Designer solvents for the extraction of glycols and alcohols from aqueous streams

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Designer Solvents for the Extraction of Glycols and Alcohols from Aqueous Streams

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dr.ir. B. Schuur

A mi familia (con un poco de ayuda de mis amigos)

To my family (with a little help of my friends)

Content

Summary

The separation of polar compounds from aqueous streams is one of the most energy intensive operations within the chemical industry, because of the formation of hydrogen bonds that should be broken and the high heat of vaporization of water. Important bulk chemicals like glycols and alcohols produced from petrochemical feedstock or renewable sources through fermentation processes are classified in this category. In this thesis, the recovery of low molecular weight diols, such as Mono Ethylene Glycol (MEG), 1,2-Propanediol also known as propylene Glycol (PG) and 2,3-Butanediol (BD) that are particularly difficult to separate due to their high water affinity and important alcohols like 1-Butanol (BuOH) were studied. Their recovery by conventional multiple effect distillation is associated with high energy consumption; therefore liquid-liquid extraction technology can be a promising alternative since it can be more energy efficient. However, for conventional solvents the distribution coefficients are generally insufficient to achieve efficient extraction at low concentrations as encountered in the chemical synthesis of diols or production through fermentation. For this reason, the use of novel extraction solvents like reactive extractants or ionic liquids is needed to improve the glycol distribution coefficient and selectivity.

Boronic acids derivatives were studied as they are known because of their good ability to form complexes with cis-diols. Naphtalene-2-Boronic Acid (NBA) was selected as extractant and it was diluted in 1-Ethyl-Hexanol and octanol. Aliquat 336 (N-Methyl-N,N-dioctyloctan-1-ammonium chloride) was applied as counterion to facilitate the complexation between NBA and MEG. 1-Ethyl-Hexanol was the better diluent. The partition coefficient of MEG in 1-ethyl-hexanol was 0.0025, and distributions and selectivities up to 0.026 and 0.089, respectively (at pH 11, 298K) were observed with NBA and Aliquat 336 in equal amounts at 0.2 mol/L. This maximum distribution is around 10 times better than the conventional solvents. Nevertheless further improvements in the distribution and selectivity towards the glycol are required, which could be provided by

advanced solvents like ionic liquids. In Chapter 2, experimental work and molecular modelling simulation with COSMO-RS were used to support the solvent screening for (MEG). The ionic liquid design and tailoring to optimize the glycol distribution coefficient (D) and selectivity (S) was done by employing the sigma electron profile. As a result, the glycol distribution coefficients improved compare to the conventional solvents when combining a tetraoctyl ammonium cation of the IL with a carboxylate, phosphinate and boronate anion. These ILs were tailor made and evaluated in LLE experiments. They outperformed the other solvents tested with D_{MEG} up to 0.45, and S up to 3.2 vs $D_{MEG} = 0.04$ and S = 0.95 for 2-ethyl-hexanol for initial feed concentrations of 20% wt MEG.

For the best performing ionic liquid tetraoctyl ammonium 2-methyl-1-napthoate [TOA MNaph], liquid-liquid equilibrium data were determined and the NRTL and UNIQUAC thermodynamic models were constructed for the three different glycols. The results, presented in Chapter 4, show that both models can properly describe the experimental data. These thermodynamic models were used to develop conceptual process designs in Aspen Plus ® and compared the different processes for the production of MEG and PG with two different technologies, conventional triple effect distillation (MED) and solvent extraction (LLE) using [TOA MNaph].The results showed that the LLE alternative could provide energy savings >50% compared to the current state-of-the-art three effect distillation technology (94% for MEG 20% wt from the petrochemical process and 54% for PG 10%wt from a fermentation process). Regarding CAPEX, the conventional technology is always preferable because less equipment is required, while for the LLE technology the CAPEX is higher due to the solvent cost, the equipment in solvent recovery section and the additional heat exchangers required for the heat integration in the process. The purification of PG has the lowest CAPEX because a lower solvent to feed ratio is required compared to MEG extraction. According to a total annualized cost analysis at the current crude oil prices, the purification of PG from a fermentation broth via LLE could be an advantageous technology to replace MED. For the MEG production we can say that currently the LLE process is not a suitable option and that a significant increase in crude oil prices should occur before the use of LLE technology with this IL can become feasible. In Chapter 6,

liquid-liquid extraction of butanol from water, employing [TOA MNaph] was evaluated against distillation and extraction with conventional solvents. The results show that this IL yields the best distribution coefficient and very high selectivity (D_{BuOH}=21, S=274), compared to the benchmark solvent oleyl alcohol (D_{BuOH}=3.42, S=192). The conceptual design study showed that butanol extraction with [TOA MNaph] requires 73% less energy than in conventional distillation (5.65 MJ/kg BuOH vs 21.3 MJ/kg for distillation). Finally it was concluded, that the feasibility of the LLE with ILs is strongly dependent on the glycol distribution coefficient and selectivity achieved. As the conceptual process design and economic evaluation showed, there are still challenges and improvements to extend the search for additional solvents (not limited to ionic liquids), especially for extremely polar compounds like MEG, which requires an even higher capacity and selectivity than could be achieved in this study.

Chapter 1.

General Introduction:

Designer Solvents for the Extraction of Glycols and Alcohols from Aqueous Streams

1.1 Overview

The separation of polar compounds from aqueous streams is one of the most energy intensive operations in chemical industry, especially if the polar compound is in low concentration and has a higher boiling point than water. Conventional processes like distillation or multiple effect evaporation are normally used to remove the water.[1] Using these technologies implies that large amount of water must be evaporated, leading to energy intensive processes because of the high heat of vaporization of water (2260 kJ/kg at atmospheric pressure and 373.15 K) which is six times higher than most organic solvents.[2] Avoiding evaporation of water could yield large energy-savings. Therefore, process alternatives to evaporation are worth investigation.

Some examples of aqueous mixtures of polar, high boiling compounds include the recovery of low molecular weight diols, such as mono ethylene glycol (MEG), 1,2 propanediol commonly known as propylene glycol (PG), and 2,3-butanediol (2,3-BD) as well as alcohols with higher boiling points that water, e.g. butanol (BuOH), as shown in figure 1-1. These chemicals can be produced from petroleum based feed stocks, but due to the increasing scarcity of fossil fuels and the corresponding increase in petroleum prices an increased interest on their production through fermentation routes causes more scientific and business attention.[3-8] In both production routes, for different reasons, the produced glycol or alcohol, needs to be recovered from a dilute aqueous solution. The work described in this thesis focuses on alternative recovery methods using extraction. In this introductory chapter, the main uses, production processes and the most common separation technologies that have been applied for their recovery from aqueous streams are described, and an outline of the thesis is given.

MEG PG 2,3BD BuOH

Figure 1-1. Polar compounds studied in this project.

1.1.1 Mono Ethylene Glycol (MEG)

MEG is one of the most important glycols in the chemical industry. The world production was 18 Mton/y in 2008 [9], of which the largest fraction (around 42%) is used as antifreeze agent, the second main application was as polymer precursor (around 35%) and a third important application of MEG is as preservative in cosmetic industry [10]. The main production route of MEG is by non-catalytic neutral hydrolysis (pH 6-10) of ethylene oxide, typically carried out in a tubular reactor at high temperatures and pressures (463.2-473.2 K and 20-30 bar). A large excess of water is applied (molar ratio 1:22) in order to avoid byproduct formation (e.g. diethylene glycol (DEG), triethylene glycol (TEG) and higher oligomers) As a result, the reactor effluent contains only 20 %wt MEG and 1% of byproducts, and as much as 79 wt% water. Consequently, large amounts of water need to be removed afterwards, this is conventionally done via multi effect distillation.[11]

1.1.2 Propylene Glycol (PG)

Propylene glycol (PG) is an important and safe glycol for uses in the food and cosmetics industries, it is also used in the chemical and in the pharmaceutical industries. The variety of its applications include as direct food additive, emulsifier and humectant agent in personal care products, and as carrier for active substance in pharmaceuticals. [12] It is also deployed as anti-freeze, industrial coolant, and as plasticizer. [13] There are two main routes for the production of PG. The first one is the petrochemical route, through a non-catalytic hydrolysis reaction of propylene oxide. This reaction is carried out at high temperature (between 393.2 – 453.2 K) and elevated pressure (around 21 atm) using an excess of water (12–20 mol water/mol propylene oxide) to maximize the conversion into propylene glycol [14]. The reactor effluent is an aqueous solution containing around 15 % wt of PG. The second route is the microbial production of PG through direct fermentation of renewable sugars using *clostridium thermosaccharolyticum* [15]. The limitation regarding the microbiological process is the low yield, therefore the concentration of PG in the fermentation broth is only around 1-10 % wt [16]. For both production routes the final product is a diluted aqueous PG solution with only 1 to 15% wt of PG, which makes the recovery of PG through thermal separation an energy intensive separation process, as water is the low boiling compound in the mixture, and large amounts of water need to be removed (around 90% wt). Two different isomers of propylene glycol can be produced: 1,2 -propanediol and 1,3-propanediol, in this thesis only the first isomer was studied.

1.1.3 2,3-Butanediol (2,3-BD)

The chemical structure of 2,3-BD makes this compound very suitable as intermediate in the production of a wide range of basic chemicals. For instance in the production of methyl ethyl ketone (MEK), an industrial solvent that can be used as fuel additive and is obtained through a dehydration reaction [17]. The ketalization of 2,3-BD with acetone produces a compound (acetone 2,3-butanediol ketal) with a high octane number that can be used as an octane booster for gasoline [18, 19]. The dehydrogenation of 2,3-butanediol leads to the formation of acetoin (acetyl methyl carbinol) and diacetyl (2,3-butanedione) food additives that are used as an aroma carrier and as flavoring compound for dairy products [19, 20]. In addition, by esterification of 2,3-BD, plasticizers and polymers can be made, [18] as well as precursors for drugs and cosmetics [21]. The microbiological route for the production of 2,3-BD is through direct fermentation of renewable substrates like wood hydrolyzates, wheat, corn and pure sugars [15, 18]. Several microorganisms are known for the conversion of sugars into 2,3-BD, the most common are *Klebsiella, Enterobacter* and *Serratia* [15]. A typical limitation in fermentation processes is the low concentration, limited to 5 - 10 %wt.

1.1.4 Butanol (BuOH)

Important alcohols like ethanol and butanol are fuels that can be produced from biomass, e.g. through fermentation of corn or lignocellulose,[22, 23] providing sustainable alternative to fossil fuel and fossil oil based chemicals.

Although ethanol is currently the most used biofuel, butanol properties like the higher energy density, the lower vapor pressure and lower flammability are leading to a growing interest in butanol over ethanol.[24] Butanol is produced from biomass via batch or pseudo-continuous fermentation processes. The traditional process for butanol production is the Acetone–Butanol–Ethanol (ABE) fermentation.[25] In this process acetone, ethanol, butanol and some carboxylic acids like acetic acid and butyric acid are produced. Of these products, butanol is the main inhibitory metabolite, concentrations higher than 1.5% wt can retard and even stop the growth of the microorganisms and therefore the process.[26] Purification of butanol is difficult, because of its high boiling point (390.2 K) and very low concentration (0.5 to 2.0 wt %) in the aqueous product streams.[25] As in the other cases desctribed above, distillation is the conventional process for butanol purification. Even though it is not necessary to evaporate all the water, due to the presence of the butanol-water heterogeneous azeotrope that induces the formation of two liquid phases, and allows a significant concentration of butanol (from around 7 %wt butanol in water to 20.1 wt% water in butanol by decantation)[24], the process is still very energy intensive and requires two distillation columns.

1.2 Alternative Separation Technologies

The difficulties in developing an efficient separation process for the compounds studied in this thesis are associated with the high affinity of the target products to water, the rather low concentrations and the high boiling points, making the recovery of these compounds challenging. Next to the already mentioned technology of distillation (the conventional process) [18], several technologies have been studied, e.g. membrane technology [27], solvent extraction [7, 28-30] and chemical conversion via acetalization [27] during the last years. However, so far the efficiency of these processes regarding purity of the product and energy consumption is still a barrier for the process scale-up. In Table 1-1, the advantages and disadvantages of the common industrial technologies for the purification of glycol and alcohols are presented.

Table 1-1. Technologies for the recovery of polar compound from aqueous streams.

Technology	Advantages	Disadvantages
Evaporation / Distillation	Mature and reliable technology to produce very pure product. Efficient to remove dilute concentrations of components with different relative volatilities.[1]	These technologies demand large amounts of energy, and even more if the lower boiling compound is in large quantity and has a high heat of vaporization.[31]
Reactive Extraction (RE)	Is an option for systems where the solute is in low concentration and it is able to react or form a complex with the extractant.[32]	The process complexity increases because the forward extraction and the back extraction need to be studied in detail to verify that the recovery of the desired product is feasible.[32]
Liquid Extraction (LLE)	Allowing very high separation factors while operating at high volumetric throughput rates.[1] Selectivities may be increased by applying reactive extraction (RE). [32]	No effective extractant has been found so far for the extraction of glycols from water.Major limitation is the hidrophilicity of these compounds. The solvent regeneration can be energy demanding.[33]
Adsorption	Specific interaction between the solute functional groups and the surface of the sorbent allow high selectivities. Adsorption area and rate can increase due to the high internal surface of the sorbents.[34]	Saturate sorbent agent must be regenerated or replaced, thus fully continuous process is not possible. Sorbents regeneration increases the energy consumption in the process. [33, 34]
Membranes	Separation of trace compounds and production of highly pure components.This technology can be used as hybrid separation systems offering interesting economics in combination with highly pure products.[35]	Most polymeric membranes have swelling problems at high water concentration. Cost can increase proportional to feed stream due to the large membrane area that is needed.[36]

Liquid-liquid extraction can be a promising technology if a highly selective solvent is used, because much less water needs to be evaporated during the recovery of the polar solute from the solvent. The possible reduction in water evaporation means a high potential to save energy [37]. However to develop a LLE process that is economically attractive, the first important step is to develop a proper solvent with a high distribution coefficient and selectivity towards the polar solute. These solvent properties are calculated with equations 1.1-3:

$$D_{MEG} = \frac{x_{solute}^{I}}{x_{solute}^{II}} \tag{1.1}$$

$$D_{H2O} = \frac{x_{H2O}^{I}}{x_{H2O}^{II}} \tag{1.2}$$

The distribution coefficients of the polar solute and water are defined as the ratio of the weight fractions of a component in the organic extract phase (*I*), and in the raffinate phase (*II*) at equilibrium. The selectivity is calculated from the ratio of the distribution coefficients (Eq. 1.3).

$$S = \frac{x_{solute}^{I} / x_{solute}^{II}}{x_{H2O}^{I} / x_{H2O}^{I}} \tag{1.3}$$

1.3 Designer Solvents-Ionic Liquids

In the search for a proper solvent, a wide range of conventional extractants for recovery of glycols and alcohols have been studied (octanol, oleyl alcohol, 2-ethyl-hexanol, boronic acid derivatives). [38, 39] In addition, ionic liquids (ILs) were identified as potential solvents for the recovery of glycols and alcohols. Ionic liquids are a particular class of solvents that have been widely studied in the last years. These compounds are salts with melting points below 373 K, and very low to negligible vapor pressure [40, 41]. Because the ILs are generally composed from an organic cation and an organic/inorganic anion, modifications in their ion structures allow for tailoring physico-chemical properties of ILs to meet the requirements for a specific task or application [42]. ILs have been reported as good solvents in several separation technologies, including reactive extraction [43, 44] extractive distillation [45, 46] and liquid-liquid extraction [47-49]. Several applications are already running on pilot plant scale and industrial scale, like the acid scavenging process (BASIL, BASF). ILs were also tested in on a pilot plant scale for extractive distillation, BASF runs this process for the separation of water/ethanol separation. [50]

In the case of extraction processes, commercially available ILs have been used in the separation of aromatic and aliphatic compounds [51-53], and for the extraction of polar compounds from aqueous streams, including alcohols (butanol) and organic acids. [24, 38, 39, 48, 54, 55]. Nevertheless, these ILs presented either a high distribution coefficient with a low selectivity or vice versa. In LLE, a suitable solvent requires both a high selectivity and a high distribution coefficient to reduce energy consumption and capital investment. The most commonly reported anions and cations for commercial available ILs are shown in figure 1-1.

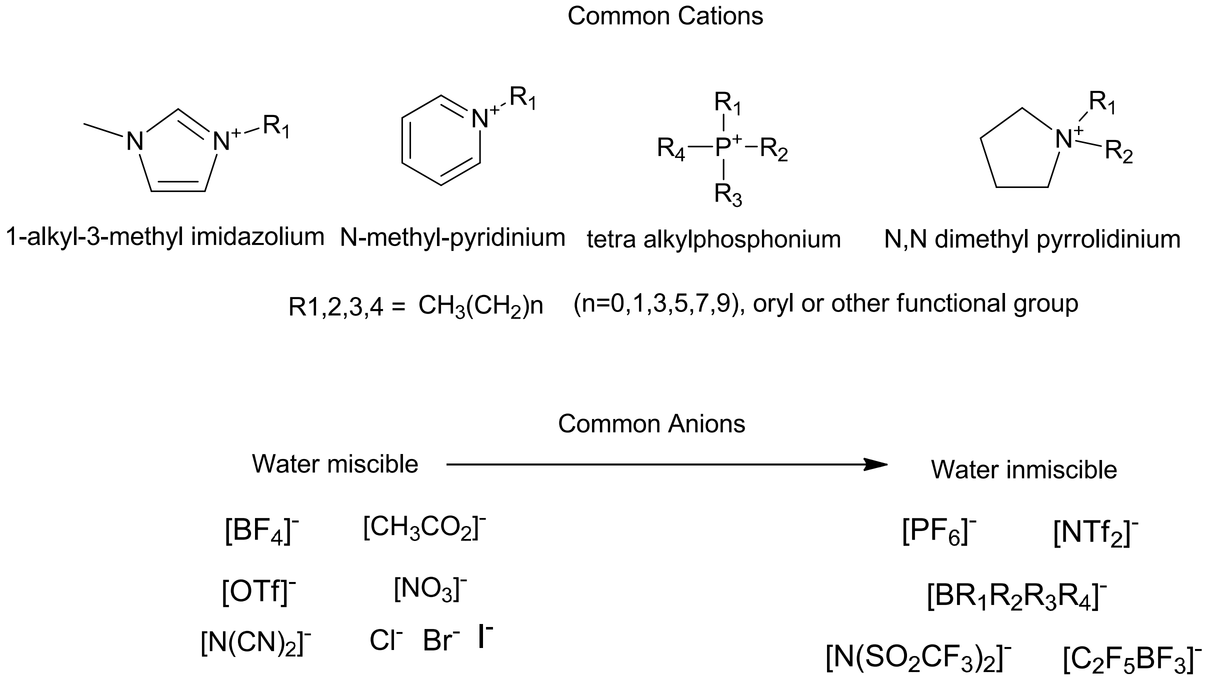

Figure 1-2. Commonly reported cations and anion for ionic liquid synthesis.[45]

1.4 Scope and Outline of this Thesis

The aim of this thesis was to investigate if LLE with task specific solvents (e.g. ILs) can be used to recover polar solutes from aqueous streams and whether the solvent extraction process is beneficial in terms of operational and capital cost compared to the conventional process. A primary focus was put on the recovery of MEG, which is a very hydrophilic compound due to its small alkyl chain and the presence of two hydroxyl groups. These characteristics make the separation of MEG from water specifically difficult, therefore if a solvent is designed with a high capability to extract MEG from aqueous streams, that solvent could also have the potential to recover other polar compounds. For this reason, in this thesis, studies on the recovery of PG, 2,3-BD and BuOH are also described. In Chapter 2, the reactive extraction of MEG with boronic acid derivatives is described. Studies on liquid-liquid extraction of MEG with ionic liquids as solvents are described in chapters 3 and 4. In chapter 3, by means of molecular modeling with COSMO-RS (Conductor like Screening Model for Realistic Solvents) and in combination with experimental work, a new hydrophobic ionic liquid, tetraoctyl ammonium 2-methy-1-naphtoate [TOA MNaph], was developed as a very promising solvent for MEG extraction [38]. The structure of this IL is shown in figure 1-2.

