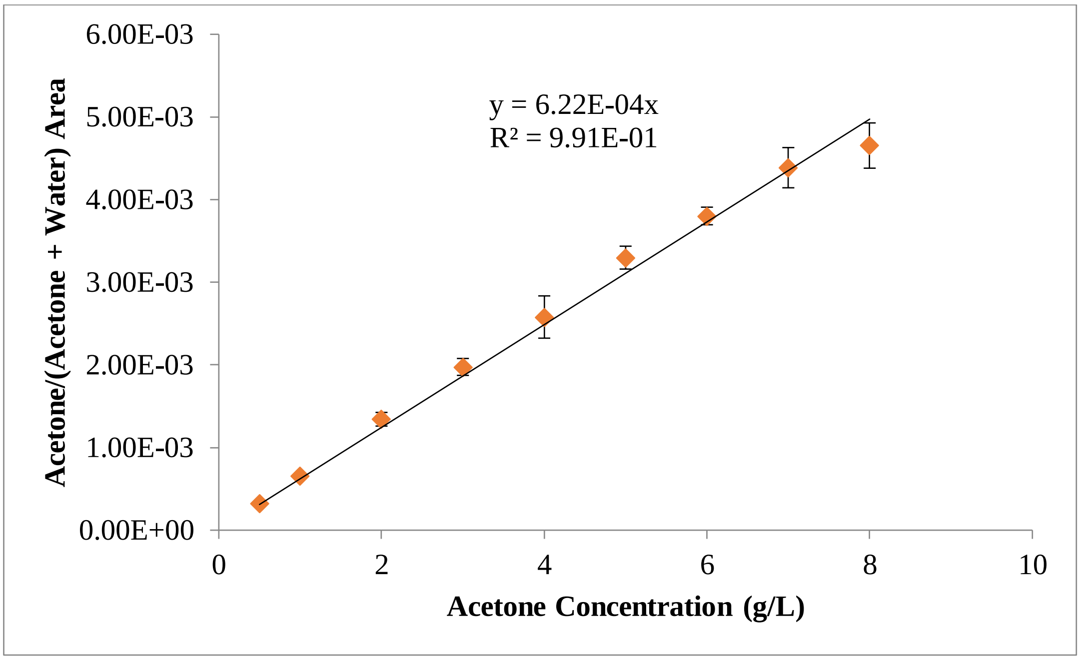

Figure B.1. Acetone Calibration Curve in Gas Chromatography at 2.0 min.

$$\text{Acetone Concentration (g/L)} = \frac{\text{Acetone Area / (Acetone + Water) Area}}{0.000622}$$

For acetone calibration curve 0.5, 1, 2, 3, 4, 5, 6, 7, 8 g/L aqueous acetone solutions were prepared. For each solution, 3 times GC measurements were conducted. For each measurement, Acetone Area / (Acetone + Water) Area was calculated. Average of these calculations were used for the calibration curve drawing.

Butanol Calibration Curve

Retention Time: 6.6 min

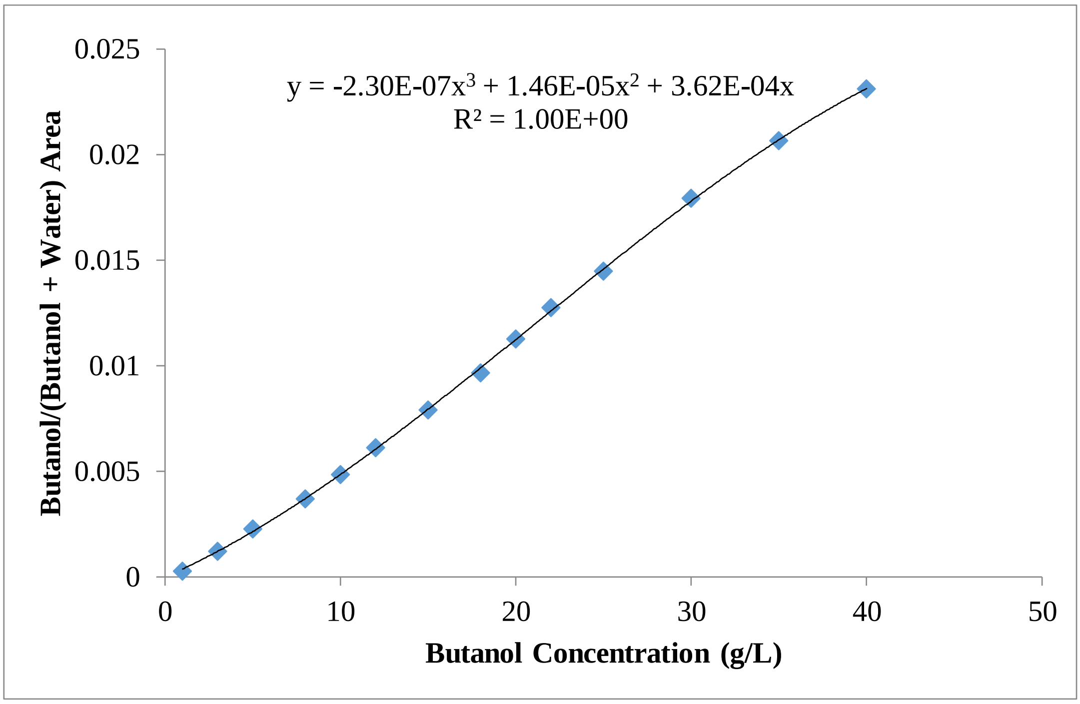

Figure B.2. Butanol Calibration Curve in Gas Chromatography at 6.6 min.

Butanol Concentration (g/L) = BC

$(-0.00000023\times(BC^3)) + (0.0000146\times(BC^2)) + (0.000362 \times (BC))$

= Butanol Area / (Butanol + Water) Area

For butanol calibration curve 1, 3, 5, 8, 10, 12, 15, 18, 20, 22, 25, 30, 35, 40 g/L aqueous butanol solutions were prepared. For each solution, 3 times GC measurements were conducted. For each measurement, Butanol Area / (Butanol + Water) Area was calculated. Average of these calculations were used for the calibration curve drawing.

Ethanol Calibration Curve

Retention Time:1.5 min

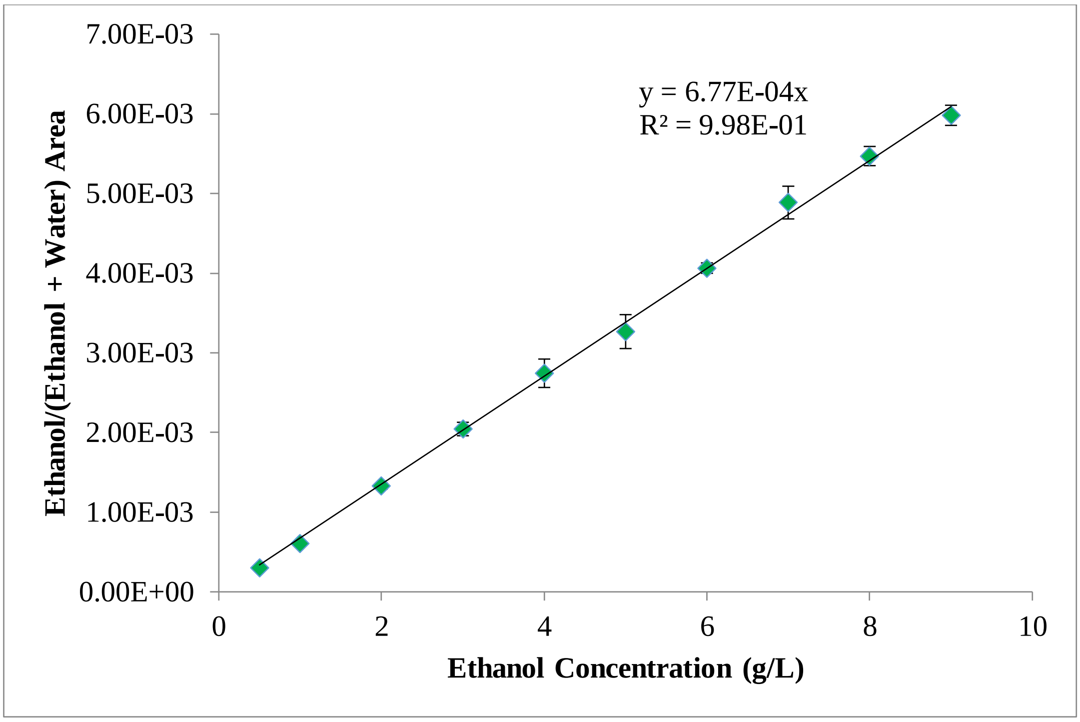

Figure B.3. Ethanol Calibration Curve in Gas Chromatography at 1.5 min.

$$\text{Ethanol Concentration (g/L)} = \frac{\text{Ethanol Area / (Ethanol + Water) Area}}{0.000677}$$

For ethanol calibration curve 0.5, 1, 2, 3, 4, 5, 6, 7, 8, 9 g/L aqueous ethanol solutions were prepared. For each solution, 3 times GC measurements were conducted. For each measurement, Ethanol Area / (Ethanol + Water) Area was calculated. Average of these calculations were used for the calibration curve drawing.

C. Surface Tension Against the Logarithm of the Pluronic

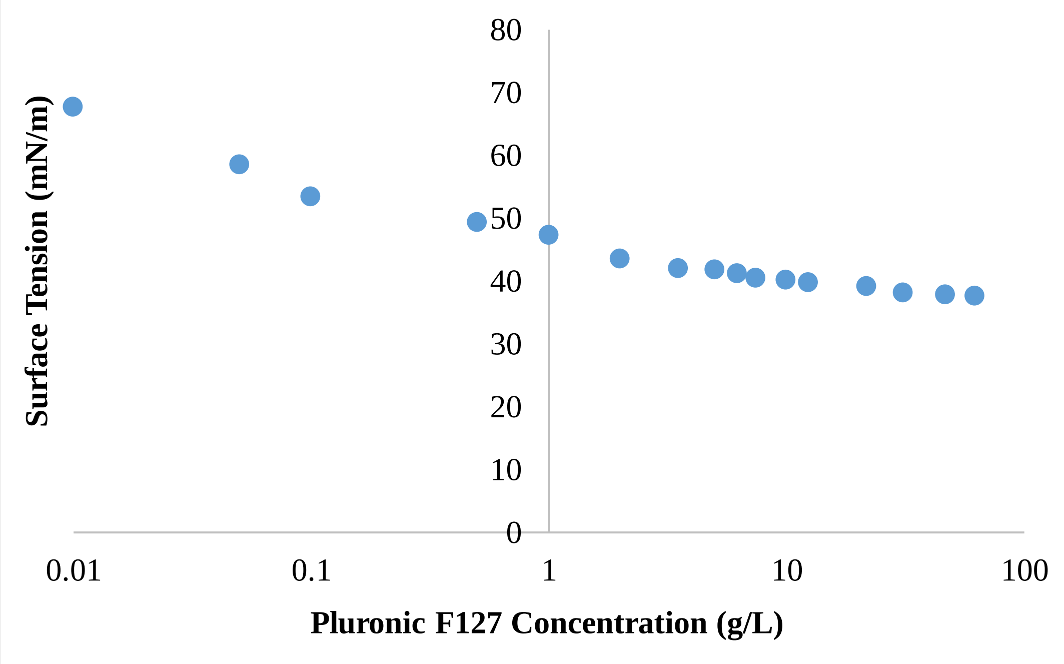

Figure C.1. Surface tension change with respect to logarithm of Pluronic F127 concentration.

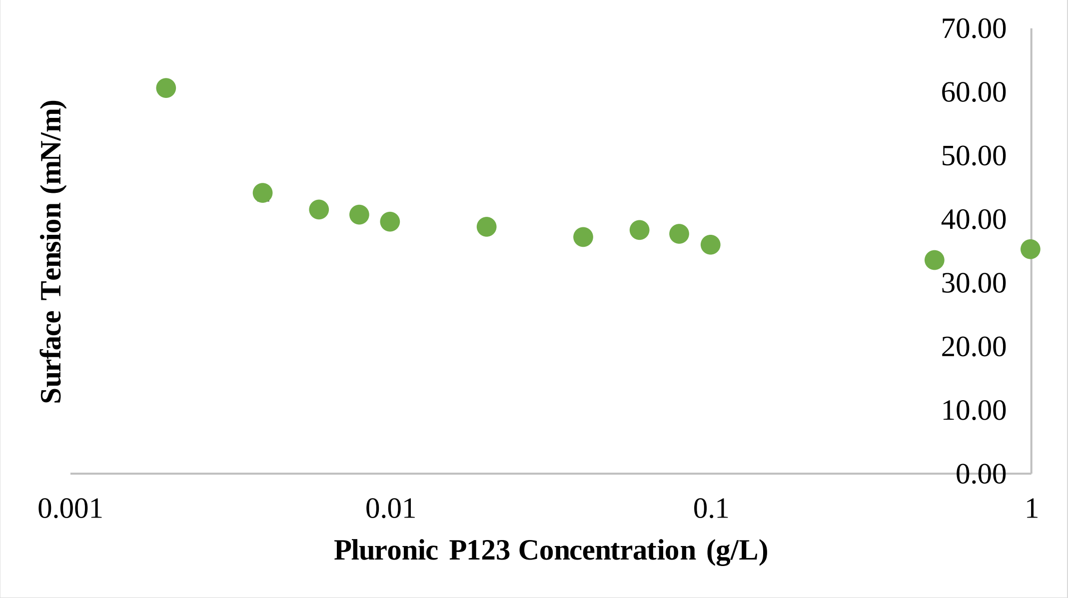

Figure C.2. Surface tension change with respect to logarithm of Pluronic P123 concentration.

D. Permeate Flux Calculations

During optimum pressure determination of selected 1 and 5 kDa UF membranes, for each pressure value, by using the interval of 28-30 ml permeate volume range of experiments, average permeate flux values were determined. To exemplify the calculation methodology, experiments of 20g/L butanol + 6.21wt.% Pluronic F127 solutions with 1kDa membrane at 4 bar were shown as an example.

As it is seen in Figure D.1., initially, experiments permeate flux vs permeate volume graphs were drawn. From calculated flux values corresponded values to the 28-30ml permeate volume in the y axis (Table D.1.) separated. Then, by taking the average of them, both average flux value and standard deviation were calculated.

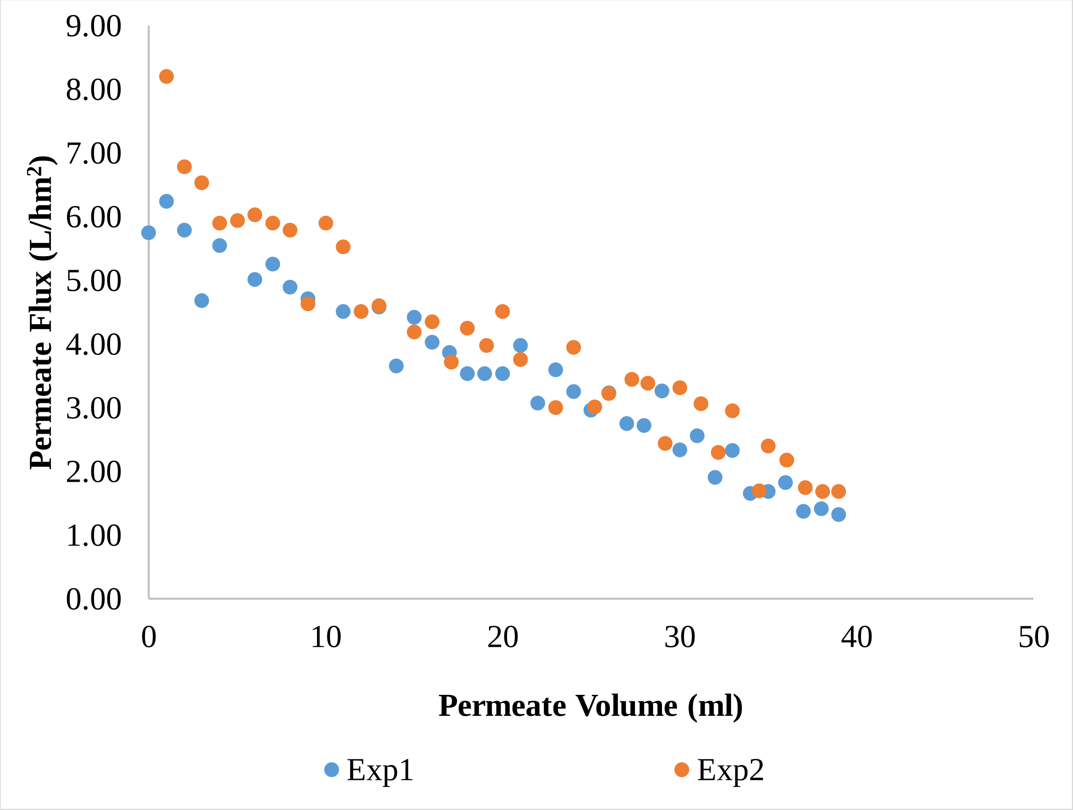

Figure D.1. Change of permeate flux of 20g/L butanol + 6.21wt.% Pluronic F127 solutions filtrations with 1kDa membrane at 4 bar with respect to permeate volume.

Table D.1. From calculated flux values of 20g/L butanol + 6.21wt.% Pluronic F127 solutions filtrations with 1kDa membrane at 4 bar corresponded values to the 28-30ml permeate volume in the y axis.

Experiments	**Permeate Volume**	**Permeate Flux**	**Average Flux**
Exp1	28 ml	2.74	
	29 ml	2.72	
	30 ml	3.26	2.91
Exp2	28.2 ml	3.44	
	29.2 ml	3.38	
	30 ml	2.43	3.09

Permeate flux value for 1kDa membrane at 4 bar;

$$\text{Average Flux} = \frac{2.91 + 3.09}{2} = 3\ \text{L/hm}^2$$

$$\text{Standard Deviation} = \sqrt{\frac{\sum(\text{Flux} - \text{Average Flux})^2}{2-1}}$$

$$= \sqrt{\frac{(2.91-3)^2 + (3.09-3)^2}{2-1}}$$

$$= 0.127$$

Then permeate flux value for 1kDa membrane at 4 bar = 3 ± 0.127 L/hm^2

E. Permeate Flux Data of The Experiments

Table E.1. At VCF 1.9, permeate flux values of single surfactant system experiments conducted with 1kDa UF membranes.