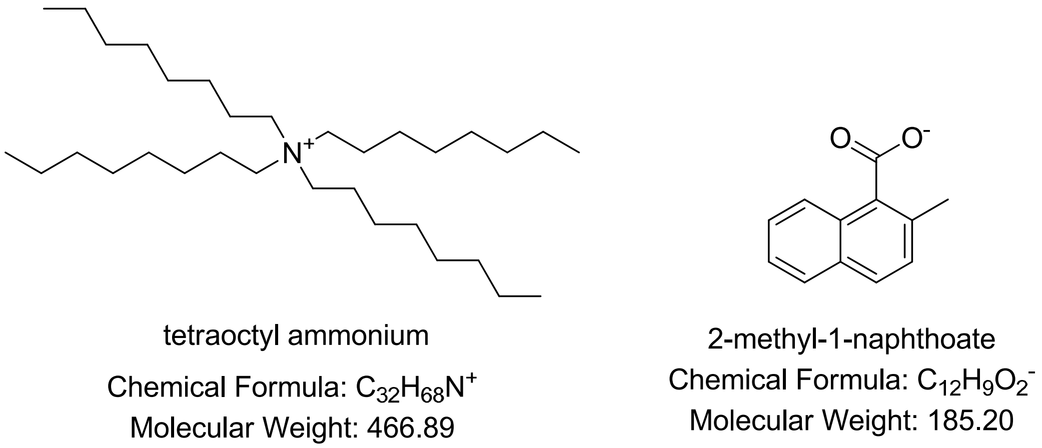

Figure 1-3. Chemical structure of tetraoctylammonium 2-methy-1-naphtoate [TOA MNaph].

Because of the promising results obtained with [TOA MNaph] for the recovery of MEG, the recovery PG and higher glycols (i.e. propylene glycol and butanediol) were studied in more detail [38, 56-58]. In Chapter 4, the experimental result of liquid-liquid equilibrium data at different temperatures and concentration of glycol-water-IL are presented, and the experimental data was correlated to the NRTL and UNIQUAC thermodynamic models, which are required to simulate the LLE process. In chapter 5, the conceptual processes design for the conventional multiple effect evaporation and the liquid-liquid extraction of MEG and PG from both petrochemical and microbiological feedstock using [TOA MNaph] are presented, this study includes the estimation of the energy demand, the capital costs and the total annualized cost at different oil fuel prices for both processes. The results on the recovery of butanol, experimental work and conceptual process design are discussed in Chapter 6 [59] and in Chapter 7, the conclusions of this research as well as some recommendations are presented.

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Chapter 2.

Glycols Recovery Using Reactive Extraction with Boronic Acid Derivatives[1]

[1]the content of this chapter was previously published as:
L.Y. Garcia-Chavez. E. Alonso, B. Schuur, A. B. de Haan (**2011**) Glycols recovery using reactive extraction with boronic acid derivatives, *Proceedings of the International Solvent Extraction Conference ISEC 2011, Santiago de Chile, Chile,* Article 194

Abstract

The recovery of important polar, high boiling bulk chemicals like mono ethylene glycol (MEG) from diluted aqueous streams using liquid extraction with conventional solvents is hindered by the low distributions of the polar compounds. In order to develop liquid extraction processes that can compete on energy consumption with the traditional thermal separation processes, novel extractants are needed that improve the distribution coefficients of the solutes. Boronic acids are known because of their good ability to form complexes with cis-diols. In this chapter, a study is presented on the use of Naphtalene-2-Boronic Acid (NBA) diluted in 1-Ethyl-Hexanol and octanol to extract MEG. Aliquat 336 (trialkylmethyl ammonium) was applied as counterion to facilitate the complexation between NBA and MEG. 1-Ethyl-Hexanol was the better diluen t. The partition coefficient of MEG in 1-ethyl-hexanol was 0.0025, and distributions up to 0.026 (at pH 11, 298K) were observed with NBA and Aliquat 336 in equal amounts at 0.2 mol/L. This maximum distribution is around 10 times better than the conventional solvents.

2.1 Introduction

Many important bulk chemicals like alcohols, glycols and organic acids are produced from fossil fuels. However they can also be manufactured from biomass through fermentation, promoting an environmentally much more sustainable production route. The main challenge for this type of production is to find an economic recovery process for these chemicals. Recovery is energy demanding, mainly due to their high boiling point, strong affinity to water and their presence at low concentrations (typically 0.5 to 5 % wt) in aqueous streams [1]. Mono Ethylene Glycol (MEG) is an important bulk chemical and one of the most important glycols in the chemical industry with the largest production volume. MEG purification is classified as an energy intensive process, since large amounts of water are removed using multiple effect evaporation. Extractive recovery strategies may save energy by avoiding the evaporation of water.

Reactive Extraction is an alternative to recover polar compounds from aqueous streams. Because of the reactive extractant in the solvent, the affinity for the solute can be much higher than in non-reactive LLE technology with conventional solvents, where the feasibility is limited by the poor affinity of the solvent for the solute [3]. In reactive extraction, the distribution of the solute over the solvents is improved by the higher affinity of the extracting agents for the solute. The extractant forms a complex with the solute, and this complexation is sometimes facilitated by a co-extractant [2].Boronic acids can reversibly form a complex with diols and are therefore good extractants for the extraction of sugars (fructose-glucose) from aqueous fermentation broths [4]. King and co-workers have also studied the recovery of several polar compounds like: glycerol, sorbitol, and 1,2-propanediol from dilute aqueous solutions using phenylboronic acid (PBA)[3,4]. However, one of the main drawbacks they found is that the borate is unstable in triagona form, mainly because it can easily be hydrolyzed in water, decreasing the capacity of the solvent and contaminating the raffinate due to leaching [4,5]. At a pH around 9 the borate becomes a stable tetrahedral anion with the ability to form a complex with the solute. To promote the solubility of the complex in the organic phase, a lipophilic counterion like Aliquat 336 a quaternary ammonium salt (N-Methyl-N,N-dioctyloctan-1-ammonium chloride) is required [6]. The mechanism of complex formation is shown in Figure 1.

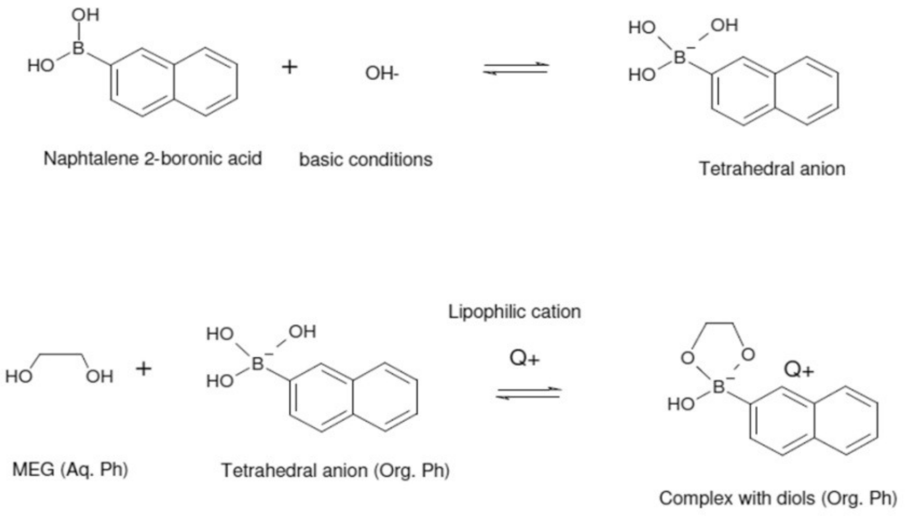

Figure 1. Complex Formation between boronate and MEG

Figure 2-1. Complex Formation between the boronate and MEG

One attempt to improve the use of boronic acids as extractants was done by Vente, who reported the use of highly lipophilic boronic acids, like hexadecyl boronic acid (HBA) to enhance the extraction of sugars like catechol, fructuose and glucose [7]. Vente showed that a high distribution ratios for extracted sugars can be reached with the use of lipohilic boronic acids, while extractant leaching was reduced. Another lipophilic boronic acid, naphthalene-2-boronic acid (NBA) was reported by Aziz and coworkers for extraction of xylose and glucose from aqueous solutions [6]. NBA was investigated with different organic solvents, showing that extraction of xylose and glucose can be up to 92% in a single stage, pH 11 and room temperature. Based on the results of Vente and Aziz and co-workers, it was decided to evaluate the highly lipophilic boronic acid NBA as extractant for the recovery of very hydrophilic compounds like MEG from aqueous streams using a reactive extraction process.

2.2 Experimental Section

2.2.1 Materials

MEG (purity ≥99 %) was obtained from VWR, diethylene glycol (purity ≥99 %), 2-ethylhexanol (purity ≥99 %), 1-octanol (purity ≥99 %), sodium bicarbonate (NaHCO2) (purity ≥99.7 %), and anhydrous sodium carbonate (Na2CO3) (purity ≥99 %) were supplied by Merck. Naphtalene-2-boronic acid (purity ≥95 %) and Aliquat 336 were supplied by Aldrich. All chemicals were used without further purification.

2.2.2 Experimental procedure

Aqueous solutions were prepared by dissolving MEG in distilled water (0.1 M). The pH of the solutions was adjusted using a NaHCO2-Na2CO3 buffer. Non-buffered aqueous MEG solutions attain a pH of 6. Solutions of NBA (extractant) and Aliquat 336 (coextractant) in 2-ethylhexanol were prepared by shaking the solutions for 24 hrs at 298.15 K. Extraction experiments were carried out by combining 10 mL of the aqueous feed phase with 10 mL of the organic extract phase in a glass cell equipped with a mantle. The temperature was controlled at 298.15 K using a water bath (Julabo F-25-MW). The system was stirred (500 - 600 rpm) for 20 hours. Afterwards the phases were allowed to settle for 2 hours. Samples from each phase were taken and analyzed. All experiments were done in duplicate.

2.2.3 Analytical methods

The MEG concentration in the aqueous phase was determined by gas chromatography using a Varian CP3800 GC apparatus equipped with a flame ionization detector (GC-FID). A Supelco fused silica capillary column with 15 m of length and 0.53 μm of diameter was used. The oven was kept isothermally at 383.15 K for 4 minutes. The injector and detector temperatures were fixed at 523.15 K. The GC response was calibrated for this particular column and conditions with known compositions of MEG-water mixtures and using diethylene glycol as internal standard. The water content in the organic phases was determined by volumetric Karl Fisher titration using a Metrohm 795 KF. The concentration of MEG in the organic phase was determined by mass balance. Repeated injections of samples of known concentration indicated a measurement accuracy of ±0.0002 and ±0.0001 mass fraction for GC and Karl Fisher respectively.

2.3 Results and Discussion

The extraction of MEG from the aqueous feed to the organic extract phase can be attributed to both physical distribution between the two phases and chemical complexation of MEG with the extractant in the organic phase. Solvent extraction equilibria are generally reported in terms of the distribution ratio D_{MEG} that is defined as concentration of MEG in organic ($X^{I}_{MEG,tot}$) and aqueous phases (X^{II}_{MEG}) in mass fraction [9,10].

$$D_{MEG} = \frac{\chi^{I}_{MEG,tot}}{\chi^{II}_{MEG}} \qquad (2.1)$$

The superscript tot in equation 2.1 is added to indicate that both physically dissolved MEG in the organic phase and MEG chemically complexed to boronic acid is taken into account. In cases where the extractant concentration is zero, the extraction process is a physical (solvent) extraction, and the D_{MEG} equals the physical partitioning. The partition coefficient m is defined as the distribution ratio in absence of extractant.

$$D_{MEG,phys} = m = \frac{\chi^{I}_{MEG}}{\chi^{II}_{MEG}} \qquad (2.2)$$

2.3.1 Solvent selection

The solvent has to be hydrophobic, able to dissolve lipophilic extractants, but it also has to show some affinity to MEG. Two fatty alcohols, octanol and 2-ethylhexanol, were selected based on the mentioned requirements. In order to evaluate the effect of physical extraction, the partition coefficient of both solvents was determined in absence of the extractant. 2-Ethylhexanol performed slightly better than 1-octanol, with a partition coefficient of m = 0.0025 compared to m = 0.0015 for octanol. The results agree with previous work, which reports that branched alcohols are favored over linear ones for extractions of glycerol and 1,2-propanediol with boronic acid carriers [4]. Based on this, further experiments were performed with 2-ethylhexanol.

2.3.2 Influence of extractant and coextractant concentration

In order to study the effect of the extractant and coextractant concentration ratio in the solvent, different experiments were carried out at a constant concentration of NBA 0.1M and different concentrations of Aliquat 336 ranging from 0.05 to 0.4 M. The experiments were done at pH 9 because it was known from previous work that the formation of a stable tetrahedral complex occurs at this pH [7,4]. The results are presented in figure 2, where it is visible that the addition of NBA increases the distribution ratio D_{MEG} up to a maximum value of 0.009 when NBA and Aliquat 336 concentrations are equimolar. In contrast, when the concentration of Aliquat 366 is higher than the concentration of NBA the trend changes and D_{MEG} starts to decrease reaching a value close to the value of m when the concentration of Aliquat 366 is four times higher than NBA. Therefore it can also be concluded that the excess of Aliquat 336 can reduce the D_{MEG}. This behaviour can be mainly due to fact that the coextraction of water increases with Aliquat 336 concentration according to Karl Fisher measurements.

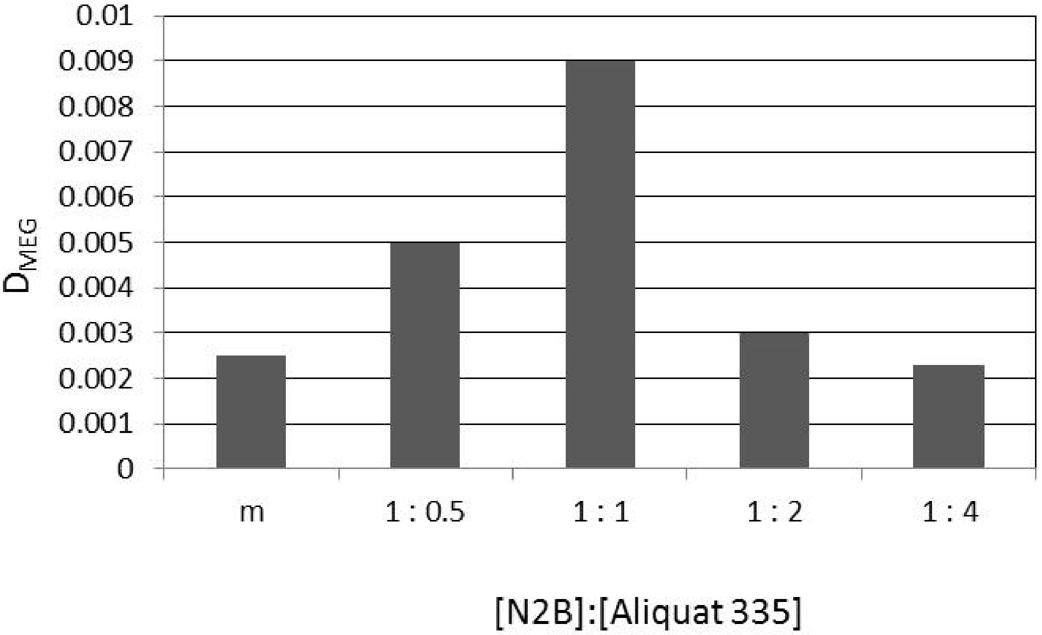

Figure 2-2. Distribution coefficient of MEG at a constant NBA concentration of 0.1M and different NBA:Aliquat 336 concentration ratios, pH 9, volume ratio 1/1, 298.15 K, 2-ethylhexanol. P represents the physical partitioning in absence of NBA and Aliquat 336

The effect of an increasing equimolar NBA and Aliquat 336 concentration was studied (Figure 3). Three different concentrations of NBA and Aliquat 336 were evaluated, being 0.1, 0.2 and 0.3 M. The MEG extraction improves when the concentration of NBA increases, but it is also visible that the increase is negligible above 0.2M, therefore experiments on the effect of the pH were done with 0.2 M.

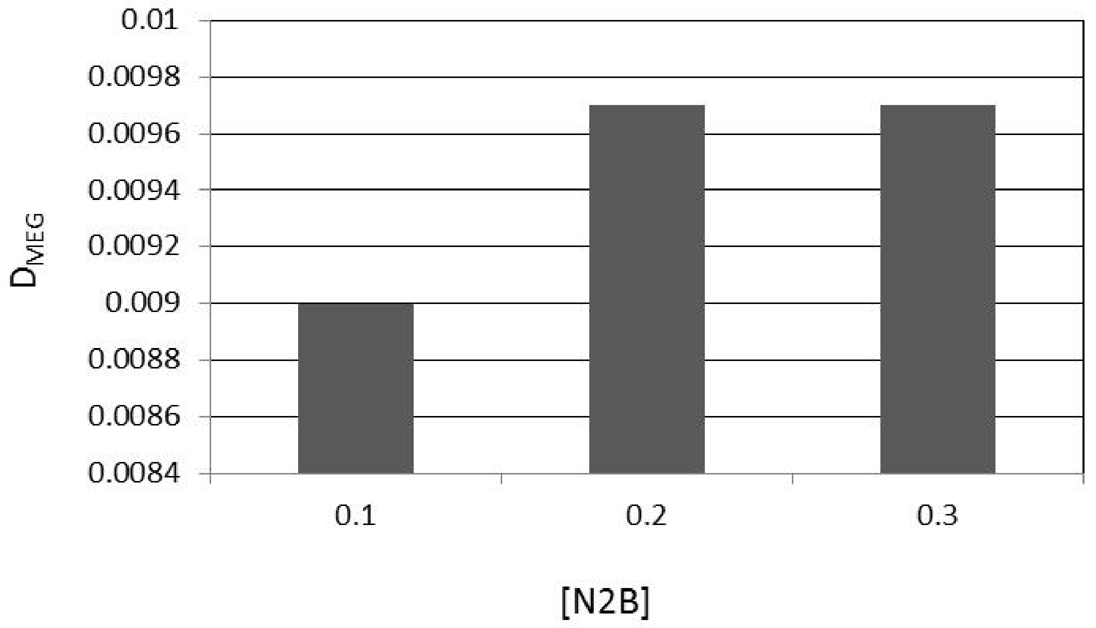

Figure 2-3. Distribution coefficient of MEG at different equimolar NBA and Aliquat 336 concentrations at pH 9, volume ratio 1/1, 298.15 K, 2-ethylhexanol.

2.3.3 Influence of pH

Three aqueous phases with different pH values, 0.2 M NBA and an equimolar concentration of NBA and Aliquat 366 were prepared. As figure 4 shows, the D_{MEG} value at pH 6 when no buffer was added to the aqueous solution is 0.0027, only slightly higher than the partition coefficient (0.0025), indicating that the effect of the chemical complexation on the distribution is negligible at this condition. The distribution ratio increased with increasing pH, which could be attributed to the formation of a stable tetrahedral complex that is formed only at higher pH.[6] The highest distribution coefficient (D_{MEG}) was obtained at pH 11, the highest pH tested. After this experiment is clear that pH optimization is a very important step because the distribution coefficient (D_{MEG}) can be increased in factor 10.

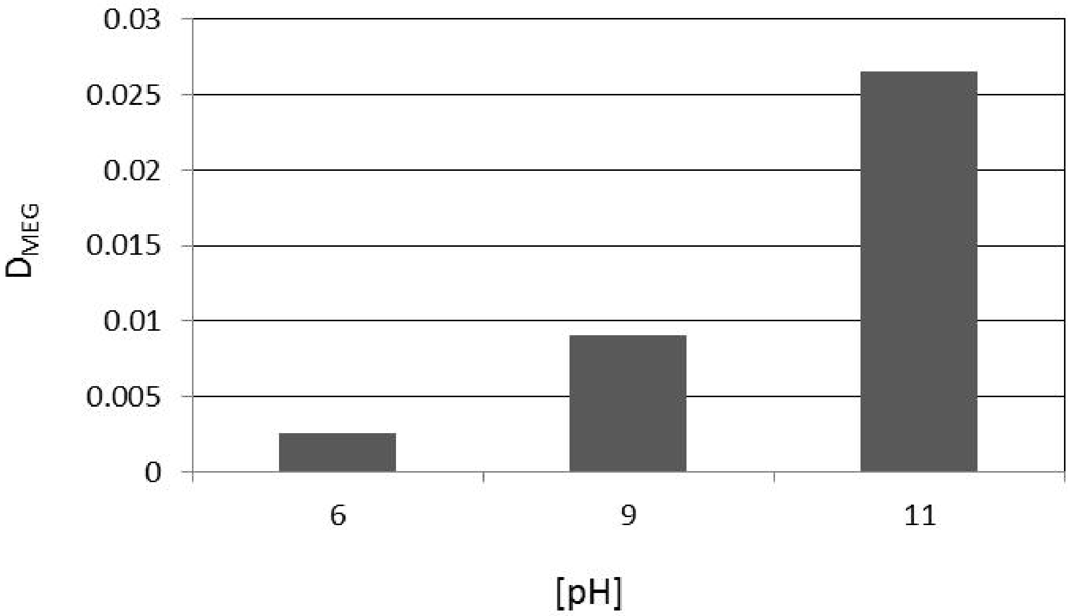

Figure 2-4. Distribution coefficient of MEG at different pH, volume ratio 1/1, 298.15 K, 2-ethylhexanol, NBA: Aliquat concentration 1:1, 0.2 M NBA.

It is known that NBA ionization and diol complex stability depend on the pH of the system and it is related to the pKa of the boronic acid. The pKa of boronic acids is expected to be around 9 and in order to keep the stability of the complex a high pH is required. In the case of MEG extraction the maximum distribution coefficient (D) was achieved at pH 11 suggesting that for MEG a stable complex is formed at higher pH. The pH of the aqueous phases at equilibrium was also measured. It was found that the pH decreased from 6, 9 and 11 to 4.8, 8.3 and 8.7 respectively. The drop of the pH is expected because of the decrease in diol groups (OH) in the aqueous phase due to the extraction of MEG into the organic phase. However it was also expected that with the addition of a buffer the change in pH will be less and it is possible that an increase in the buffering capacity improved the extraction performance.

2.4 Conclusions

The presented reactive extraction results show that extraction of MEG from diluted aqueous streams with conventional solvents can be improved by the addition of boronic acid extractants with basic co-extractants. The reactive extraction of MEG with lipophilic extractant NBA and Aliquat **366** as co-extractant improved the MEG distribution with a factor 10 compared to physical partitioning. The optimal extraction conditions were found at pH 11, extractant concentration of 0.2M and equimolar extractant-coextractant ratio. Under these conditions, a distribution coefficient of 0.026 at 298.15 K was obtained in a single stage extraction.

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Chapter 3

COSMO-RS assisted solvent screening for liquid-liquid extraction of mono ethylene glycol from aqueous streams[1]

[1] the content of this chapter was published under the same title as:
Lesly Y. Garcia-Chavez, Annelies J. Hermans, Boelo Schuur, André B. de Haan
(2012) Separation and Purification Technology

Abstract

The distribution of mono ethylene glycol and the co-extraction of water are key parameters that depend on the characteristics of the solvent. We here report on the solvent screening for mono ethylene glycol (MEG) extraction from water to maximize the distribution coefficient (D_{MEG}) and selectivity (S) of MEG over water. To speed-up the screening process and avoid unnecessary experiments, COSMO-RS was used to predict the LLE performance of both real and hypothetical solvents for the extraction of MEG from aqueous streams. Based on the σ-electron density-profile analysis, hypothetic tetraoctyl ammonium carboxylate, phosphinate and boronate ILs were considered as potentially interesting. These ILs were tailor made and evaluated in LLE experiments. They outperformed other solvents tested thus far with D_{MEG} up to 0.45, and S up to 3.2 vs D_{MEG} = 0.08 and S = 1.5 for α-terpineol.

3.1 Introduction

Liquid-liquid extraction (LLE) is a unit operation with high potential for the recovery of polar compounds from aqueous streams with low energy costs [1,2]. The main challenge in developing a LLE process is the identification of an appropriate solvent. The extraction of MEG from aqueous streams requires solvents with a high affinity for MEG, but a low affinity for water to avoid excessive co-extraction of water. Therefore a solvent that combines polar and hydrophobic behavior is required. Based on literature on the extraction of butanol and propanediol from aqueous solutions [3-6] fatty alcohols were identified as a promising class of traditional solvents, and hydrophobic ionic liquids (ILs) [7,9] as a promising, relatively new class of solvents for the extraction of aqueous MEG.

ILs have been studied as potential solvents for different applications in separation technology, including extractive distillation, absorption and liquid-liquid extraction.[10,11] They have been used for the separation of close boiling point compounds ethylbenzene-styrene [12] and azeotropic mixtures like tetrahydrofuran –water or ethanol-water[13] by extractive distillation, and for absorption of carbon dioxide [14]. In LLE processes, ILs also have been used as solvents for the separation of aromatic and aliphatic compounds[15], as well as, polar compounds like alcohols and organic acids from aqueous streams [7-9,16]. The ability of tailoring the properties of the ILs by combining different cations and anions opens a tremendous wide window of possible solvents for the extraction of MEG from aqueous streams, and a proper solvent screening method is desired.[17] Solvent selection can be carried out experimentally by measuring both the equilibrium distribution of MEG and water over the solvent phase and the aqueous phase. The desired properties of solvents are a high distribution coefficient and selectivity towards MEG, and little or no miscibility with the aqueous stream. The experimental distribution coefficients are defined according to the following equations:

$$D_{MEG} = \frac{x^{I}_{MEG}}{x^{II}_{MEG}} \tag{3.1}$$

$$D_{H2O} = \frac{x^{I}_{H2O}}{x^{II}_{H2O}} \tag{3.2}$$

The distribution coefficients of MEG and water are given as the ratio of the weight fractions in the organic extract phase (x^{I}), and in the aqueous raffinate phase (x^{II}) at equilibrium. The selectivity is defined as the ratio of the distribution coefficients (Equation 3-3).

$$S_{MEG} = \frac{D_{MEG}}{D_{H2O}} \tag{3.3}$$

The main drawback of experimental solvent screening is that it can be expensive and time consuming, due to the large number of possible solvents that could fulfill these requirements. Several alternatives for solvent screening have been reported, including heuristic methods and Computer-Aided Molecular Design (CAMD) to assist the solvent selection procedure.[6,18] Although CAMD can speed up the solvent selection, group contribution methods like UNIFAC [19-21] are needed to calculate activity coefficients and other thermodynamic properties in liquid mixtures. However, the required UNIFAC interaction parameters are not always available in literature, especially for relatively new compounds [22].

The COnductor like Screening MOdel for Realistic Solvents (COSMO-RS), is a known as a powerful method for molecular description and solvent screening based on a quantum-chemical approach proposed by Klamt and co-workers [23,24]. COSMO-RS combines quantum chemical considerations and statistical thermodynamics to determine and predict thermodynamic properties without using experimental data. Successful application of COSMO-RS has been reported recently for solvent selection for the extraction of phenol, aromatics, aliphatic and flavonoids from different streams (aqueous and non-aqueous).[16,20,25-28] Because of these promising results, we decided to use COSMO-RS in our solvent screening for MEG extraction from aqueous streams.

3.2 Application of COSMO-RS for solvent screening

COSMOTherm C2.1 is a software package that calculates thermodynamic properties using the COSMO-RS theory. The theory is based on quantum chemical computations and statistical thermodynamics.[23] Evaluation of a possible solvent with COSMO-RS involves 1) quantum chemical calculations to approximate the electron density functions of the compounds (solvents and solutes) by molecular surface sigma-electron density profiles, and 2) using the surface sigma-electron profiles in statistical thermodynamics to estimate the activity coefficient of the solute in the solvent, and with that the distribution coefficient. In COSMO-RS, the distribution coefficients are calculated according to equations 3.4 and 3.5, where $\gamma^{\infty}{}_{\mathrm{MEG}}$ and $\gamma^{\infty}{}_{\mathrm{H2O}}$ are the activity coefficients of MEG and water at infinite dilution in different solvents and ILs.

$$D_{MEG}^{Cosmo} = \frac{1}{\gamma_{MEG}^{\infty}} \tag{3.4}$$

$$D_{H2O}^{Cosmo} = \frac{1}{\gamma_{H2O}^{\infty}} \tag{3.5}$$

The COSMO-RS selectivity is calculated according to the equation 3.6.

$$S^{Cosmo} = \frac{\gamma_{H2O}^{\infty}}{\gamma_{MEG}^{\infty}} \qquad (3.6)$$

Distribution coefficient and selectivity at infinite dilution calculated by COSMO-RS are compared with the distribution and selectivity at finite dilution obtained experimentally (equations 3.1 and 3.3). Alternatively, because many researchers have already found that the distribution coefficients calculated by the statistical thermodynamic procedures of COSMO-RS are seldom quantitatively predicted [16,23,25], we decided to develop a qualitative evaluation of the solvents, based on their σ- profiles. In this evaluation, the experimental distribution coefficients were measured for a series of commercially available solvents, and the performance of these solvents in terms of D_{MEG} and S were compared with the σ-profiles of the solvents.

The σ-profile is a description of the polar electronic charge distribution of a molecular surface and it is represented as a probability plot p(s) or histogram, which gives information about how much of the molecular surface we can find in a certain polarity interval (σ) [23]. The σ-profiles of our aqueous solution system MEG-Water is shown in Figure 3-1, a short discussion on this system is given to facilitate further discussion. The surface charge that is displayed in Figure 3-1 on the x-axis of the σ-profile plot is the charge that is located on the surface of the molecules, which is opposite to the charge in the molecule itself. Therefore, the negative charges of the molecules result in positive charges at the surface and hence, are plotted as positive region called "hydrogen bond acceptor region"), we can see that the σ-profiles of MEG and water span in the range from + 2 e/nm^2 to -2 e/nm^2, which correspond to normal σ values for stable organic molecules. COSMO-RS theory considers σ regions beyond +1 e/nm^2 and behind -1 e/nm^2 as strong polar with the potential to form hydrogen bonds (HB), while the region between ± 1 e/nm^2 is considered as non-polar [28]. This polarity explanation is reflected in the σ-profiles for water and MEG. The profile for water only shows an electropositive region (the hydrogen atoms) and an electronegative region (the oxygen), whereas MEG contains also some non-polar hydrocarbon bonds visual in the σ-profile as a peak around 0 e/nm^2.

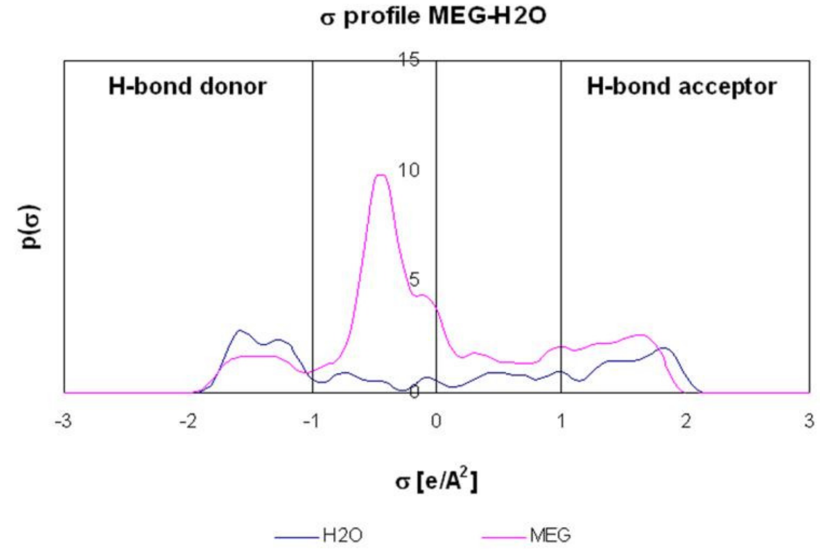


Figure 3-1. σ-profiles of water and MEG obtained by COSMO-RS.

3.3 Experimental Section

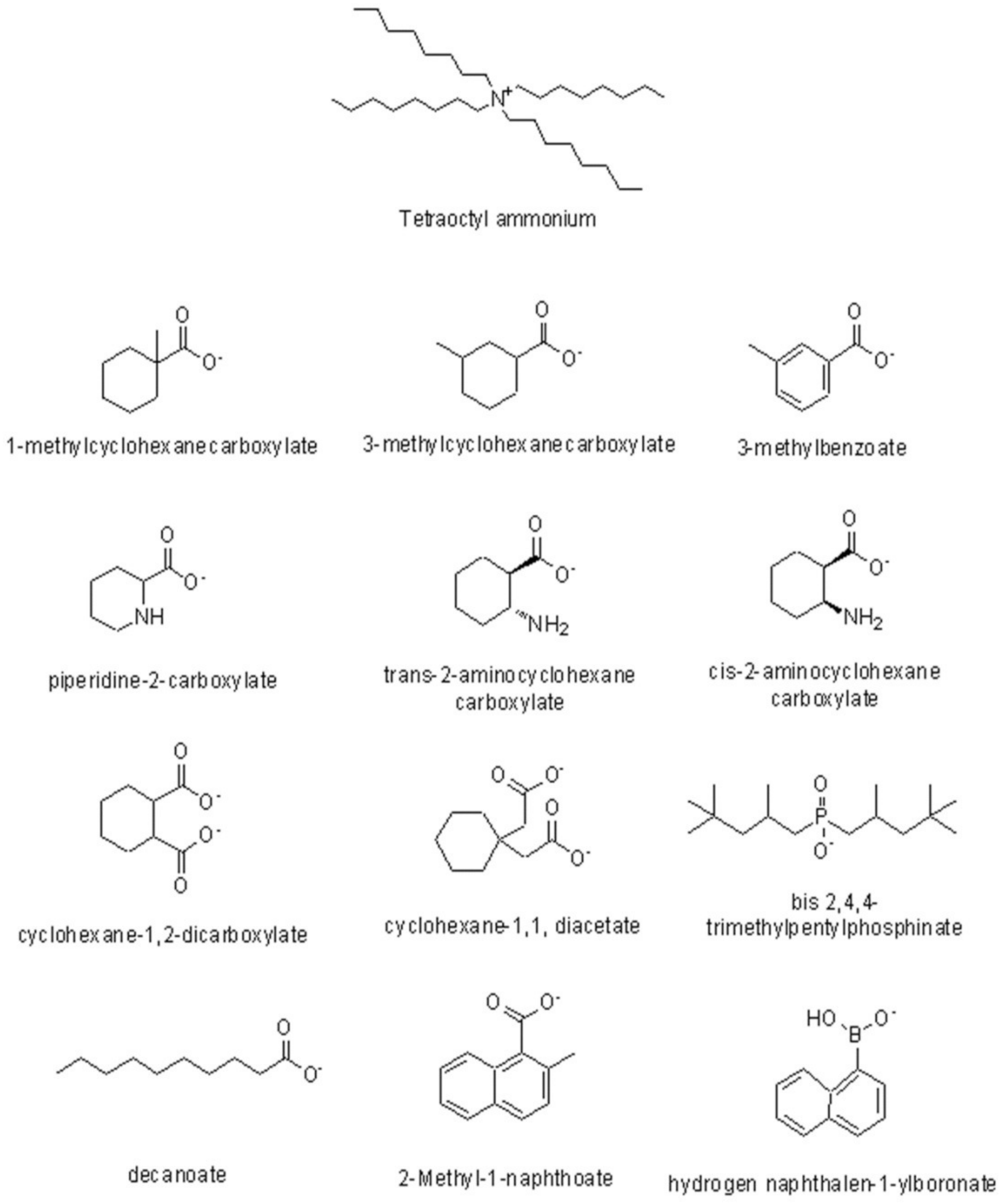
3.3.1 Materials

MEG (purity ≥99.9 %) was supplied by VWR. 1-Octanol (purity≥99.5 %) and 1-decanol (purity ≥ 99 %) were provided by Fluka. 2-ethyl-hexanol (purity ≥99 %) and α-terpineol (purity ≥ 98%) were provided by Merck, and oleyl alcohol (purity ≥ 80%) was provided by Acros Organics. In this study, seventeen commercially available ILs were tested and all chemicals were used without further purification, these are presented in Table 1.