Pluronic Type	**Pluronic Concentration (wt.%)**	**Experiment Temperature (℃)**	**Butanol Concentration (g/L)**	**Permeate Flux (L/hm^2)**
Pluronic F127	6.21	26	-	4.22 ± 0.71
Pluronic F127	6.21	26	20	3 ± 0.02
Pluronic F127	6.21	26	10	3.62 ± 0.09
Pluronic F127	6.21	26	5	3.47 ± 0.37
Pluronic F127	6.21	26	1	3.74 ± 0.32
Pluronic P123	6.21	26	20	7.01 ± 0.34
Pluronic P123	6.21	26	10	7.02 ± 0.45
Pluronic P123	6.21	26	5	7.53 ± 0.06
Pluronic P123	2.56	26	20	6.98 ± 0.16
Pluronic P123	2.56	26	10	7.31 ± 0.25
Pluronic P123	2.56	26	5	7.35 ± 0.43
Pluronic P123	1	26	20	6.97 ± 0.35
Pluronic P123	1	26	10	8.05 ± 0.68
Pluronic P123	1	26	5	7.92 ± 0.32
Pluronic F127	6.21	37	20	3.59 ± 0.15
Pluronic F127	6.21	37	10	4.09 ± 0.29
Pluronic F127	6.21	37	5	3.89 ± 0.17
Pluronic P123	6.21	37	-	9.54 ± 0.07
Pluronic P123	6.21	37	20	4.42 ± 0.17
Pluronic P123	6.21	37	10	7.81 ± 0.06
Pluronic P123	6.21	37	5	8.56 ± 0.09
Pluronic L61	0.22	37	20	16.92± 0.83

Table E.2. At VCF 1.9, with permeate flux values of single surfactant system experiments conducted with 1kDa UF membranes at the existence of ethanol.

Pluronic Type	**Pluronic Concentration (wt.%)**	**Experiment Temperature (°C)**	**Ethanol Concentration (g/L)**	**Permeate Flux (L/hm^2)**
Pluronic F127	6.21	26	4.5	4.41 ± 0.14
Pluronic F127	6.21	2	2.25	4.55

Table E.3. At VCF 1.9, permeate flux values of single surfactant system experiments conducted with 1kDa UF membranes at the existence of acetone.

Pluronic Type	**Pluronic Concentration (wt.%)**	**Experiment Temperature (°C)**	**Acetone Concentration (g/L)**	**Permeate Flux (L/hm^2)**
Pluronic F127	6.21	26	4	4.14 ± 0.28
Pluronic F127	6.21	26	2	4.13 ± 0.02

Table E.4. At VCF 1.9, permeate flux values of mixed surfactant system experiments conducted with 1kDa UF membranes at 37°C with 20g/L butanol.

Co-surfactant Type	**Co-surfactant wt.%**	**Pluronic P123 wt.%**	**Permeate Flux (L/hm^2)**
Pluronic L61	0.22	6.21	2.16 ± 0.08
Pluronic L101	0.008	6.21	3.01 ± 0.15
Pluronic L101	0.08	6.21	2.96 ± 0.28
Pluronic L101	0.5	6.21	2.07 ± 0.1
Pluronic L101	1	4	2.66 ± 0.3
Pluronic L101	1	3	3.07 ± 0.81
Pluronic L101	1	1	8.94 ± 0.5

Table E.5. Permeate flux values of mixed surfactant system experiments conducted with NF90 membranes at 37°C with 20g/L butanol existence.

Co-surfactant Type	**Co-surfactant wt.%**	**Pluronic P123 wt.%**	**VCF**	**Permeate Flux (L/hm^2)**
Pluronic L101	1	1	1.9	0.85 ± 0.0001
Pluronic L101	1	3	1.9	0.60 ± 0.04
Pluronic L101	1	1	5.7	0.74 ± 0.06

Table E.6. Permeate flux values of ABE experiments conducted with NF90 membranes at 37°C with mixed surfactant system.

Co-surfactant Type	**Co-surfactant wt.%**	**Pluronic P123 wt.%**	**VCF**	**Permeate Flux (L/hm^2)**
Pluronic L101	1	1	1.9	0.76 ± 0.01
Pluronic L101	1	1	5.7	0.69 ± 0.001

Table E.7. Permeate flux values of ABE experiments conducted with 1kDa membranes at 37°C with mixed surfactant system.

Co-surfactant Type	**Co-surfactant wt.%**	**Pluronic P123 wt.%**	**VCF**	**Permeate Flux (L/hm^2)**
Pluronic L101	0.5	6.21	1.9	2.19 ± 0.08
Pluronic L101	0.5	6.21	5	0.31 ± 0.01

F. Graphs of Fouling Analysis

In addition to the obtained butanol rejection values as a result of filtrations, searching how membrane fouling was affected according to the changing parameters became another research subject within the scope of this study. Membrane properties, solution properties, and operating conditions are the factors that affect the fouling of the membrane (Abdelrasoul et al., 2013). In addition to the fouling, these factors also became critical while deciding experimental parameters and best rejection performances. Therefore, with the solutions used for rejection analysis, also fouling study was conducted. Analysis of the mixtures of 6.21wt.% Pluronic F127 and 6.21wt.% Pluronic F127 + 20, 10, 5, and 1g/L butanol solutions were the starting point of the fouling studies. As it can be seen from Figure F.1, in these experiments, with increasing butanol concentration increment in the fouling resistance was noticed. Pluronic P123 was another surfactant that was used for the filtration of solutions that were at different butanol concentrations. As a result of filtration using 6.21wt.% Pluronic P123 and 6.21wt.% Pluronic P123 + 20, 10, and 5g/L butanol solutions, the results was supported the increase in fouling due to the increase in butanol (Figure F.2.).

Any increase in the viscosity of the feed solution makes easy the membrane fouling by facilitating the adhesion of the solution to the membrane surface and makes it difficult to filter the solution (Du et al., 2020). This means is anything that causes to increase in the solution viscosity will result in a decrease in the permeate flux. As aforementioned Pluronic are the compounds which exist in the unimers form under certain temperature and concentration values.

However, when this temperature (CMT) or concentration (CMC) barrier was overcome, they form micelles. Moreover, continuation of increment at the temperature and concentration cause viscosity increases and above the CGT or the CGC values solution ends up with gel formation (Cho, 2009). The existence of the additives, such as butanol, causes a decrease in CGC and CGT values (Parekh et al., 2014; Ricardo et al., 2011).

In other words, an elevation in the butanol concentration was increased the solution viscosity. Hence, this increase in viscosity caused by butanol was made the increase in fouling resistance an expected result.

Fouling analysis at the existence of butanol and surfactant followed by the analysis of solutions which included ethanol + surfactant and acetone + surfactant. For these analyses, for ethanol and surfactant solutions, 6.21wt.% Pluronic F127 + 2.25, 4.5g/L ethanol contained solutions were prepared. On the other hand, for acetone and surfactant solutions, 6.21wt.% Pluronic F127 + 2g/L, 4g/L acetone contained solutions were prepared. On contrary to the butanol solutions, in the ethanol and acetone included solutions, no clear change in the fouling had been observed due to the ethanol or the acetone concentration change (Figure F.3. & Figure F.4.). The reason for it might be the in these low concentrations ethanol and acetone don't have any positive or negative effect on surfactants' gel formation.

In the study of Chaibundit et al., 2010, it was observed that when Pluronic F127 concentration kept constant, CGT of Pluronic F127 slightly lowered for 10wt.% and 20wt.% ethanol concentrations. On the other hand, contrary to the butanol, when ethanol concentration increased to 30wt.% at the same Pluronic F127 concentration CGT increased, and gel formation gets harder. Also, in another study of Chaibundit et al., 2008, it had been seen that adding ethanol raised the necessary minimum concentration of Pluronic P123 from 26wt.% (in the water) to 28wt.% (in the 20wt.% ethanol) for the gel formation. When these relatively high ethanol concentrations had such a small effect on gel formation, used ethanol or acetone concentrations did not affect the fouling became an expected result. Therefore, it was concluded that no change occurs in the fouling due to the change in worked ranged ethanol and acetone concentration.

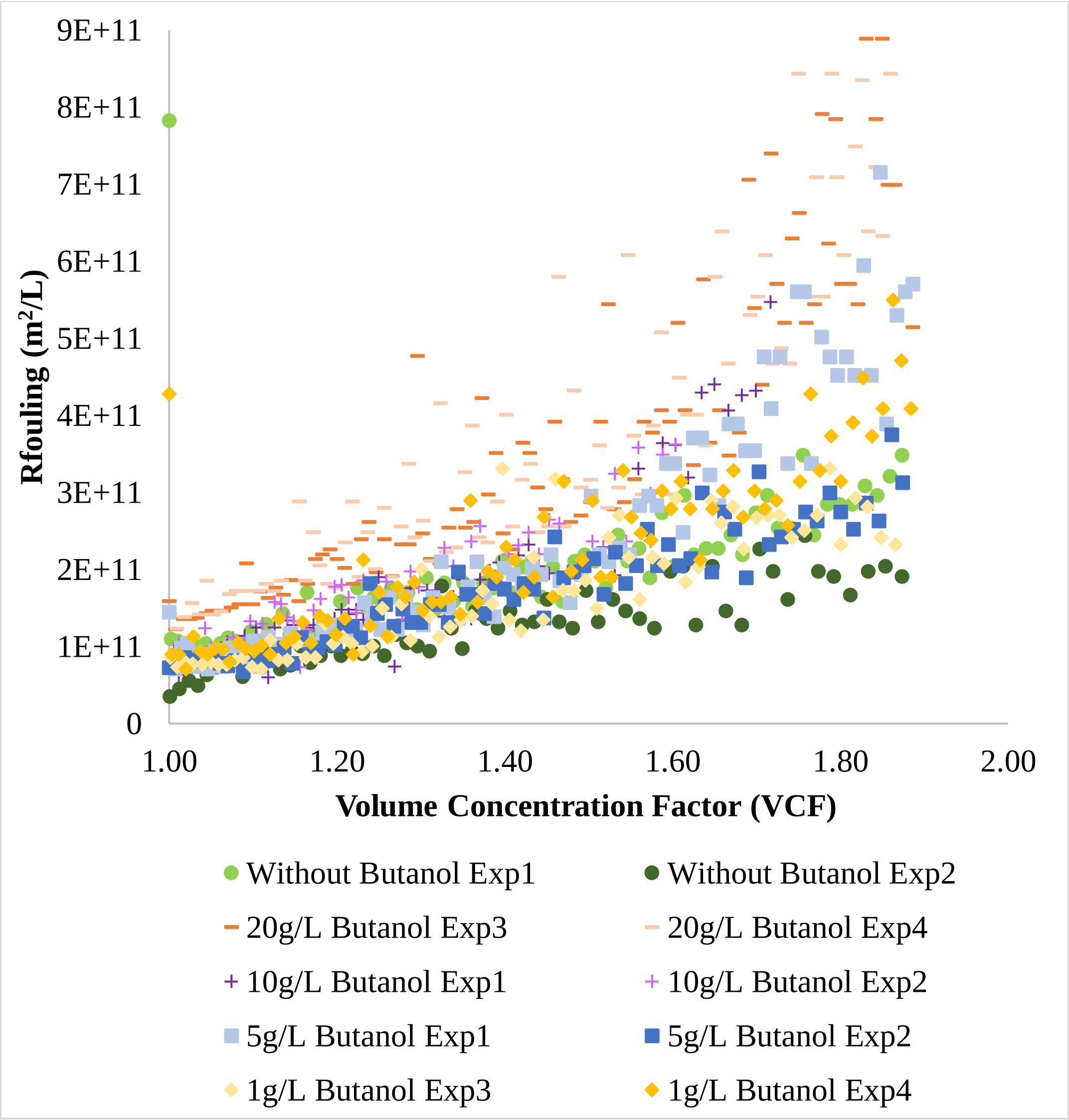

Figure F.1 Change of fouling resistance of 6.21wt.% Pluronic F127 and 6.21wt.% Pluronic F127 + 20, 10, 5, and 1g/L butanol solutions at 26°C with respect to volume concentration factor (VCF).

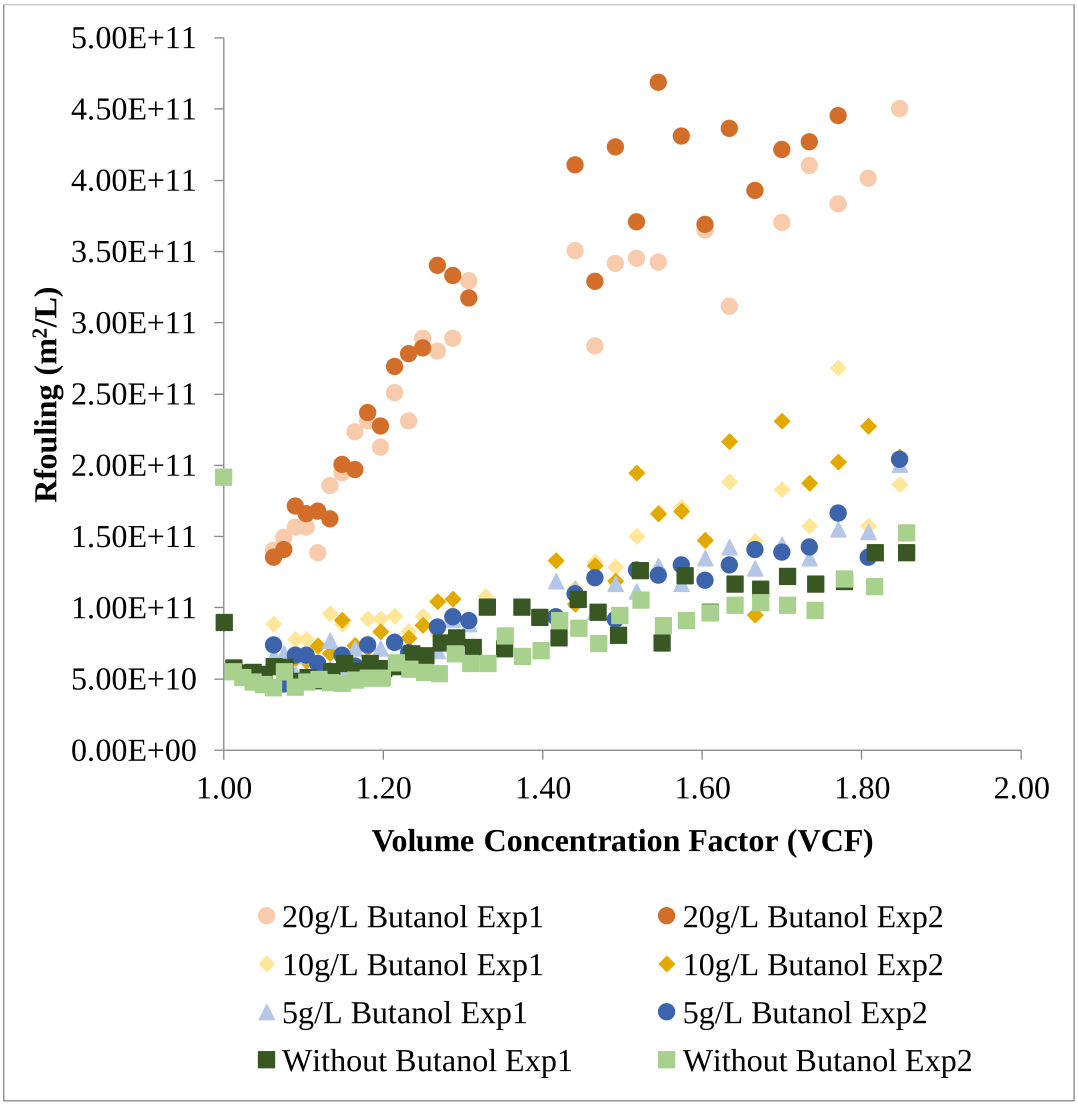

Figure F.2 Change of fouling resistance of 6.21wt.% Pluronic P123 and 6.21wt.% Pluronic P123 + 20, 10, and 5g/L butanol solutions at 37°C with respect to volume concentration factor (VCF).