The ILs that were synthesized in this study, all contained a tetraoctyl ammonium cation, and were formed by acid-base reaction of the tetraoctyl ammonium hydroxide with the appropriate acid. The chemicals used for these syntheses are: Tetraoctyl ammonium hydroxide solution (20% in methanol), 1-methyl-1-cyclohexane carboxylic acid (purity 99%), 3-methyl-1-cyclohexane carboxylic acid, m-toluic acid (purity 99%), cyclohexane-1,1-dicarboxylic acid, trans-cyclohexane-1,2-dicarboxylic acid (purity 95%), trans-2-aminocyclohexane carboxylic acid, cis-2-aminocyclohexane carboxylic acid, pipecolinic acid (purity 98%), 2-methyl-1-naphtoic acid (purity 97%), decanoic acid (purity 98%), diisooctylphosphinic acid (purity 90%), naphtalene-2-boronic acid (purity 95%),all provided by Sigma-Aldrich. The chemical structures of the synthesized ILs are presented in Figure 3-2.

Table 3-1. Commercial ionic liquids tested in this research.

	Name	Supplier	Purity
[BMIM PF_6]	1-butyl-3-methylimidazolium hexafluorophosphate	Merck	98%
[HMIM NTf_2]	1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide	Merck	≥99 %
[EMIM FAP]	1-ethyl-3-methyl-imidazolium tris(pentafluoroethyl) phosphate	Merck	≥99 %
[BMPy FAP]	1-butyl-3-methylpiridinium tris(pentafluoroethyl) phosphate	Merck	≥99 %
[ETMGu FAP]	N''-ethyl-NNN'N tetramethylguanidinium tris(pentafluoroethyl) phosphate	Merck	≥99 %
[PMIM NTf_2]	1-propyl-3-methylimidazolium bis(triofluoromethylsulfonyl)imide	Iolitec	99%
[OHEMIM NTf2]	1-(hydroxyethyl)-3-methylimidazolium bis(triofluoromethylsulfonyl)imide	Iolitec	98%
[BMIM PFBu]	1-butyl-3-methylimidazolium perfluorobutanesulfonate	Iolitec	98%
[OMIM Doc]	1-octy-3-methyimidazolium docusate	Iolitec	97%
[TBA Doc]	tertrabutyl ammonium docusate	Iolitec	98%
[MTOA Oct]	1-methyl trioctyl ammonium octanoate	Iolitec	95%
[MTOA Dec]	trioctylmethylammonium decanote	Iolitec	95%
[MTOA Chol]	1-methyl trioctyl ammonium cholate	Syncom BV	95%
[MTOA TS]	1-methyl trioctyl ammonium thiosalicylate	Fluka	≥95%
[Cyphos 109®]	tetradecyl(trihexyl)phosphonium bistriflamide	CYTEC	98.6%
[Cyphos 104®]	tetradecyl(trihexyl)phosphonium bis 2,4,4-trimethylpentyl-phosphinate	CYTEC	93.7%
[Cyphos 103®]	tetradecyl(trihexyl)phosphonium decanote	CYTEC	94%



Tetraoctyl ammonium

1-methylcyclohexanecarboxylate

3-methylcyclohexanecarboxylate

3-methylbenzoate

piperidine-2-carboxylate

trans-2-aminocyclohexane carboxylate

cis-2-aminocyclohexane carboxylate

cyclohexane-1,2-dicarboxylate

cyclohexane-1,1, diacetate

bis 2,4,4-trimethylpentylphosphinate

decanoate

2-Methyl-1-naphthoate

hydrogen naphthalen-1-ylboronate

Figure 3-2. Hydrophobic Ionic Liquids synthesized and tested in this study, based on tetraoctylammonium cation and carboxylate, phosphinate and boronate anions.

3.3.2 Ionic Liquid Synthesis

The acid-base reactions to synthesize the twelve different ILs from carboxylic, phosphinic and boronic acids and tetraoctyl ammonium hydroxide were carried out in a 100 mL round bottom flask equipped with a reflux condenser and magnetic stirrer. To 0.01 moles of the appropriate acid were added slowly 0.01 moles of tetraoctyl ammonium hydroxide (20% in methanol) at room temperature. The mixture was heated to 343.15 K for 2 hours; after the synthesis the formed water and the methanol were removed using a rotavapor (VWR RV 10 digital). For carboxylic acids this synthesis was done using a mol ratio of 2:1 (tetraoctyl ammonium hydroxide: carboxylic acid). NMR spectroscopy is a useful and rapid standard method to assess IL authenticity and purity [30]. The ionic liquids synthesized in this research were identified by NMR using ^{1}H-NMR on a Varian 200 MHz NMR spectrometer.

Tetraoctyl ammonium 1-methylcyclohexane carboxylate [TOA MCA] Yield: ~99%.^{1}H-NMR (DMSO-d_6): 3.13 (t, 11H), 2.25 (t, 1 H), 1.86 (m, 2H), 1.53 (s, 8H), 1.24 (m, 44 H), 0.91 (s, 3H), 0.84 (t, 12H).

Tetraoctyl ammonium 3-methylcyclohexane carboxylate [TOA 3MCA] Yield: ~95%.^{1}H-NMR (DMSO-d_6, ppm fixed with $CHCl_3$ at 8.27 ppm): 3.95 (m, 1H), 3.35 (m, 22H), 3.08 (m, 6H), 2.45 (m, 2H), 2.25 (t, 1H), 1.75 (m, 1H), 1.54 (m, 5H), 1.25 (m, 28 H), 1.05 (t, 7H), 0.85 (m, 12H).

Tetraoctyl ammonium 3-methylbenzoate [TOA MBA] Yield: ~97%. ^{1}H-NMR (DMSO-d_6, ppm fixed with $CHCl_3$ at 8.27 ppm): 7.60 (m, 2H), 7.04 (m, 2H), 3.42 (d, 2H), 2.25 (s, 3H), 1.54 (m, 8H), 1.25 (m, 43H), 1.04 (t, 3H), 0.85 (m, 12H).

Tetraoctyl ammonium piperidine-2-carboxylate [TOA PIP] Yield: ~97%.^{1}H-NMR (DMSO-d_6): 3.17 (m, 10H), 2.86 (d, 2H), 1.56 (m, 11H), 1.28 (m, 43 H), 0.87 (m, 12H).

Tetraoctyl ammonium trans-2-aminocyclohexane carboxylate [TOA t-NH2CA] Yield: ~ 96%. ^{1}H-NMR (DMSO-d_6): 3.98 (t, 1H), 3.17 (m, 8H), 1.56 (m, 15H), 1.26 (m, 44 H), 0.85 (m, 12H).

Tetraoctyl ammonium cis-2-aminocyclohexane carboxylate [TOA c-NH2CA] Yield: ~ 97%.^{1}H-NMR (DMSO-d_6): 3.99 (t, 1H), 3.18 (m, 8H), 1.55 (m, 12H), 1.27 (m, 44 H), 0.87 (m, 12H).

Tetraoctyl ammonium cyclohexane-1,1-diacetate [TOA 11CHDA] Yield: ~ 96% ^{1}H-NMR (DMSO-d_6): 3.92 (m, 2H), 3.38 (m, 2H), 3.15 (m, 14H), 1.66 (m, 2H), 1.55 (m, 16H), 1.26 (m, 84H), 1.03 (t, 2H), 0.84 (t, 24H).

Tetraoctyl ammonium cyclohexane-1,2-dicarboxylate [TOA 12CHDA], white solid at room temperature. Yield: ~ 98% .^{1}H-NMR (DMSO-d_6): 3.18 (m, 16H), 2.02 (m, 4H), 1.59 (m, 24H), 1.28 (m, 84H), 0.87(t, 24H).

Tetraoctyl ammonium bis 2,4,4-trimethylpentylphosphinate [TOA 104] Yield: ~98%. ^{1}H-NMR (DMSO-d_6): 3.14 (m, 8H), 1.55 (m, 9H), 1.26 (m,40H), 0.98 (s,3H), 0.94 (s, 3H), 0.89-0.81 (m, 21H).

Tetraoctyl ammonium decanoate [TOA Dec] Yield: ~ 97%.^{1}H-NMR (DMSO-d_6): 3.41(s,1H), 3.14 (m,8H) , 1.65 (t, 4H), 1.55 (m, 8H), 1.26 (m,40H),1.26 (m, 52H), 0.87-0.89 (m, 15H).

Tetraoctyl ammonium hydrogen naphthalene-1-ylboronate [TOA MNaph], brown solid at room temperature. Yield: ~99%.^{1}H-NMR (DMSO-d_6): 7.9-7.46 (3H,m) ,7.31-7.15(2H,m), 3.34 (s,2H), 3.16 (m,8H), 2.5 (s,2H), 1.55 (m,10H),1.27 (m, 38H), 0.85 (m, 12H).

Tetraoctyl ammonium naphtalene-2-ylboronate [TOA N2B]. Yield: ~ 98%.^{1}H-NMR (DMSO-d_6): 7.79(s,1H), 7.69-7.56 (m, 3H), 7.47 (dd, 1H) 7.34-7.18 (m,2H) , 3.14 (m, 8H), 1.53 (s, 10H),1.25 (m, 40H), 0.85 (t, 12H).

3.3.3 Liquid-liquid Extraction Experiments

Aqueous 20 wt% MEG solutions were prepared by dissolving MEG in distilled water. Extraction experiments were carried out by combining equal volumes (4 mL) of the aqueous phase and the organic solvent phase in a glass cell equipped with a mantle. The temperature was controlled at two different temperatures, i.e. 298.15 K and 333.15 K, using a water bath (Julabo F-25-MW). The system was stirred mechanically (800 rpm) for 20 hours. Afterwards the phases were allowed to settle for 2 hours. Samples from both phases were collected and analyzed. All experiments were done in duplo.

3.3.4 Analytical Methods

Analysis of the MEG content in both the aqueous and the organic phase was done by gas chromatography. The GC was equipped with a Nukol Fused silica capillary column with 15 m of length and 0.53 μm diameter, and a flame ionization detector. An uncoated capillary pre-column was used to prevent the IL from contamination the column. The oven program was set from 393.15 K for 1 minute, increasing up to 473.15 K with a ramp 10 K/min. The injector and detector temperatures were fixed at 523.15 K. Quantitative analysis (3% accuracy) was enabled by diluting 0.1mL of the sample in 1.0 mL of a mixture ethanol-DEG (with 5 wt% DEG). DEG was used as internal standard. The water content in the organic phase was determined by volumetric Karl Fisher titration using a Metrohm 795 KF (accuracy 0.5%). The ionic liquid or solvent content in the aqueous phase was assumed to be negligible; therefore the water content in aqueous phase was calculated by difference.The quantification of the IL in the raffinate is very important to evaluate the extraction process and to determine the amount of solvent that leaches in order to decide whether additional recovery steps are required. For the selected ionic liquid, the content in the raffinate was quantified using UVvis spectrophotometry, detailed information is presented in Chapter 4.

3.4 Results and Discussion

3.4.1 MEG extraction with commercially available solvents

To evaluate the activity coefficients at infinite dilution as calculated by COSMO-RS, and with that the screening method for the extraction of aqueous MEG, the σ-profiles of a series of commercially available solvents were calculated, and the distributions of MEG and water determined experimentally as described in section 3.3. A comparison of the experimentally determined D_{MEG} and the D_{MEG} predicted by COSMO-RS based on the simulated activity coefficients is given in Figure 3-3.It is clearly visible in Figure 3-3, that solvent screening for the MEG extraction from aqueous solutions cannot be performed using the predicted activity coefficients at infinite dilution by COSMO-RS. Especially the distribution coefficients of ILs with polar groups in the anion (acetate, phosphinate, cholate and tosylate) are heavily overpredicted, which is in agreement with results obtained by others [16,23,26,29,30]. From the experimentally observed distribution coefficients, it may be concluded that the ILs Cyphos 103, Cyphos 104, MTOA Octanoate, and MTOA decanoate are the most promising solvents that were tested. Therefore, the σ-profiles of these ILs were analyzed. The σ-profiles of the Cyphos ILs are given in Figure 3-4.

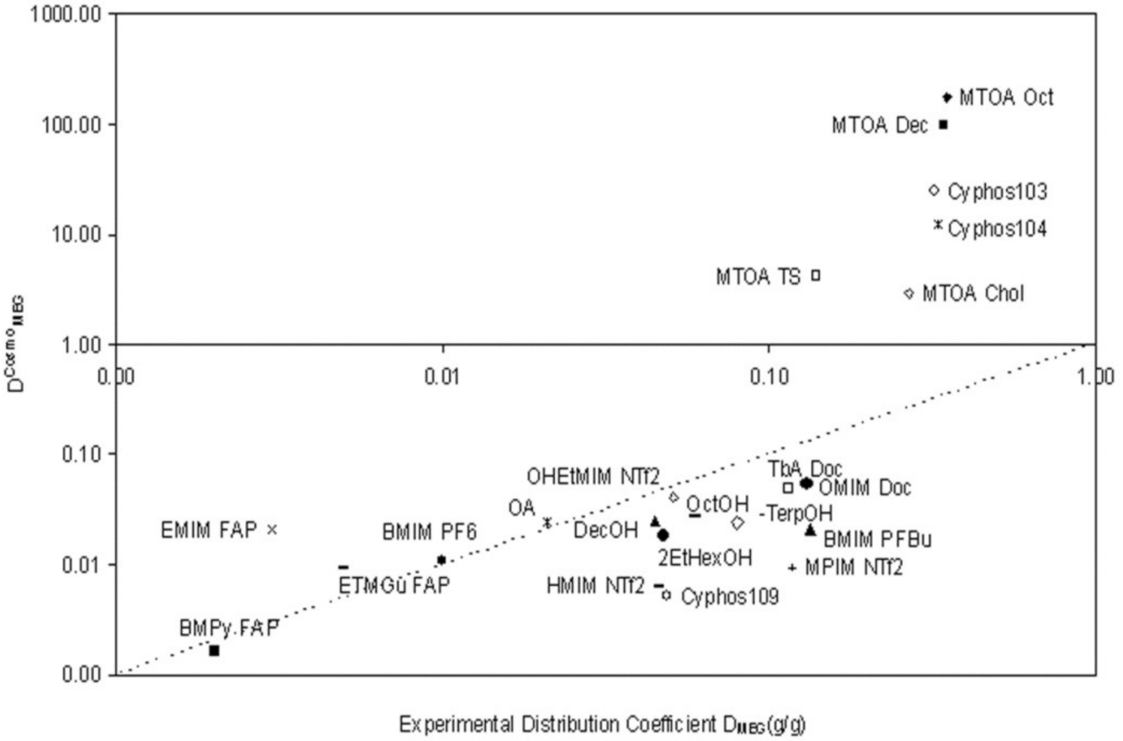


Figure 3-3. Comparison of experimental MEG distribution coefficients vs those predicted by COSMO-RS at infinite dilution (commercially available solvents).

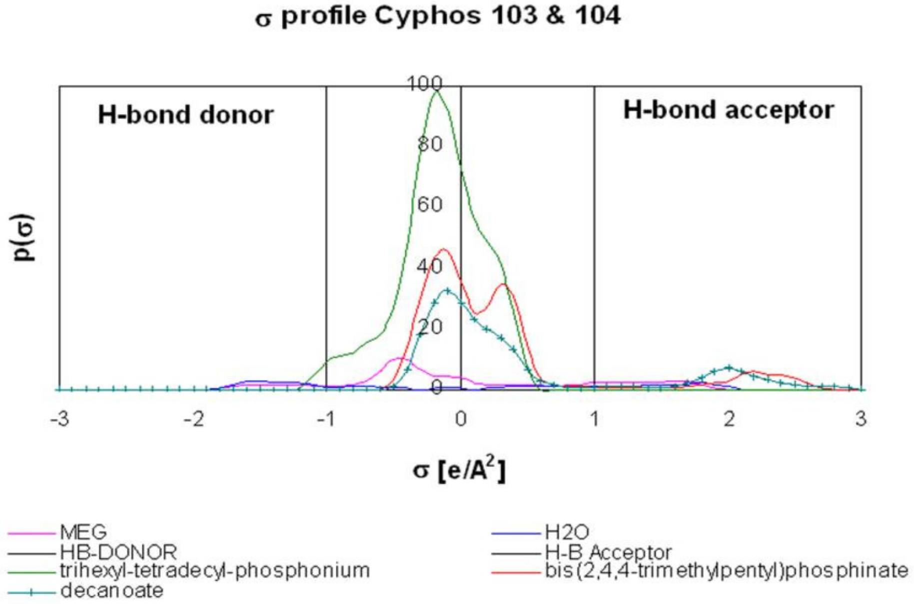


Figure 3-4. σ -profile of phosphonium ionic liquids with decanoate and phosphinate anions.

In the σ-profiles the trihexyl-tetradecyl-phosphonium cations show a huge density around zero, which corresponds with the hydrocarbon bonds in the long alkyl chains. This hydrophobic region is beneficial, because it reduces the amount of co-extracted water (see Figure 3-6 below for the results regarding selectivity). What is furthermore interesting is that both the phosphinate and decanoate anions show an electronegative region reflected in the high probability density around +2 e/A^2. In order to verify whether this is a characteristic only found in solvents with high MEG distribution, the σ-profiles of the less performing ILs and the conventional solvents were also evaluated. Figure 3-5 displays the σ -profiles of some ILs (Figure 3-5a) and conventional solvents (Figure 3-5b) that performed less good. None of the less performing solvents displayed a high probability density in the electronegative region around +2e/A^2, thus confirming this characteristic as beneficial. On the basis of these characteristics in the σ -profiles, it was suggested that the electronegative region of the COO^- and PO_2^- group in the anion, in combination with the large neutral region of the long alkyl chains in the cation form the ideal extractant for MEG.