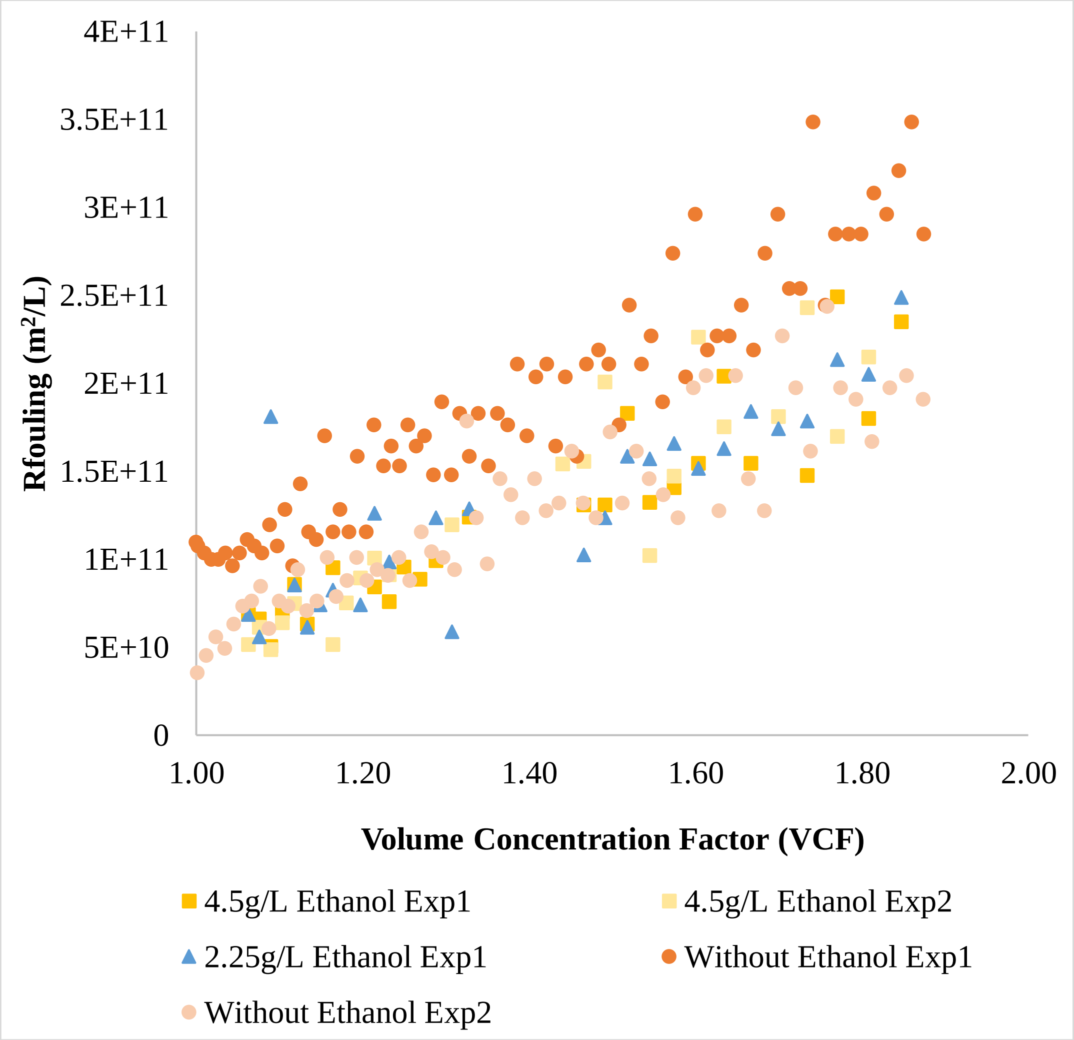

Figure F.3 Change of fouling resistance of 6.21wt.% Pluronic F127 and 6.21wt.% Pluronic F127 + 4.5 and 2.25g/L ethanol solutions at 26°C with respect to volume concentration factor (VCF).

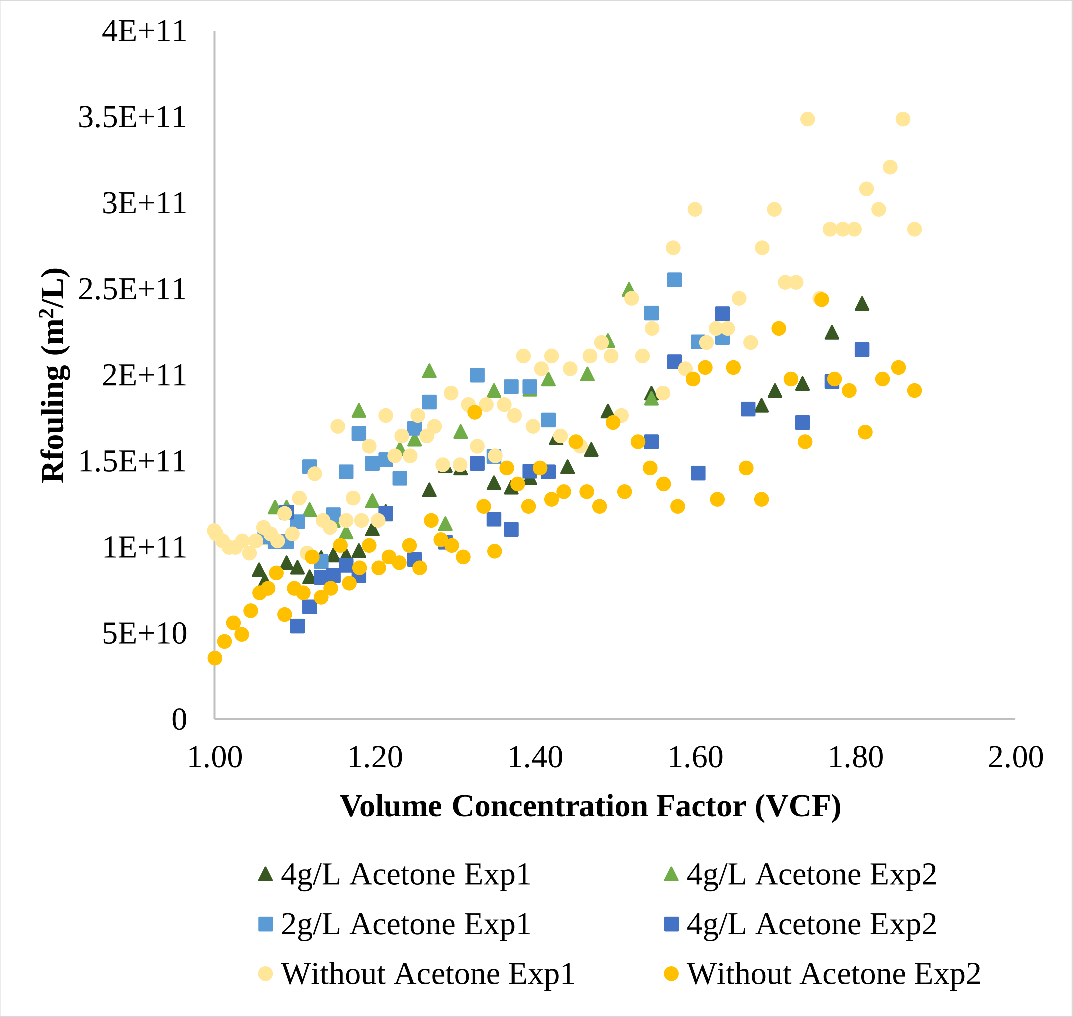

Figure F.4 Change of fouling resistance of 6.21wt.% Pluronic F127 and 6.21wt.% Pluronic F127 + 4 and 2g/L acetone solutions at 26°C with respect to volume concentration factor (VCF).

Temperature and concentration were the two of the other factors examined about the contribution to the fouling in the prepared filtration solutions. During the filtration experiments of both Pluronic F127 and Pluronic P123 solutions, due to the temperature rise, a decrease in the permeate fluxes was observed (Figure F.5.).

At the same time, due to the increase in surfactant concentration, there was an increase in fouling resistance (Figure F.6.). The main reason for this increase, due to the increase in concentration, was thought to because of the increment in the amount of foulants in the solution. On the other hand, it was known that the elevation in temperature had an effect on changing the physical state of the solution. In other words, the rise up in temperature had brought the solution one step closer to gel formation, that was, it had improved the viscosity value. This rise up in viscosity, with the elevation of temperature, had increased the fouling resistance. Both in the experiments of P123 and F127, there was an elevation in the fouling depending on the temperature. However, it was seen that while this increment was decreasing the P123 solutions flow rate up to half, not significantly lowering the flow of solutions containing F127. When the phase change and turbidity analysis of both surfactants due to temperature changes was considered, the reason for this difference had thought that solutions containing 6.21wt.% P123 + 20g/L butanol was showing gel formation at a temperature of 50°C. In the interval where the temperature elevation was observed, the viscosity suddenly raised and gel had formed. On the other hand, in solutions containing 6.21wt.% F127 + 20g/L butanol, there was no discernible increment in viscosity at temperature increases up to 80°C. This difference in the temperature values required for the gel formation of the two solutions at the same Pluronic concentration and the butanol amount had been thought to cause the difference in their reaction to the temperature.