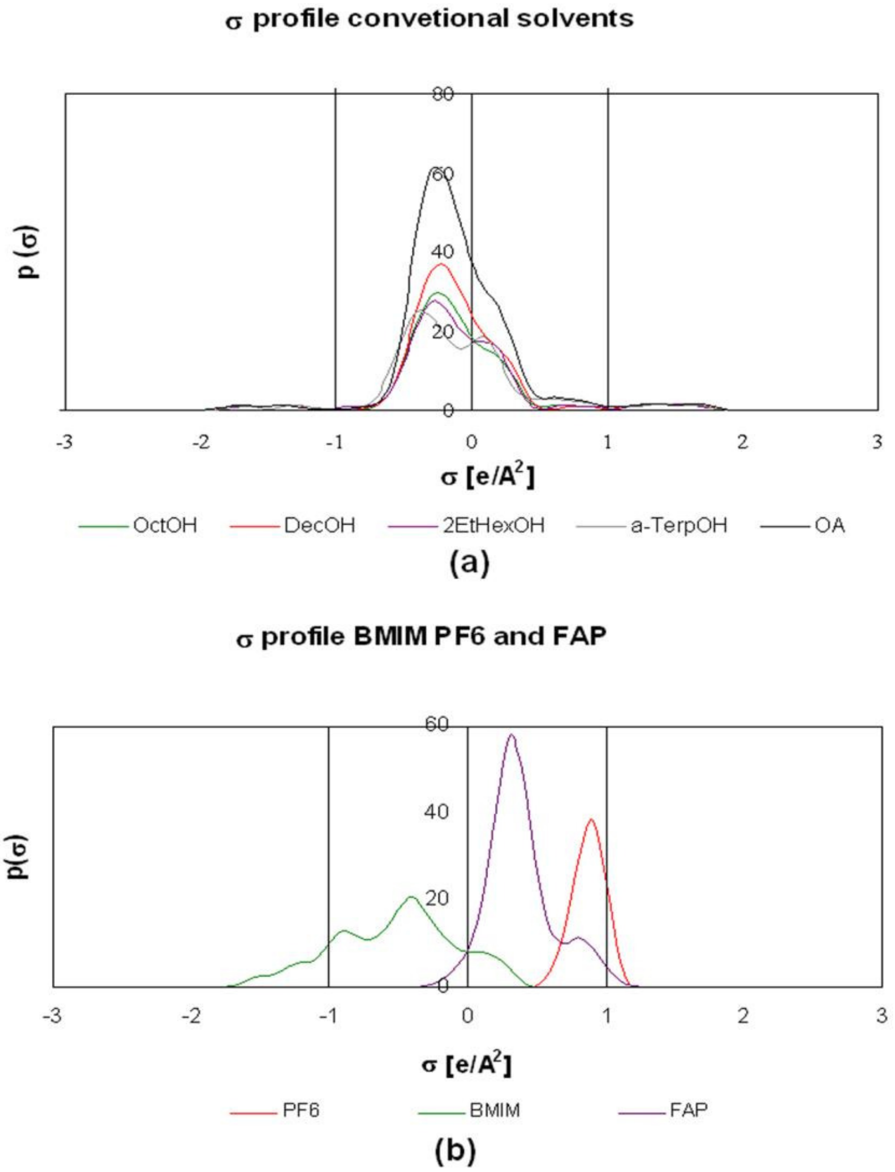


Figure 3-5. (a) σ– profile of fluorinated ionic liquids and, (b) σ -profile of conventional solvents.

3.4.2 MEG extraction with tailor made solvents

Based on the conclusions regarding the ideal σ -profile as discussed in section 4.1, it was possible to draw structures of hypothetical ILs and evaluate their opportunities for the LLE of MEG on the basis of their σ -profile as calculated by COSMO-RS. Because of the ease of synthesis, it was decided to focus on ILs that can be made from simply combining tetra octyl ammonium hydroxide and an organic acid. The σ -profiles of a range of ILs were thus predicted, and the most promising, presented in Figure 3-2, were synthesized and evaluated in LLE experiments.

Because not only D_{MEG} is important, but also a high selectivity in order to reduce the amount of co-extracted water, in the experimental evaluation this factor was also taken into account. The results from all solvents tested (thus also the commercially available ones) are displayed in Figure 3-6. With D_{MEG} on the x-axis, and *S* on the y-axis, the best solvents are found in the upper right corner. It can be seen that, without exception, all tailor made solvents based on the σ -profile screening using COSMO-RS are located towards the upper right corner. This is a clear proof that qualitative evaluation of σ -profiles can be used as a screening method in solvent selection for LLE processes.

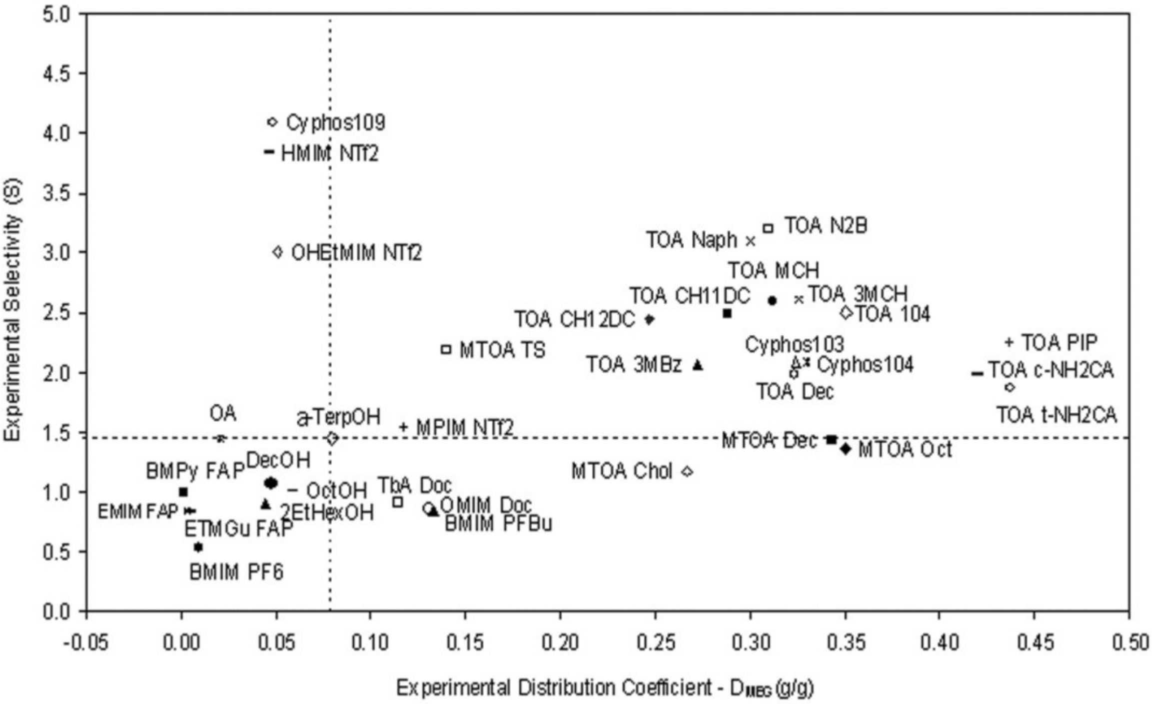


Figure 3-6. Plot of experimental D_{MEG} and S for all solvents used in this study. α-terpineol (α-TerpOH) was used as reference system.

The σ profiles of the tailor made solvents are given in Figure 3-7. The σ -profiles of [TOA CH11DA], [TOA 3MBz] and [TOA 3MCH] are shown in Figure 3-7a. The presence of a cyclic aliphatic chain in the anion increases the hydrophobicity of the IL (thus the selectivity) more than the cyclic aromatic. Although the diacetate IL [TOA CH11DA] was designed with the objective to improve the affinity towards MEG by increasing the molecular surface in the electronegative region > +2.0 e/nm^2 (as it can be seen it the σ– profile), the experimental D_{MEG} did not improve and the selectivity decreased due to higher water co-extraction.

ILs containing anions with amine group and cyclic acetate group [TOA PIP], [TOA t-NH2CA] and [TOA c-NH2CA] are presented in Figure 7b. These ILs showed the higher D_{MEG} (around 0.4) compared to other ILs, but not a high selectivity. Unfortunately no significant change in the σ -profile of these compounds that could give us an explanation about the significant increment on D_{MEG} could be found. Our interpretation is that the presence of the amine group in an ortho position to the carboxylate group strengthens the hydrogen bond interaction between the MEG and carboxylate peak, but it also increases water co-extraction.

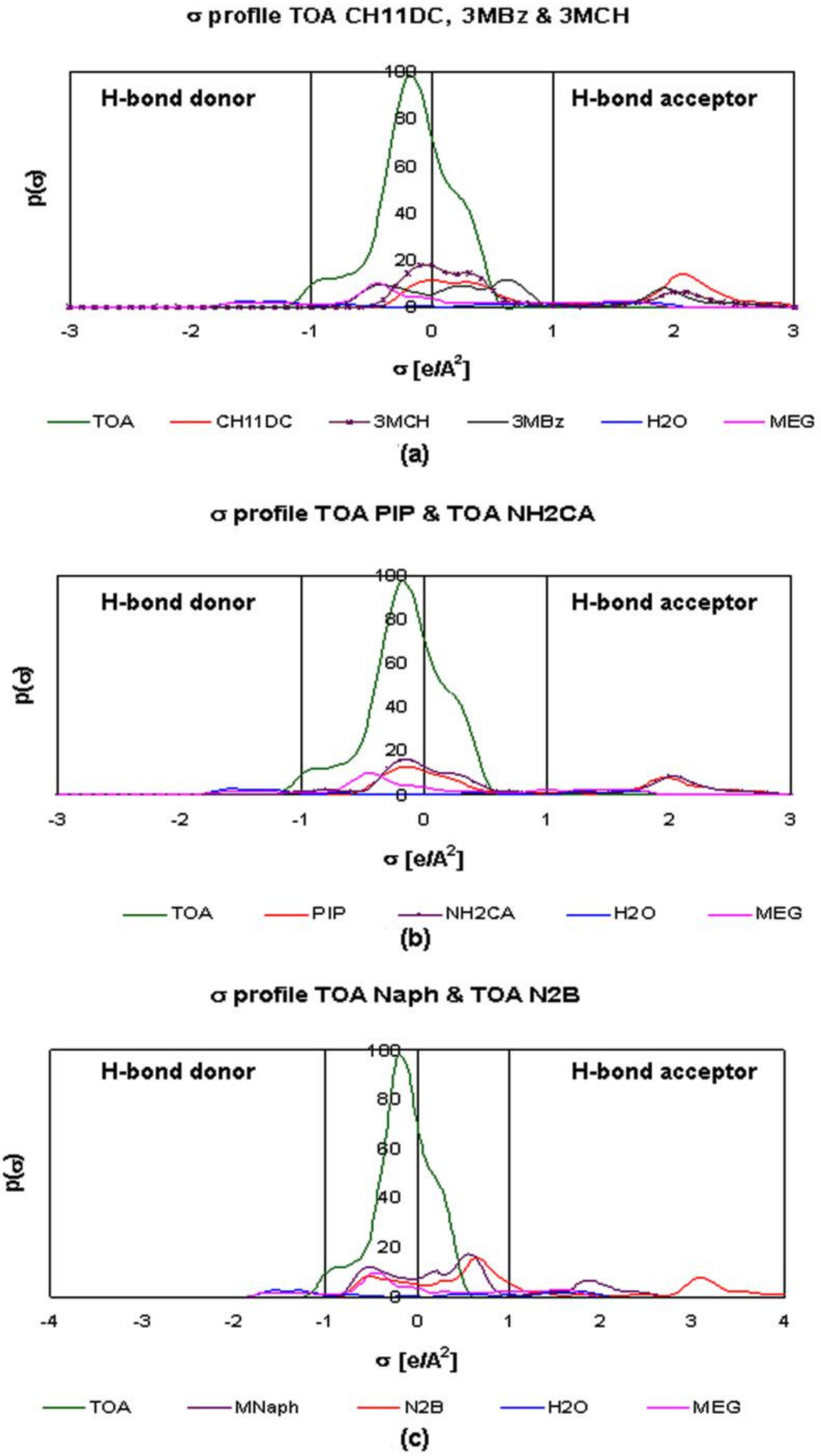


Figure 3-7. σ -profile of IL with tetraoctylammonium cations and cyclic aliphatic and aromatic carboxylate anions.

In Figure 3-7c, the σ -profiles of ILs containing a bicyclic aromatic anions like [TOA Naph] and [TOA N2B] are shown. These ILs reported a good balance between high distribution coefficient (D_{MEG} = 0.3 ,0.31) and high selectivity (S = 3.1, 3.2). From the σ profiles, we can see that N2B is a more polar anion reaching values up to + 4.0 e/nm^2. Therefore a big improvement in D_{MEG} would be expected, nevertheless the experimental values of both IL are similar. An important finding is that the presence of a bicyclic aromatic structure in the anion improves the selectivity of ILs, this is likely due to the very large hydrophobic area they exhibit.

3.5 Conclusions

In this study, the extraction of MEG from aqueous streams using LLE with hydrophobic ILs is presented as an energy efficient alternative to technologies using the evaporation of water. COSMO-RS software was used as a tool for solvent screening. Because of the limited correlation between experimental distribution of MEG using commercially available solvents, and the simulated distribution based on activity coefficients calculated by COSMO-RS, a qualitative analysis of the σ-profiles of solvents by COSMO-RS was developed. A combined electronegative region for affinity towards MEG, and a large electroneutral region for hydrophobicity were found as optimum solvent characteristics. Simulations of hypothetic solvents yielded tetraoctylammonium carboxylates, phosphinates, and boronates as most promising. All ILs that were selected to be synthesized and experimentally evaluated in LLE processes, performed very good with high distribution and high selectivity. The presented data on distribution and selectivity show that a range of easy to synthesize quaternary ammonium ILs performs much better than conventional fatty alcohol solvents. Further studies are needed to accurately measure the leaching of solvent and to estimate the required energy and sizing of equipment.

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Chapter 4.

Equilibrium Data for Glycols +Water + Tetraoctyl ammonium 2-Methyl-1 Naphthoate[1]

[1]the content of this chapter was previously published as:

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Journal of Chemical Thermodynamic 51. p. 165-171.

L.Y. Garcia-Chavez. M. Shazad, B. Schuur, A. B. de Haan (2012) Liquid-Liquid Equilibrium Data for the system Propylene Glycol + Water + Tetraoctyl Ammonium 2-Methyl-1-Naphtoate.
Journal of Chemical Thermodynamic 54. p. 238-244.

L.Y. Garcia-Chavez. M. Shazad, B. Schuur, A. B. de Haan (2012) Liquid-Liquid Equilibrium Data for Separation of 2,3-Butanediol form aqueous streams using Tetraoctyl Ammonium 2-Methyl-1-Naphtoate.
Journal of Chemical Thermodynamic 55. p. 85-91.

Abstract

Tetraoctyl ammonium 2-methyl-1-naphtoate [TOA MNaph] is a tailor made hydrophobic ionic liquid that may be applied for the recovery of glycols from aqueous streams. In this chapter, the liquid-liquid equilibrium data for: MEG+ water + [TOA MNaph], PG+ water + [TOA MNaph] and 2,3-BD + water + [TOA MNaph] at 313.2, 333.2 and 353.2 K have been obtained and correlated to the NRTL and UNIQUAC activity coefficient models. Root square mean deviations (RMSD) values of 1.34%, 1.51% and 1.54% with the NRTL model, and 0.89%, 1.20% and 1.88 %, with UNIQUAC were obtained for MEG, PG and 2,3-BD, respectively. The analysis showed that both models can properly describe the experimental data. Compared to conventional solvents, [TOA MNaph] presents a good balance between distribution coefficient and selectivity for the three glycols. The highest values were D = 0.36, 0.8, 1.08 and S= 3.31, 8.20, 11.47 respectively [1,2] for MEG, PG and 2,3-BD.

4.1 Introduction

Liquid-liquid extraction has been evaluated as technology to remove glycols from aqueous streams (chapters 2 and 3), and the main reason why liquid-liquid extraction appears promising is because it could avoid the evaporation of large amounts of water. Key for the separation of glycols from aqueous streams through liquid-liquid extraction is that the solvent is highly selective because then, hardly any water is co-extracted that needs to be evaporated during the recovery from the solvent. Traditional solvents that have been described for the extraction of aqueous glycols are octanol, 2-ethylhexanol, decanol, and oleyl alcohol for MEG [3-11]. The reported distribution coefficients for MEG were 0.059, 0.045, 0.048 and 0.021 with selectivities of 1.02, 0.90, 1.07 and 1.17 for octanol, 2-ethyl-hexanol, decanol and oleyl alcohol, respectively. For PG, oleyl alcohol, 4-methyl-2-pentanone, isopropyl acetate, ethyl acetate, tributyl phosphate, oleic oil, soya oil and castor oil have been studied [3-6], however, all reported distributions of PG are very low (between 0.01-0.13 mass fraction for low concentrations of PG) and consequently large amounts of solvent will be needed to have an effective extraction [4]. The obtained selectivities towards PG with conventional solvents vary from S = 2 to 20, but there appeared a tradeoff between this two properties and for solvents with high values of S, very low values of D were observed [3,4].

Solvent extraction of 2,3-BD from aqueous solutions has been studied by several authors [7-9]. The distributions of 2,3-BD ($D_{2,3BD}$) and the selectivity of conventional solvents reported by different authors showed that butanol has the highest $D_{2,3BD}$ with 0.89 at a low selectivity of 2.9, and the highest selectivity is reached with methyl vinyl carbinol acetate (MVCA) at S=19.7, but with this solvent the distribution is only about 0.35. It may be concluded that there is clear trade-off between these two parameters, which is important because of their influence on the design of the extraction process. An ideal solvent should have a high distribution coefficient for 2,3-BD, while also exhibiting a high selectivity, in order to avoid co-extraction of extensive amounts of water.

As described in Chapter 3, from the study on the solvent selection for MEG extraction from aqueous streams that included experimental studies and molecular modeling with COSMO-RS (Conductor like Screening Model for Realistic Solvents), a new hydrophobic ionic liquid, tetraoctyl ammonium 2-methy-1-

naphtoate [TOA MNaph], was found as one of the most promising solvents for this system [10]. After obtaining the promising results for MEG-water separation with [TOA MNaph], the scope of the study on the extraction of glycols was extended and in this chapter the liquid-liquid equilibria of 1,2 propanediol (propylene glycol PG) and 2,3-butanediol (2,3-BD) in aqueous – [TOA MNaph] biphasic systems are presented. The experimental data is modeled using NRTL and UNIQUAC models. Thermodynamic modeling is required to develop a conceptual design of the glycols extraction using the new IL [TOA MNaph] and obtain good estimates of the capital costs and the energy consumption. A crucial basis for such a conceptual design is a validated thermodynamic model. Well known thermodynamic models, including the activity coefficient models NRTL, UNIQUAC, UNIFAC and Wilson [11-15], and equation of state models [16-17] have been used to describe mixtures containing ILs. Because both the NRTL and the UNIQUAC models have been found very suitable for describing liquid-liquid equilibria involving ILs, even though the NRTL model was developed for molecular systems and not for ionic ones [18], in the current work these two activity coefficient models have been deployed to correlate the LLE data of the ternary system MEG + Water + [TOA MNaph], PG + Water + [TOA MNaph], and 2,3-BD + Water + [TOA MNaph].

4.2 Theory

4.2.1 Solvent Extraction for the Recovery of Glycols

Important parameters in solvent extraction are the distribution coefficient (D) and the selectivity (S). Equations 4.1 and 4.2 show the calculation of the distribution coefficient of the glycol and water respectively, given by the ratio of the weight fractions of the component in the extract phase (*I*), and in the raffinate phase (*II*) at equilibrium.

$$D_{glycol} = \frac{\chi^{I}_{glycol}}{\chi^{II}_{glycol}} \tag{4.1}$$

$$D_{H2O} = \frac{\chi^{I}_{H2O}}{\chi^{II}_{H2O}} \qquad (4.2)$$

The selectivity is defined as the ratio of the distribution coefficients of 2,3-BD and water as given in equation 4.3.

$$S = \frac{\chi^{I}_{glycol} \Big/ \chi^{II}_{glycol}}{\chi^{I}_{H2O} \Big/ \chi^{II}_{H2O}} \qquad (4.3)$$

4.2.2 Thermodynamic activity coefficient models: NRTL and UNIQUAC

For correlation of the experimental equilibrium data, the NRTL and UNIQUAC thermodynamic models have been applied, because they are known to be able to describe the behavior of systems including ionic liquids [11-15]. The expression for the NRTL activity coefficient model and the required interaction parameters are presented in equations 4.4 and 4.5 [19].

$$\ln(\gamma_i) = \frac{\Sigma_j x_i \tau_{ji} G_{ji}}{\Sigma_k x_k G_{ki}} + \sum_j \frac{x_j G_{ij}}{\sum_k x_k G_{kj}} \left(\tau_{ij} - \frac{\sum_k x_k \tau_{kj} G_{kj}}{\sum_k x_k G_{kj}} \right) \qquad (4.4)$$

where, $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $\tau_{ij} = a_{ij} + \frac{b_{ij}}{T}$ and $\tau_{ii} = 0$, $G_{ii} = 1$, $\alpha_{ij} = \alpha_{ji}$

(4.5)

where a_{ij} and b_{ji} are the interaction parameters between the molecules i and j, and α_{ij} the non-randomness parameter, which represents the local composition of the system.The equation of the UNIQUAC model for the activity coefficients calculation and the required parameters are presented in equations 4.6 and 4.7 [20]:

$$\ln(\gamma_i) = \ln\frac{\Phi_i}{x_i} + \frac{z}{2} q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\theta_i}{x_i}\sum_j x_j l_i + q_i\left(1 - \ln\sum_j \theta_j \tau_{ij} - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_K \tau_{kj}}\right) \tag{4.6}$$

where

$$\Phi_i = \frac{r_i x_i}{\sum_k r_k x_k};\ \theta_i = \frac{q_i x_i}{\sum_k q_k x_k};\ l_i = \frac{z}{2}(r_i - q_i) + 1 - r_i,\ \tau_i = \exp(a_{ij} + b_{ij}(T/K)^{-1}) \tag{4.7}$$

In these equations, the binary parameters are represented by a_{ij}, a_{ji}, b_{ij} and b_{ji} and the van der Waals volume and surface area are r_i and q_i, respectively.

4.3 Experimental Section

4.3.1 Materials

The starting materials for synthesis of the IL tetraoctylammonium 2-methyl-1-naphtoate [TOA MNaph] were tetraoctylammonium hydroxide (20% in methanol) and 2-methyl-1-naphthoic acid (purity > 0.97). MEG (purity ≥0.999) was purchased from VWR, propylene glycol (1,2-propanediol, purity ≥99.9 %) was supplied by Merck, meso 2,3-butanediol (purity > 0.99). All chemicals were supplied and used without further purification.

4.3.2 Ionic Liquid Synthesis

[TOA MNaph] was synthesized using a single step acid-base reaction, also known as the neutralization method [21]. In a 100 mL round bottom flask equipped with a reflux condenser and magnetic stirrer, 0.015 moles (2.75 g) of 2-methyl-1-naphthoic acid were added slowly to 0.015 moles (7.25 g) of tetraoctyl ammonium hydroxide (diluted 20% in methanol) at room temperature. The reaction was carried out at 343.2 K for 2 hours. Afterwards the formed water and the methanol were removed in a rotary evaporator (VWR RV 10 digital) at 383.2 K and 200 mbar for 6 h, the purity of the IL was checked by ^{1}H-NMR at > 0.95 mass fraction, the major impurity, being the starting material tetraoctyl ammonium hydroxide was proven to be present in < 1% (based on the 2.2 ppm signal). The density of the

IL was estimated, using a graduated cylinder and a balance, the obtained value was 0.88 g/ml at 333.2 K. The product was characterized using ^{1}H-NMR on a Varian 200 MHz NMR spectrometer. [TOA MNaph] Yield: (97%) ^{1}H-NMR (DMSO-d_6): 7.9-7.46 (3H,m) ,7.31-7.15(2H,m), 3.34 (s,2H), 3.16 (m,8H), 2.5 (s,2H), 1.55 (m,10H),1.27 (m, 38H), 0.85 (m, 12H). See Appendix A.

4.3.3 Liquid-liquid Extraction Experiments

Extraction experiments were carried out by combining equal masses (3 g) of the aqueous feed phase and the organic solvent phase in a glass cell equipped with a mantle. The experiments were done at three different temperatures, T/K = (313.2, 333.2 and 353.2), using a water bath (Julabo F-25-MW) to maintain the temperature constant, temperature deviation was 0.1K. The system was stirred mechanically (800 rpm) for 2 hours (it was experimentally verified that equilibrium was reached within 15 minutes). Afterwards the phases were allowed to settle for 2 hours. Samples from both phases were collected and analyzed. The mass fraction of the aqueous glycol solutions was between 0.05 and 1.0 for MEG and PG, and for 2,3-BD between 0.01 and 0.85 and were prepared by dissolving the appropriate amount of glycol in distilled water.

4.3.4 Analytical Methods

Analysis of the MEG content in both the aqueous and the organic phase was done by gas chromatography. The GC was equipped with a Nukol Fused silica capillary column (15 m x 0.53 µm), and a flame ionization detector. An uncoated capillary pre-column was used to prevent the IL from contaminating the column. The GC method for the different glycols is: For MEG, the temperature of the column was initially 393.2 K for 1 minute, followed by a 10 K/min ramp up to 453.2 K. The injector and detector temperatures were fixed at 250 °C. Quantitative analysis (0.003 accuracy) was enabled using diethylene glycol as internal standard. For PG and 2,3-BD the temperature of the column was initially 358.2 K for 3 minutes, followed by a 40 K/min ramp up to 418.2 K. The injector and detector temperatures were fixed at 523.2 K. Quantitative analysis (0.001 deviation in the mass fraction) was enabled using mono ethylene glycol as internal standard and ethanol as diluent. The water content in the organic phase was determined by volumetric Karl Fisher titration using a Metrohm 795 KF (accuracy 0.005). The quantification of the IL in the raffinate is very important to evaluate the extraction process and to determine the amount of solvent that leaches in order to decide whether additional recovery steps are required. The ionic liquid content in the raffinate was quantified using UV-vis spectrophotometry (Cary 300 Conc UV/VIS). The samples were diluted with ethanol, and the ionic liquid band was observed at $\lambda = 225$ nm, corresponding to the π-π^* excitation of electrons in the naphthoate ring (the molar extinction coefficient in ethanol was determined at $\varepsilon = 40{,}480$ L/ (mol cm). The error of this method is approximately 0.002.

4.4 Results and Discussion

4.4.1 Correlation of LLE data with NRTL and UNIQUAC models

The NRTL and UNIQUAC models were used to correlate the experimental data, the regression was done using ASPEN Plus V7.1. data regression tool. The models have been chosen based on the good correlations in vapor-liquid equilibria and liquid-liquid equilibria of multicomponent systems including ionic liquids that were reported in literature [13,17,22-24].

For the NRTL thermodynamic model regression, only 3 parameters for each pair of compounds were regressed (b_{ij},b_{ji} and α_{ij}) using the experimental data. The parameters a_{ij} and a_{ji} were fixed to zero. In the case of the UNIQUAC model the binary parameters (a_{ij}, a_{ji}, b_{ij} and b_{ji}), which were regressed on the experimental data. The van der Waals volume (r_i), and surface area (q_i) were estimated for the different glycols and water using the Bondi method [18] and for the ionic liquid [TOA MNaph], the parameters were estimated with the correlations given in equations 8 and 9 [14-25]:

$$r_i = 0.029281(V_i / cm^3 mol^{-1}) \quad (4.8)$$

$$q_i = \frac{(z-2)r_i}{z} + \frac{2}{z} \quad (4.9)$$

The molecular volume V_i for the ionic liquid [TOA MNaph] was predicted with COSMOtherm C21.0110, which is an accurate method to predict molar liquid volumes as was reported by Palomar and coworkers [26]. The molecular volume of the ionic liquid can also be estimated using the experimentally density, however minimal differences in the regression results are typically observed [2]. The coordination number z is assumed to be 10 [2] and the calculated values of the surface and volume and the predicted molar volume of the ionic liquids are presented in table 4-1.

Table 4-1. Van der Waals volume and surface parameters (required for the UNIQUAC model).

Parameter	MEG	PG	2,3-BD	H_2O	[TOA MNaph]
r_i	2.41	3.30	3.89	0.92	20.70
q_i	2.25	3.10	3.94	1.42	16.75
$V_i/(cm^3\ mol^{-1})$	---	---	---	---	706.90

4.4.2 Experimental Results

Liquid-liquid equilibrium experiments were performed at 313.2, 333.2 and 353.2 K. The experimental compositions of glycol and water in the extract phase, and of glycol and [TOA MNaph] in the raffinate phase were determined analytically, the main components in each phase (water and [TOA MNaph], respectively) by mass balance. The feed, extract, and the raffinate compositions as well as the glycol distribution coefficient and the selectivity calculated with equation 1-3 are presented in Appendix B.

Mono Ethylene Glycol

The experimental data showed that the solubility of the IL in the raffinate phase increases with increasing MEG content in the mixture (up to 0.033 mass fraction with pure MEG). The observed behavior is an indication that the IL has more affinity towards MEG, for which it was actually designed. A similar effect of increasing IL solubility in the raffinate with increasing solute concentration was observed for a completely different application, the separation of aliphatics and aromatics [27]. It has observed that the solubility of the IL in aqueous phase is almost independent of the temperature. In figures 4-1 and 4-2 the ternary diagrams are shown for the mixture [TOA MNaph] + MEG + Water. In figure 4-1 the comparison with the NRTL model correlation, and in figures 4-2 the comparison with the UNIQUAC model. From the comparison of the calculated ternary diagrams with the experimental liquid-liquid equilibrium data, it is clearly visible that both models are well capable to describe the ternary system. It can furthermore be seen that the tie lines range from 0 to 1.0 mass fraction of MEG in the feed. An equal mass ratio of IL over MEG-water mixtures was considered for all experiments. The ternary diagrams show that the system is immiscible over the complete range of concentration and temperature that were studied.

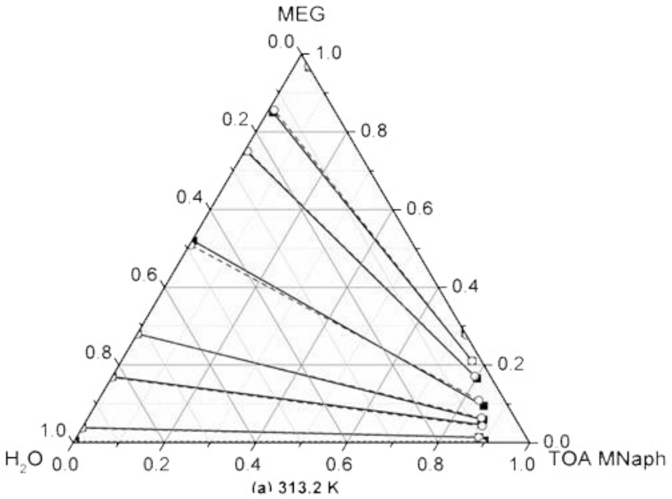
The binary parameters for MEG and water that were taken from ASPEN Plus, the other binary interaction parameters (aij, aij, bij and bji) were obtained after regression of the UNIQUAC model to the experimental data. For the NRTL model, all parameters were regressed. The calculated model parameters for both the NRTL and the UNIQUAC models are presented in table 4-2. For both thermodynamic models the linear temperature-dependent binary interaction parameters were taken into account.

Table 4-2 Binary interaction parameter for MEG, NRTL and UNIQUAC models.

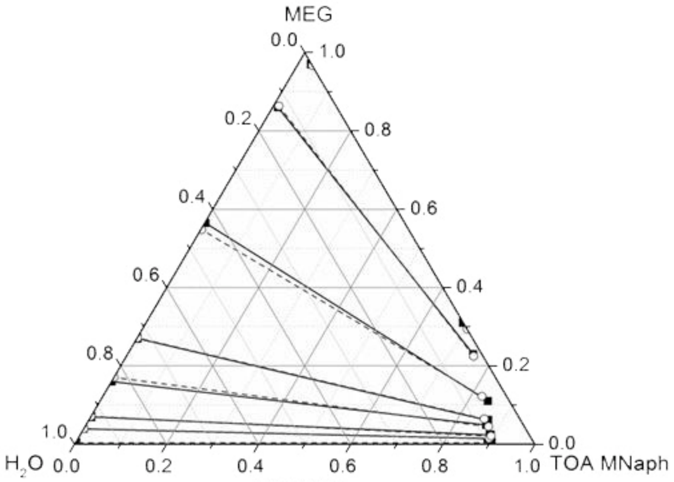
	H_2O / MEG (i) / (j)		H_2O / [TOA MNaph] (i) / (j)		MEG/[TOA MNaph] (i) / (j)	
	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
a_{ij}	2.295	-0.6018[a]	14.101	-0.072	5.291	2.020
a_{ji}	-0.848	0.6018[a]	-16.064	-0.645	13.990	0.325
b_{ij}	338.796	-282.079	-1414.56	102.52	200.688	-186.765
b_{ji}	617.606	-71.031	6497.79	475.533	3732.64	42.026
α_{ij}	0.73	--	0.36	--	0.57	--

[a] these values were taken from the ASPEN PLUS database, and not regressed

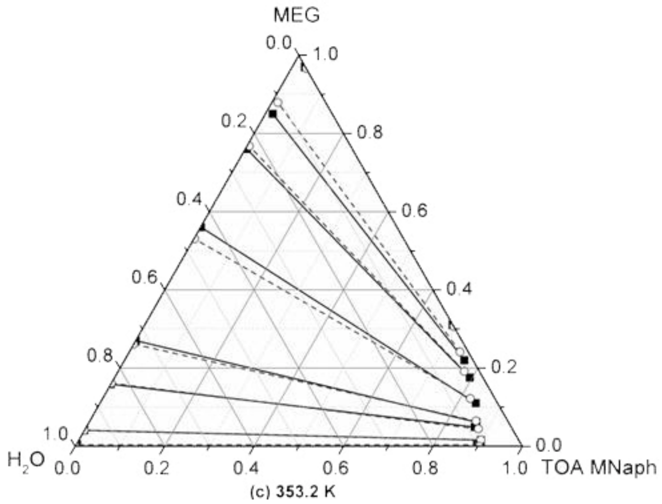
The experimental D_{MEG} and selectivity were calculated with equations 4.1 – 4.3, and compared with the calculated values using the NRTL and UNIQUAC models, respectively. From these figures it can be seen that both models give a good description of the distribution coefficient and selectivity for the whole range of X_{II}^{MEG}. Nevertheless the UNIQUAC model correlated slightly better the experimental data at low MEG concentration, while the NRTL model provides a better description of selectivity at high concentrations of MEG in the raffinate, which according to the experiments remains almost constant after $x_{II}^{MEG} = 0.5$ and not decreasing as the UNIQUAC model propose. Figure 4.3 and 4.4 also show that the distribution coefficient of MEG and the selectivity are hardly affected by the temperature. This behavior is in accordance with previously reported temperature dependencies of IL containing systems [28-30]. The D_{MEG} was found to be highest for low concentrations of MEG in the aqueous phase, and reduced with increasing MEG fraction in the raffinate, to reach a minimum value when equal mass concentrations of both components (MEG-Water) are present in the raffinate. Beyond this point the D_{MEG} increases again with the concentration of MEG in the raffinate. This behavior could be related to the decrease of water content in the system and the higher concentration of MEG (which is a less polar compound than water), therefore the affinity mixture towards the hydrophobic IL increases. The behavior of the MEG distribution is beneficial for an extraction process, since the increasing D_{MEG} with decreasing x_{II}^{MEG}, enables effective extraction even at low concentrations of MEG.



(a) 313.2 K

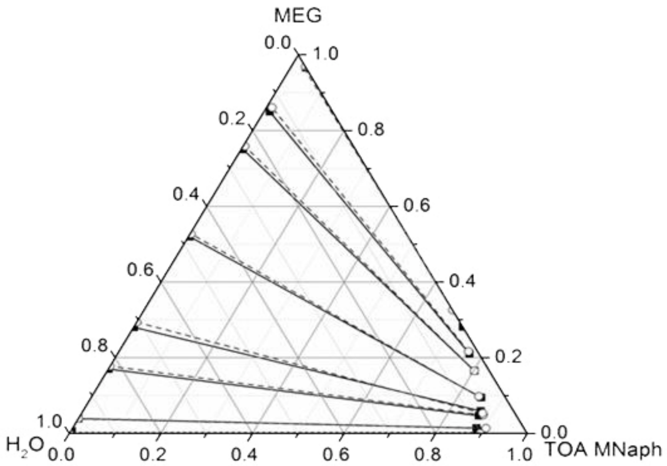


(b) 333.2 K

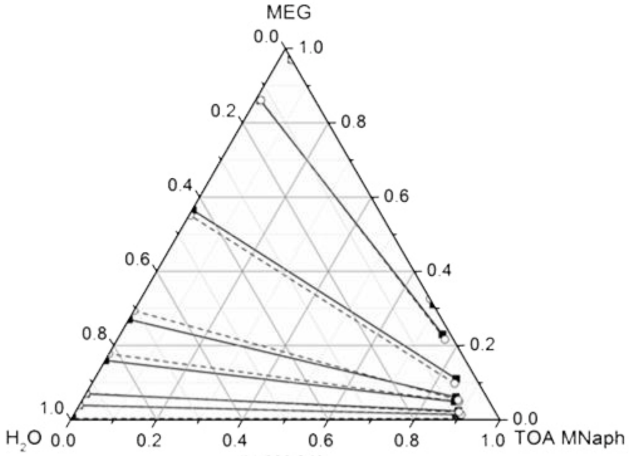


(c) 353.2 K

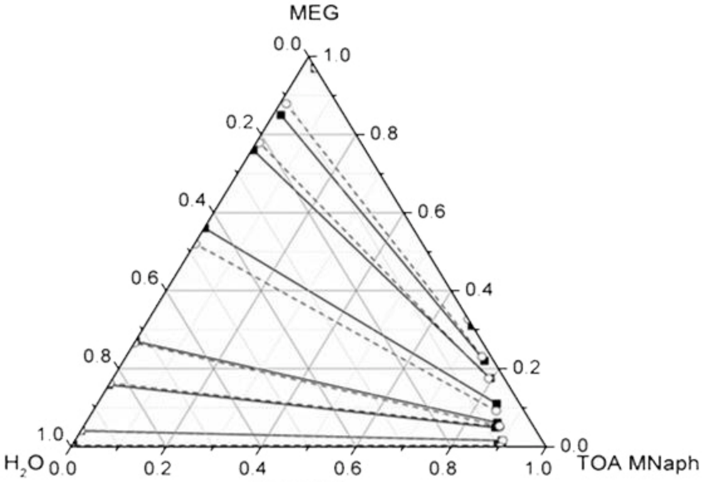
Figure 4-1. Ternary liquid-liquid equilibrium diagrams in mass fraction for the system [TOA MNaph] + MEG + Water at (a) 313.2 K, (b) 333.2 K and (c) 353.2 K. Experimental data (■ —) and NRTL model (○ ---).