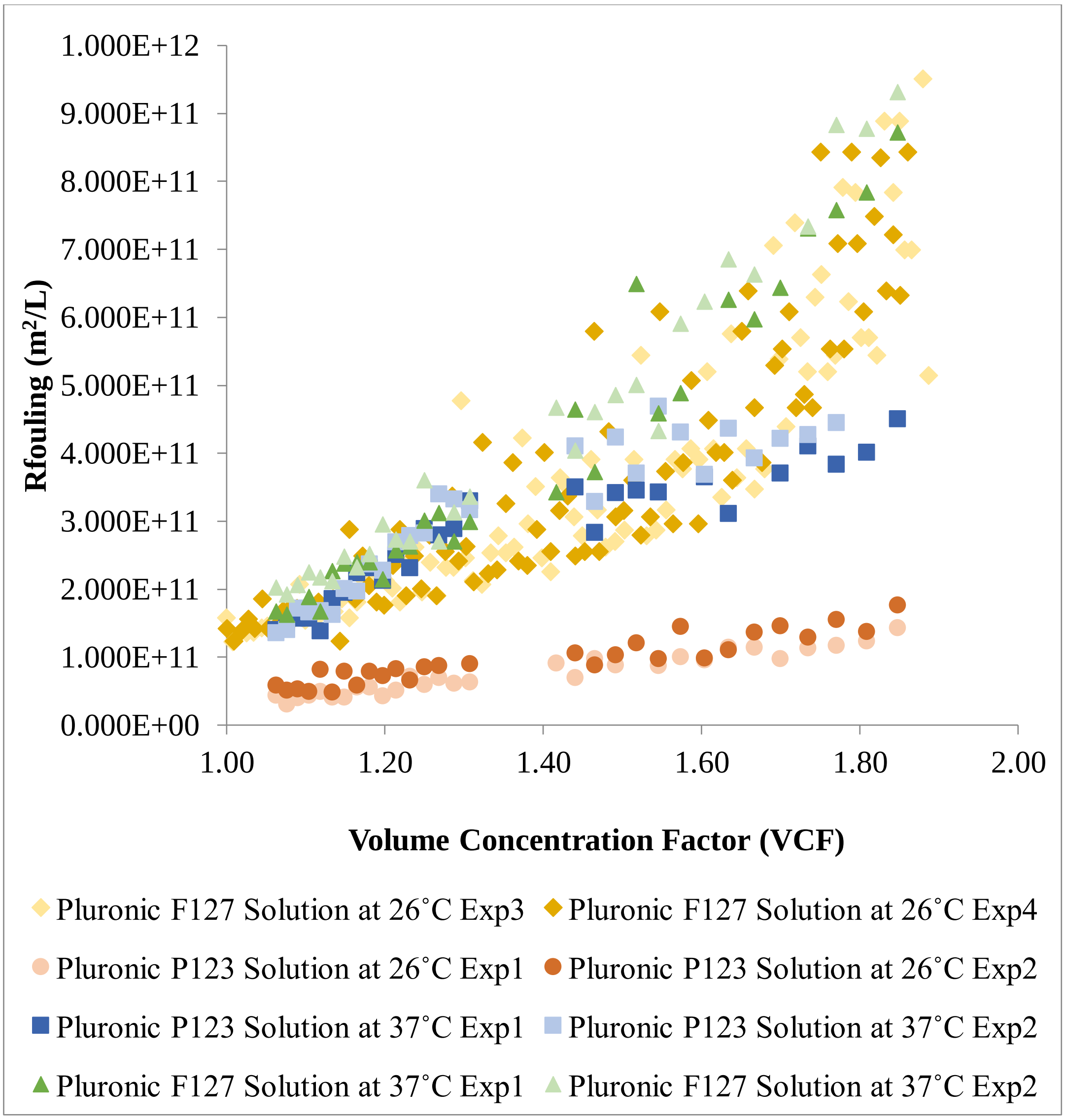

Figure F.5 Change of fouling resistance of 6.21wt.% Pluronic F127 + 20g/L butanol and 6.21wt.% Pluronic P123 + 20g/L butanol solutions with respect to volume concentration factor (VCF) at 26°C and 37°C.

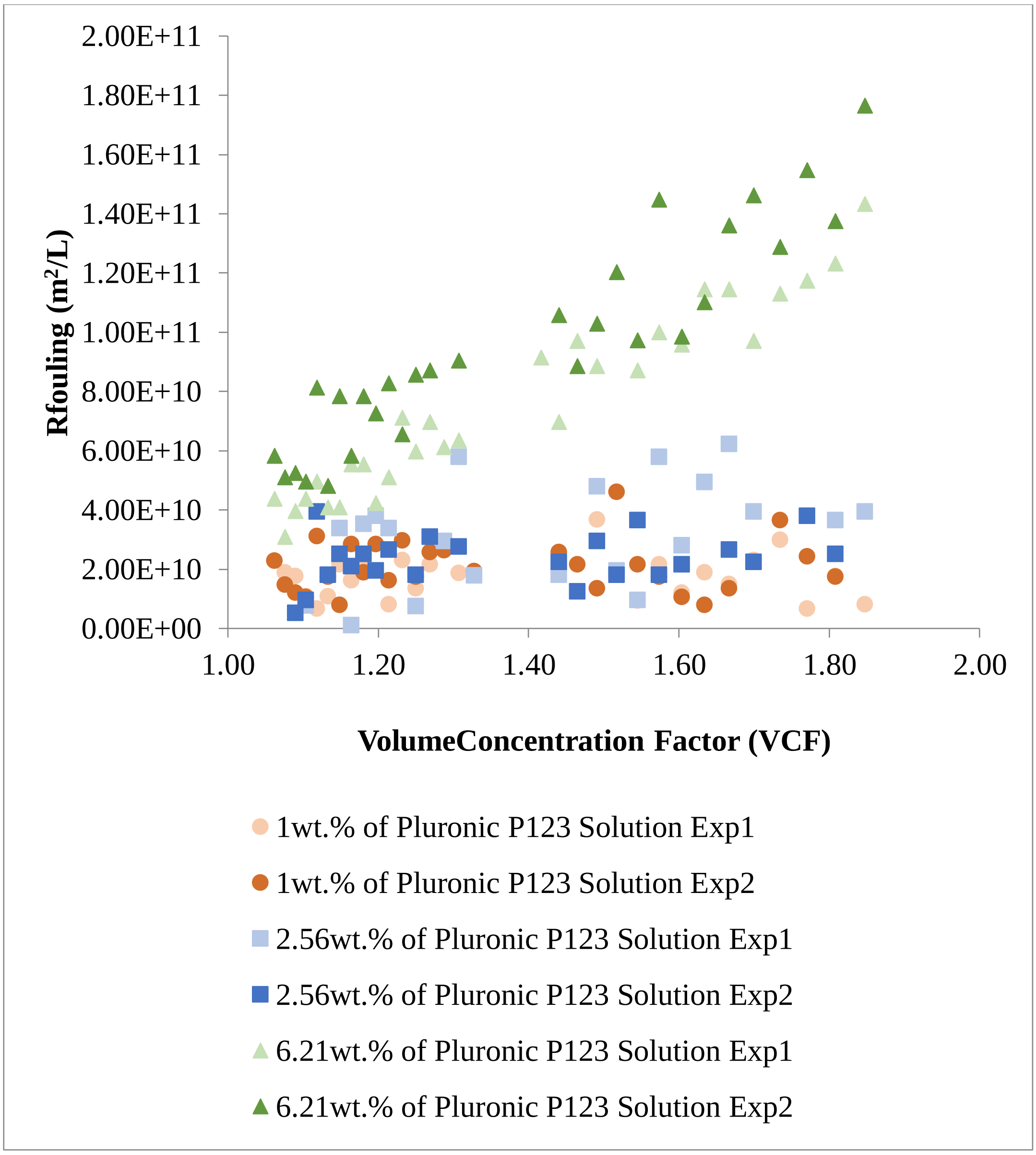

Figure F.6 Change of fouling resistance of 1, 2.56 and 6.21wt.% Pluronic P123 + 20g/L butanol solutions at 26°C with respect to volume concentration factor (VCF).

G. For ABE Filtration Raw Concentration Datas & Rejection Calculations

Similar to the other experiments in this thesis study, 1wt% Pluronic L101 + 1wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solutions filtration experiments were conducted twice, too. In these experiments, for Exp1 and Exp2 separately 12 permeate were collected. For each collected permeate sample, acetone, butanol, and ethanol concentration calculations had been done (Figure G.1., G.2., G.3.). Later, by taking the average of acetone, butanol, and ethanol concentrations for two different experiments, in the same permeate volumes, average acetone, butanol, and ethanol concentration was calculated (Figure G.4.). So that, in the end, by using two experiments' acetone, butanol, and ethanol concentration data single concentration value for each permeate volume was calculated. From these values and measured feed concentrations, the retentate concentration values, for each permeates volume, were calculated by using mass balance. Then passed to the rejection calculations.

For better understanding when permeate volumes are 10 ml acetone rejection calculations can be given as an example.

For exp1 and exp2 feed solution acetone concentration ($C_{F,acetone}$) was 5g/L. For exp1 when collected permeate volume was 10 ml, measured permeate acetone concentration ($C_{Pexp1,p1,acetone}$) was 5.09g/L. On the other hand, for exp2 when collected permeate volume was 10 ml, measured permeate acetone concentration ($C_{Pexp2,p1,acetone}$) was 4.89g/L. So that, as a result of 1wt.% Pluronic P123 + 1wt.% Pluronic L101 + 5 g/L acetone + 20 g/L butanol + 5 g/L ethanol solutions filtration when permeate volume was 10ml, average measured acetone permeate concentration ($C_{Pavg,p1,acetone}$) was

$$C_{Pavg,p1,acetone} = \frac{C_{Pexp1,p1,acetone} + C_{Pexp2,p1,acetone}}{2}$$

$$\mathrm{C_{Pavg,p1,acetone}} = \frac{5.09 + 4.89}{2} = 4.99\ \mathrm{g/L}$$

From mass balance when permeate volume was 10ml, calculated acetone retentate concentration ($\mathrm{C_{R,acetone}}$) was

$$\mathrm{C_{Pavg,p1,acetone}} \times \text{Permeate Volume} + \mathrm{C_{R,acetone}} \times \text{Retentate Volume} = \mathrm{C_{F,acetone}} \times \text{Feed Volume}$$

$$5\ \mathrm{g/L} \times 85\ \mathrm{ml} = 4.99\ \mathrm{g/L} \times 10\ \mathrm{ml} + \mathrm{C_{R,acetone}} \times 75\ \mathrm{ml}$$

$$\mathrm{C_{R,acetone}} = 5.001\ \mathrm{g/L} \cong 5\ \mathrm{g/L}$$

For rejection calculations used feed side concentration was

$$\mathrm{C_{Ravg,acetone}} = \frac{\mathrm{C_{F,acetone}} + \mathrm{C_{R,acetone}}}{2}$$

$$\mathrm{C_{Ravg,acetone}} = \frac{5 + 5}{2} = 5\ \mathrm{g/L}$$

So, when the permeate volume was 10 ml, obtained acetone rejection was

$$\mathbb{R}_i\% = \left(1 - \frac{C_{\mathrm{Pavg,p1,acetone}}}{C_{\mathrm{Ravg,acetone}}}\right) \times 100$$

$$\mathbb{R}_i\% = \left(1 - \frac{4.99\ \mathrm{g/L}}{5\ \mathrm{g/L}}\right) \times 100 = 0.2\ \%$$

Other than ABE experiments, for none of the experiments, average permeate concentration had been calculated. In other experiments, by using the permeate and the feed of the solutions, with GC analysis, butanol concentration measurements had been conducted. From measured data, by using mass balance, retentate concentrations were calculated. Then from calculated feed side concentration used for rejection calculation and permeate concentration % butanol rejection of experiments were calculated. Later on, by taking the average of % rejection values for exp1 and exp2 of the same solution %rejection and standard deviation had been calculated.