(a) 313.2 K



(b) 333.2 K



(c) 353.2 K

Figure 4-2. Ternary liquid-liquid equilibrium diagrams in mass fraction for the system [TOA MNaph] + MEG + Water at (a) 313.2 K , (b) 333.2 K and (c) 353.2 K. Experimental data (■ —) and UNIQUAC model (○ ---).

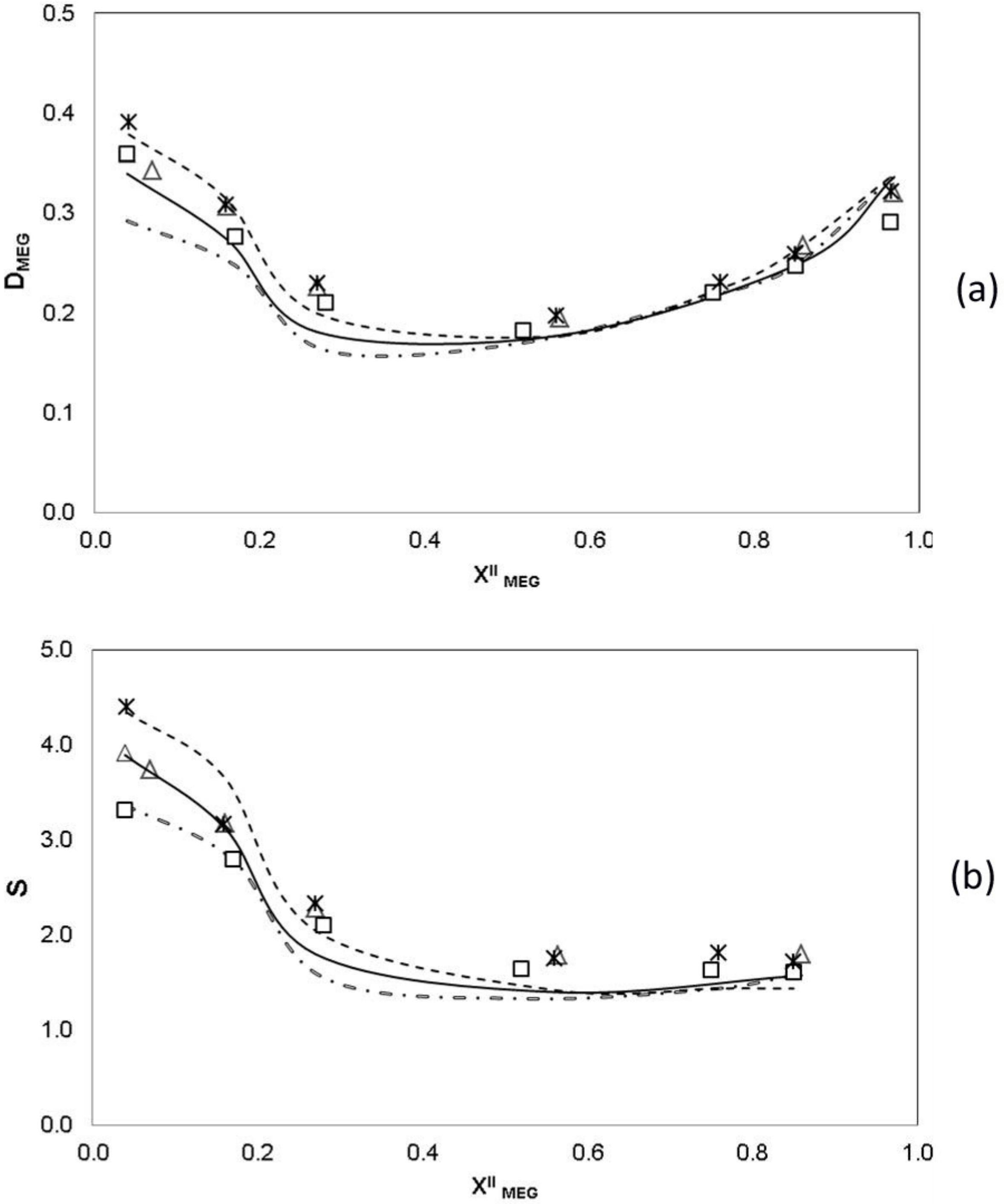


Figure 4-3. Distribution coefficient of MEG (a) and selectivity (b).Experimental data and NRTL model at 313.2 K (□) exp, (–· –·) NRTL ; 333.2 K (Δ) exp, (—) NRTL and 353.2 K (*) exp, (---) NRTL.

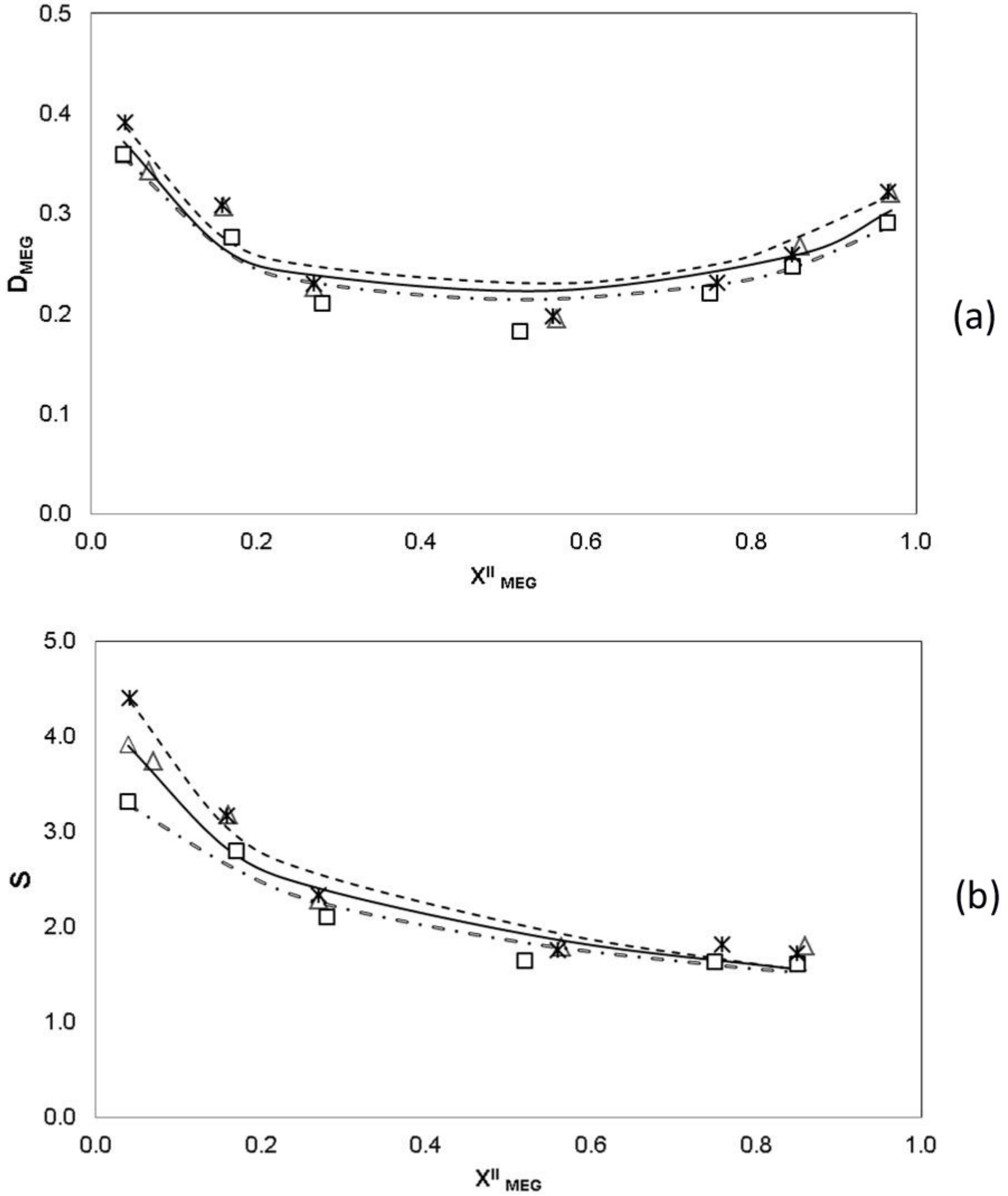


Figure 4-4. Distribution coefficient of MEG (a) and selectivity (b).Experimental data and UNIQUAC model at. 313.2 K (□) exp, (–· –·) UNIQUAC ; 333.2 K (Δ) exp, (—) UNIQUAC and 353.2 K (*) exp, (--) UNIQUAC.

Propylene Glycol

The second glycol studied was proplene glycol. For this glycol, the all the binary interaction parameters for NRTL model and UNIQUAC model, were regressed (a_{ij}, a_{ji}, b_{ij},b_{ji} and α_{ij}) and (a_{ij}, a_{ij}, b_{ij} and b_{ji}) respectivetly, were obtained by regression of the experimental data. The calculated binary interaction parameters for both models NRTL and UNIQUAC are presented in table 4-3.

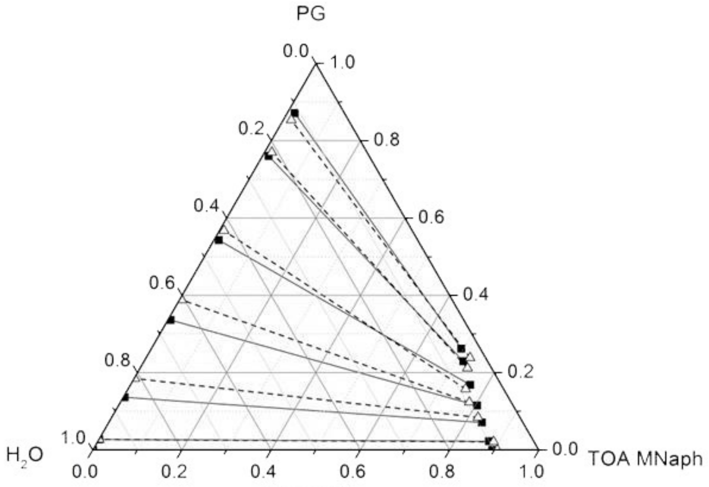
Table 4-3. Binary interaction parameter for PG, NRTL and UNIQUAC models.

	H_2O /PG (i) / (j)		H_2O / [TOA MNaph] (i) / (j)		PG/[TOA MNaph] (i) / (j)	
	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
a_{ij}	1.32	1.11	3.92	0.90	6.18	-1.01
a_{ji}	-5.198	-0.59	6.195	0.24	1.02	0.83
b_{ij}	189.05	-632.63	1537.69	728.69	477.41	907.18
b_{ji}	2036.3	363.55	-1774.70	349.78	-997.19	381.144
α_{ij}	0.84	--	0.39	--	0.24	--

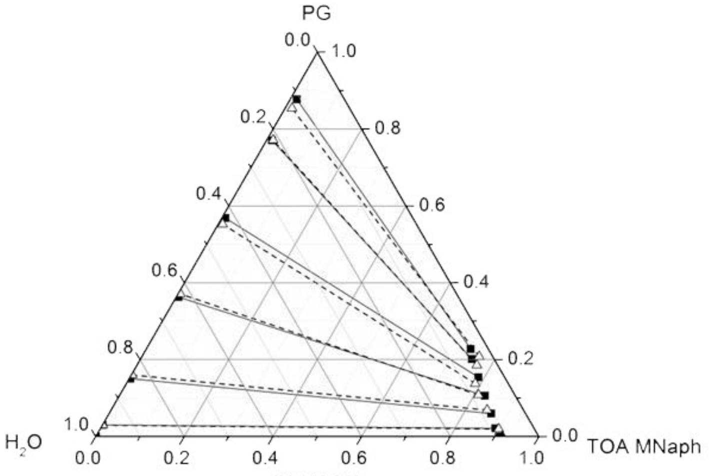
For propylene glycol, it was found that the imisibility of the system is limited, during the experiments it was observed that at 313.2 K and 333.2 K , a biphasic exists up to X_{PG},overall = 0.45. At 353.2 K, the last experiment with a X_{PG}, overall = 0.45, a single liquid phase appears. Because at all experimental temperatures the binary mixture PG – IL is always miscible, it is expected that the plait point is near to the concentration $X_{PG,overall}$= 0.47, $X_{H2O,\ overall}$ = 0.03, $X_{IL,\ overall}$=0.5 for 313.2 K and 333.15 K. At 353.2 K, the plait point is expected close to $X_{PG,overall}$= 0.45, $X_{H2O,\ overall}$ = 0.05, $X_{IL,\ overall}$=0.5. The trend in plait points can be observed in figures 4.6 (a), 4.6 (b) and 4.6 (c). Nevertheless more experimental points would be needed to exactly quantify the binodal curve, which is outside the scope of this work.

As in the case of MEG, for PG the IL content in the raffinate phase also increases with the glycol concentration in the mixture, which is an indication of the high affinity of the IL towards the glycol and the IL content for high values of x^{II}_{PG} (>0.5) decreases slightly with the temperature from 1.7 to 1.4 wt% for 313.2 to

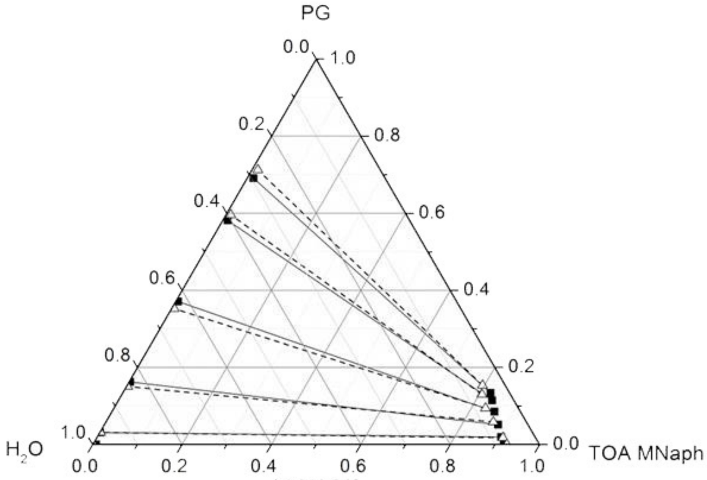
353.2 K, respectively. Nevertheless at low PG concentrations in the raffinate (x^{II}_{PG} <0.37) the solubility of the IL is almost independent of the temperature. In figures 4-5 and 4-6, the ternary diagrams for the mixture [TOA MNaph] + PG + Water and the data obtained from the NRTL and the UNIQUAC models are presented. It can be seen that both thermodynamic models can provide a good correlation with the experimental data. Nevertheless, the tie lines calculated with UNIQUAC model are somewhat better in agreement with the experimental tie lines.The experimental distribution coefficient of PG (D_{PG}), the distribution coefficient of water (D_{H2O}), and the selectivity (S) are compared with the values obtained with the NRTL and UNIQUAC models in figures 4-7 and 4-8, respectively. Here, it can be seen that both models give a good description of the distribution coefficients of PG and selectivity over the whole range of x^{II}_{PG}. Nevertheless, for the distribution coefficient of H2O the UNIQUAC model provided a somewhat better correlation. The solvent capacity of glycol, $D_{PG,}$ decreases with increasing concentration of glycol in the aqueous phase (x^{II}_{PG}), while for the distribution coefficient of water D_{H2O} the opposite effect is observed. This causes a decline in the selectivity with increasing glycol concentration. With respect to temperature, it was found that the D_{PG} and D_{H2O} decrease slightly with increasing temperature. The change in D_{PG} and D_{H2O} could be related to the fact that the strength of the intermolecular hydrogen bonds between glycol-ionic liquid and also water decreases with increasing the temperature as studied by Miran and coworkers [31], and thus the solubility of both PG and water in the IL phase decreases. The highest D_{PG} (0.85) and selectivity (8.2) were found at $x^{II}_{PG} = 0.027$ at 313.2 K.