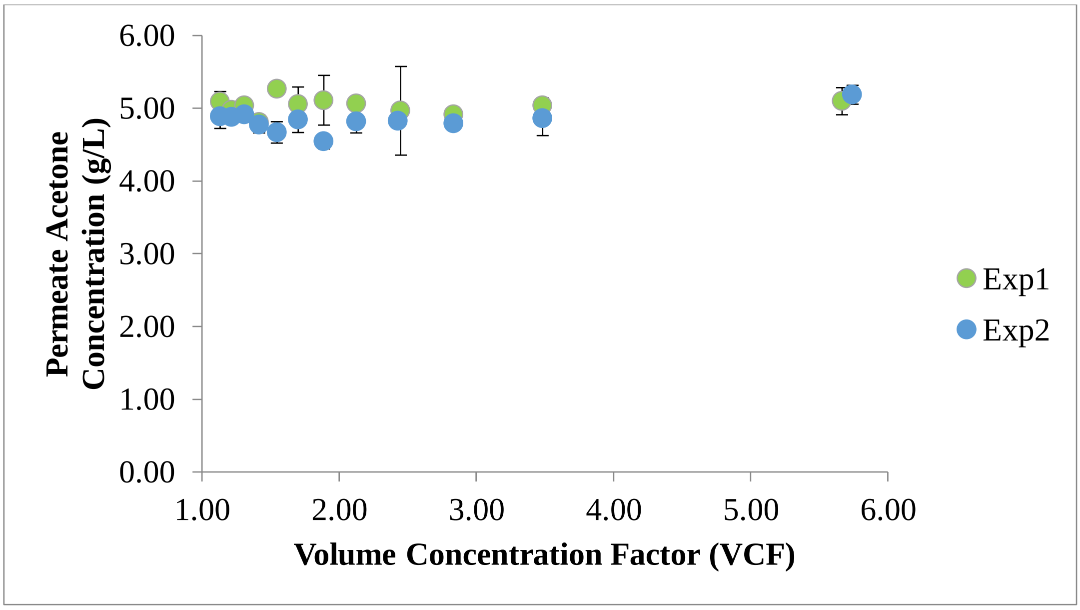

Figure G.1. Permeate acetone concentration as a result of 1wt% Pluronic L101 + 1wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with NF90 membrane.

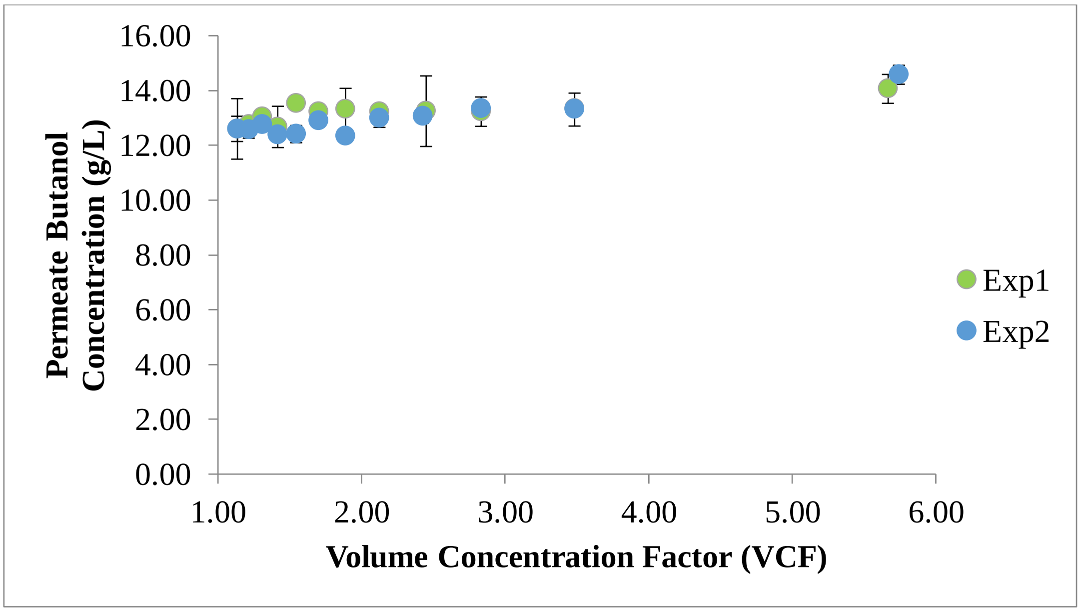

Figure G.2. Permeate butanol concentration as a result of 1wt% Pluronic L101 + 1wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with NF90 membrane.

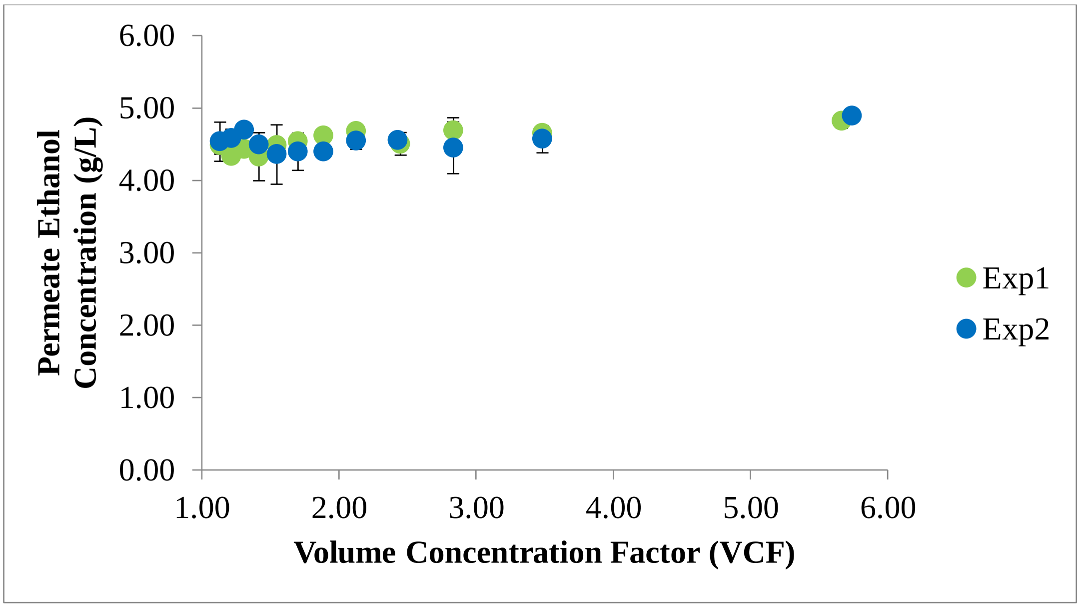

Figure G.3. Permeate ethanol concentration as a result of 1wt% Pluronic L101 + 1wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with NF90 membrane.

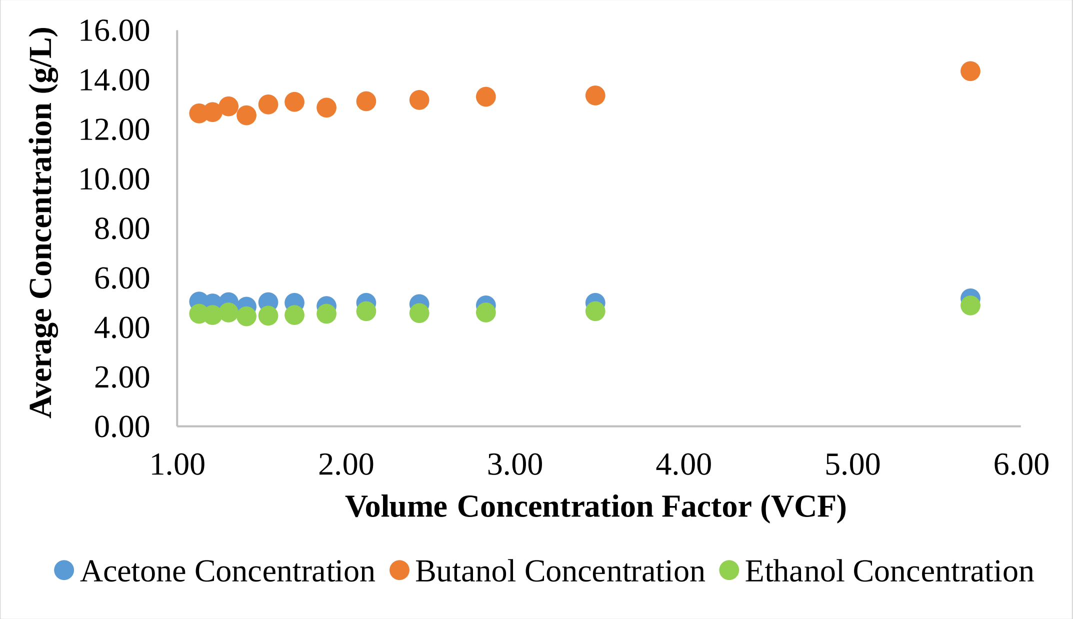

Figure G.4. 1wt% Pluronic L101 + 1wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solutions' experiments average acetone, butanol, and ethanol concentration values.

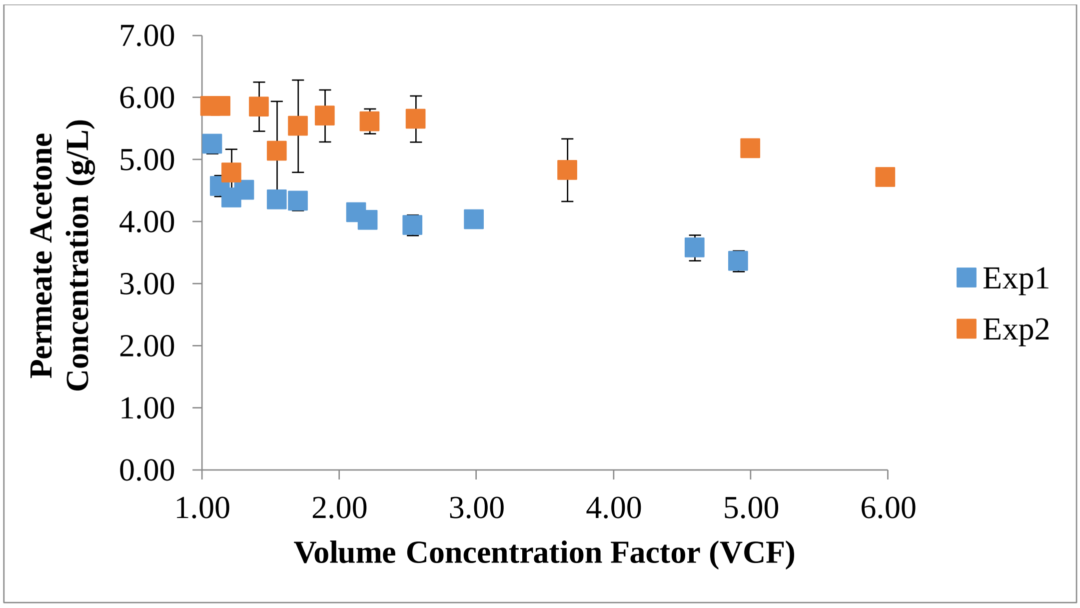

Figure G.5. Permeate acetone concentration as a result of 0.5wt% Pluronic L101 + 6.21wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with 1kDa UF membrane.

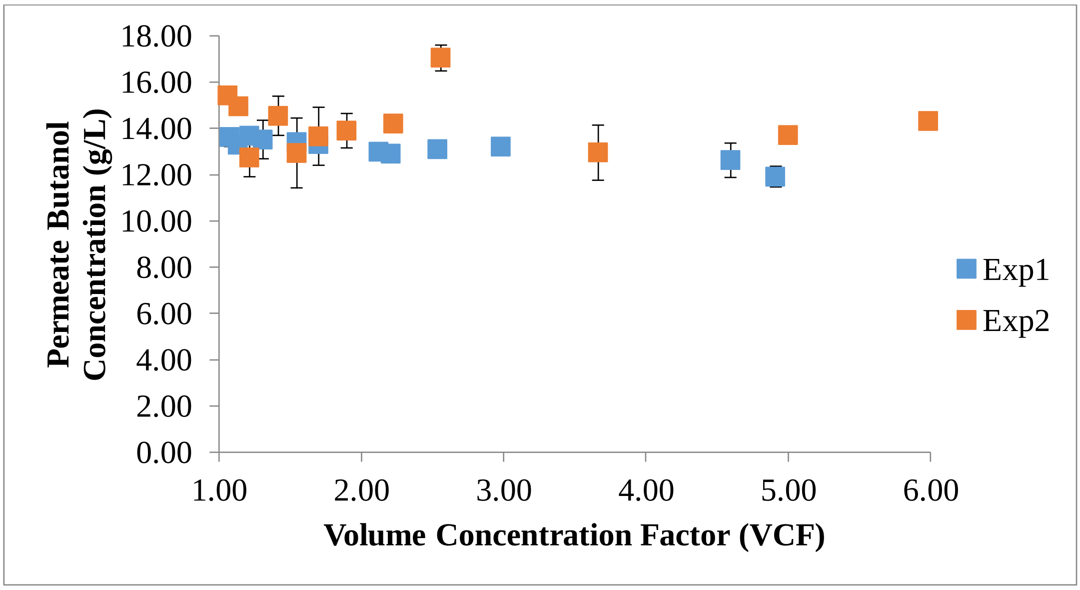

Figure G.6. Permeate butanol concentration as a result of 0.5wt% Pluronic L101 + 6.21wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with 1kDa UF membrane.

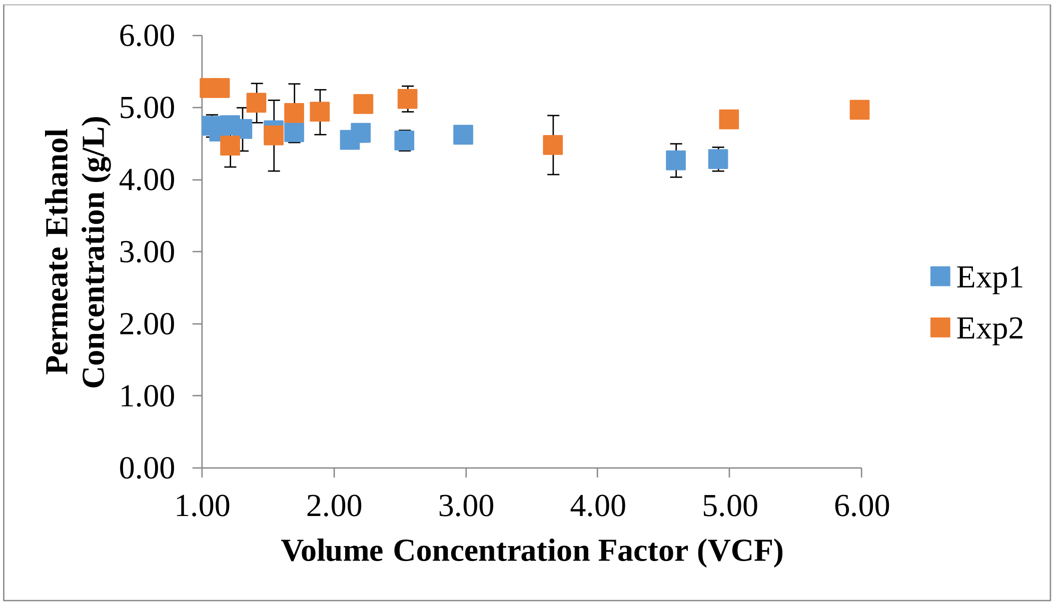

Figure G.7. Permeate ethanol concentration as a result of 0.5wt% Pluronic L101 + 6.21wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solution filtration with 1kDa UF membrane.

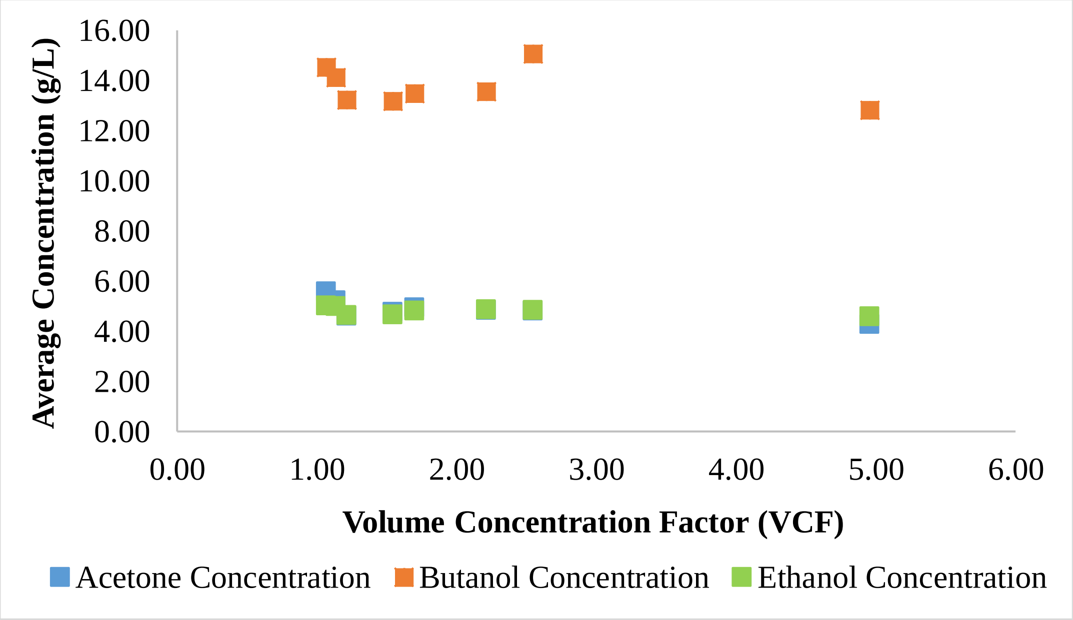

Figure G.8. 0.5wt% Pluronic L101 + 6.21wt% Pluronic P123 + 5g/L Acetone + 20g/L Butanol + 5g/L Ethanol solutions' experiments average acetone, butanol, and ethanol concentration values.