(a) 313.2 K

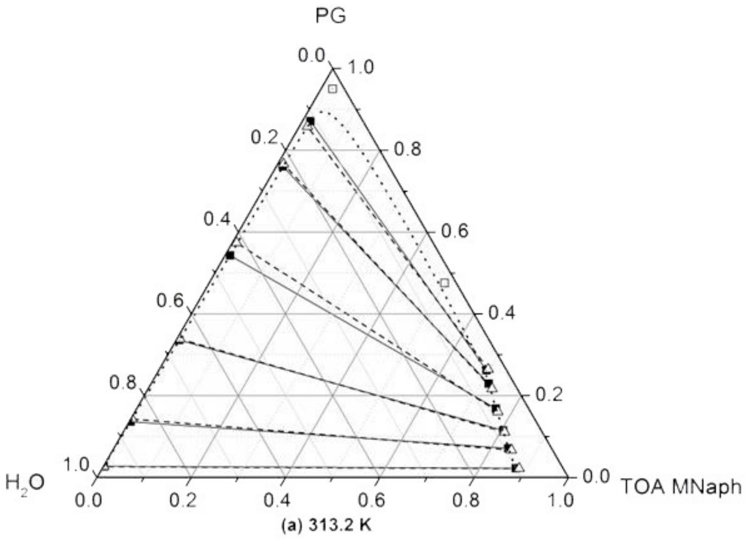


(b) 333.2 K

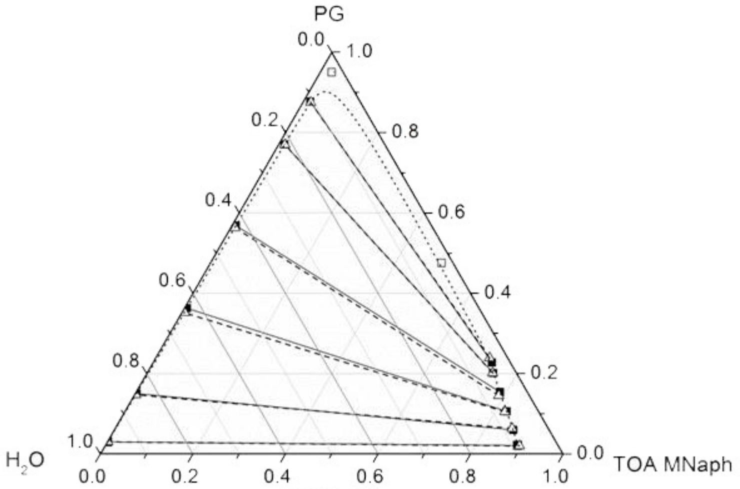


(c) 353.2 K

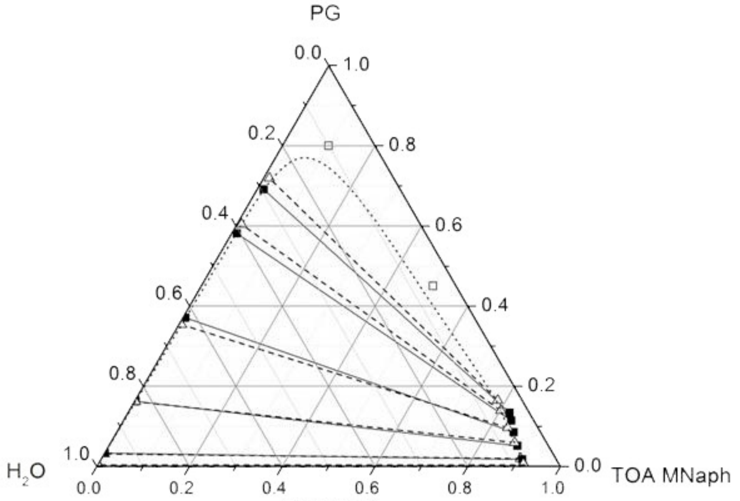
Figure 4-5. Ternary liquid-liquid equilibrium diagrams in mass fraction for the system [TOA MNaph] +PG + Water. Experimental data (■ —) and NRTL model (Δ ---).



(a) 313.2 K



(b) 333.2 K



(c) 353.2 K

Figure 4-6. Ternary liquid-liquid equilibrium diagrams in mass fraction for the system [TOA MNaph] + PG + Water. Experimental data (■ —), UNIQUAC model (Δ ---), experimental data single phase (□) and binodal curve trend (…).

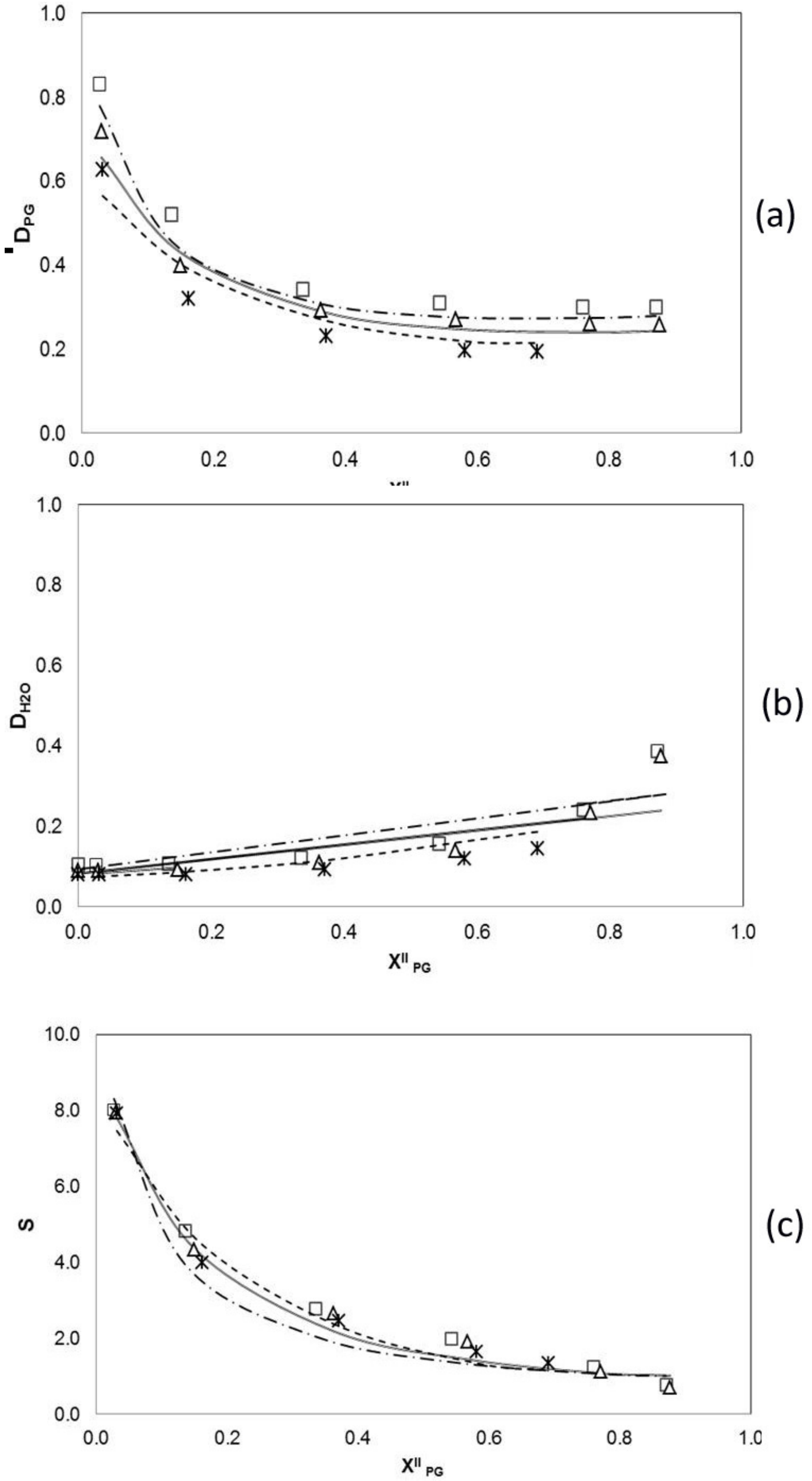


Figure 4-7 . Distribution coefficient of PG (a), distribution coefficient of H2O (b) and selectivity (c).Experimental data and NRTL model at 313.2 K (□) exp, (–· –·) NRTL ; 333.2 K (Δ) exp, (—) NRTL and 353.2 K (*) exp, (---) NRTL.

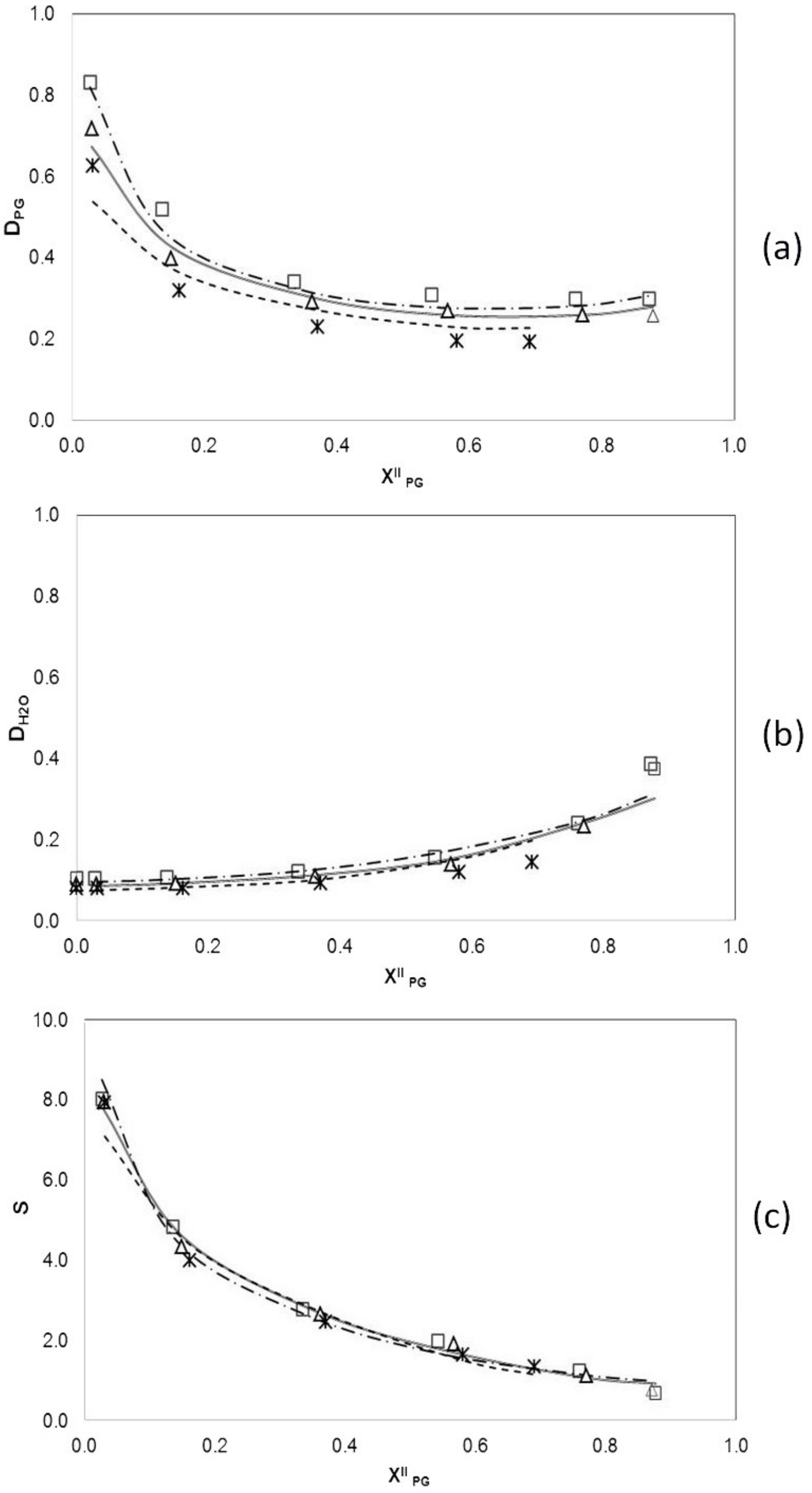


Figure 4-8. Distribution coefficient of PG (a) and selectivity (b).Experimental data and UNIQUAC model at. 313.2 K (□) exp, (–· –·) UNIQUAC ; 333.2 K (Δ) exp, **(—)** UNIQUAC and 353.2 K (*) exp, (--) UNIQUAC.

2,3-Butanediol

For 2,3-BD it was found that is completely miscible with [TOA MNaph] over the whole range of binary compositions and the three investigated temperatures, and also several ternary mixtures with a high 2,3-BD content formed a single homogeneous liquid phase. This type I phase behavior observation is comparable to the behavior of the ternary system water + [TOA MNaph] + propylene glycol [1]. The system water + [TO MNaph] + mono ethylene glycol in contrary, exhibits a type II ternary phase diagram [2]. The regression results for the calculated binary interaction parameters for both thermodynamic models NRTL and UNIQUAC are presented in table 4-4.

Table 4-4. Binary interaction parameters for 2,3-BD, NRTL and UNIQUAC models.

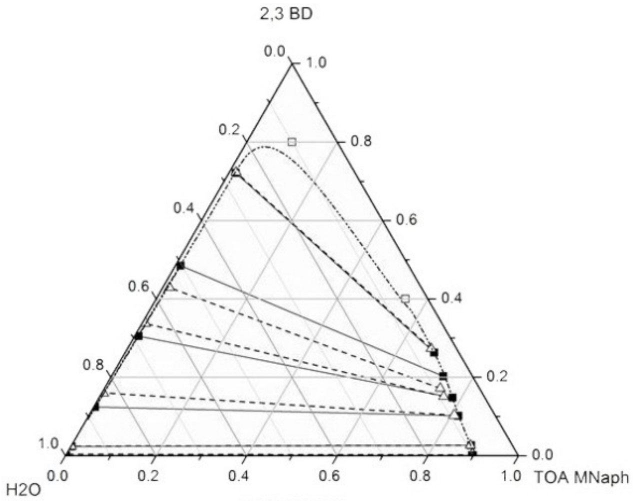
	H_2O /2,3-BD (i)/(j)		H_2O / [TOA MNaph] (i)/(j)		2,3-BD /[TOA MNaph] (i)/(j)	
	NRTL	UNIQUAC	NRTL	UNIQUAC	NRTL	UNIQUAC
a_{ij}	0^a	1.04	0^a	-2.16	0^a	-1.65
a_{ji}	0^a	6.01	0^a	-1.62	0^a	3.01
b_{ij}	3199.50	-97.46	21024.35	284.70	15678.62	563.62
b_{ji}	-2020.71	2896.10	-11448.3	232.04	-7457.96	321.80
α_{ij}	0.069	--	0.018	--	0.039	--

^{a} fixed values in the regression

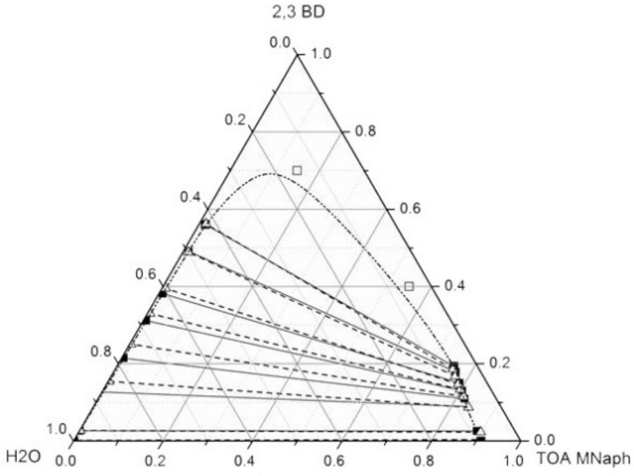
The binodal curve of 2,3-BD was estimated based on the compositions at which just biphasic behavior was observed, e.g. $X_{2,3\text{-BD,overall}} = 0.40$ $X_{H2O,\ overall} = 0.1$, $X_{IL,\ overall}=0.5$ at 313.2 K, and some experimental points with close overall composition, e.g. $X_{2,3\text{-BD,overall}} = 0.3$ $X_{H2O,\ overall} = 0.2$, $X_{IL,\ overall} = 0.5$ at 313.2 K that showed a single liquid phase. As a result of this miscibility between [TOA MNaph] and 2,3-BD, the leaching of [TOA MNaph] to the raffinate phase increases with the 2,3-BD content in the mixture. At $x^{II}_{2,3\text{-BD}} < 0.3$, the leaching of the IL is negligible, and is not affected by the temperature. The phase behavior is illustrated in the ternary diagrams in figures 4-9 (including the modeled tie lines using the NRTL model) and 4-10 (including the modeled tie lines using the UNIQUAC model).

The area of the two-phase region decreases with the hydrophobicity of the glycol in the following order MEG > PG > 2,3BD, which is a logical result due to the hydrophobic character of the IL. The comparison of the experimental distribution coefficients of 2,3-BD ($D_{2,3\text{-}BD}$) and water (D_{H2O}), as well as the selectivity (S) against the with the NRTL and UNIQUAC models results are shown in figures 4-11 and 4-12. It is visible that, the $D_{2,3\text{-}BD}$, increases with decreasing concentration of 2,3-BD in the aqueous phase ($x_{II2,3\text{-}BD}$), while the distribution coefficient of water D_{H2O} slightly decreases, resulting in an increasing selectivity with decreasing 2,3-BD concentration. The same effect was observed for PG and MEG [1,2] and this behavior is especially interesting since in situ extractions from fermentations are typically done at low solute concentrations.

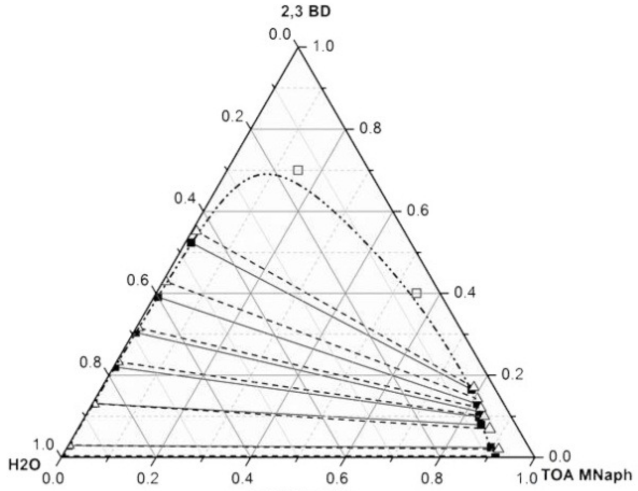
Regarding the effect of temperature in the $D_{2,3\text{-}BD}$ and D_{H2O}, it can be seen that both decrease with increasing temperature. This behavior was previously reported for the propylene glycol [1], and is likely due to the reduced strength of the hydrogen bonds between glycol-ionic liquid and water- ionic liquid [31]. As shown in figure 4-11 and 4-12 the distribution coefficient of water showed bigger deviations compared to the experimental data, this can be due to these thermodynamic models are develop for the molecular systems and not for ionic species as the IL, therefore these thermodynamic models do take into account the possible dissociation of the IL in aqueous phase, as explained by Simoni and coworkers [27]. The highest $D_{2,3\text{-}BD}$ (1.08) and selectivity (11.47) were found at $x^{II}_{2,3\text{-}BD} = 0.024$ at 313.2 K. In comparison with the solvents presented in table 1, [TOA MNaph] has a higher distribution coefficient and selectivity than butanol ($D_{2,3\text{-}BD}$= 0.89, S=2.9), the conventional solvent with the highest reported distribution coefficient. Even though [TOA MNaph] does not have a selectivity as high as methyl vinyl carbinol acetate (which has a selectivity of S=19.7), the combination of the best D and a high S, makes [TOA MNaph] a promising solvent for the extraction of 2,3-BD from aqueous streams.



(a) 313.15 K

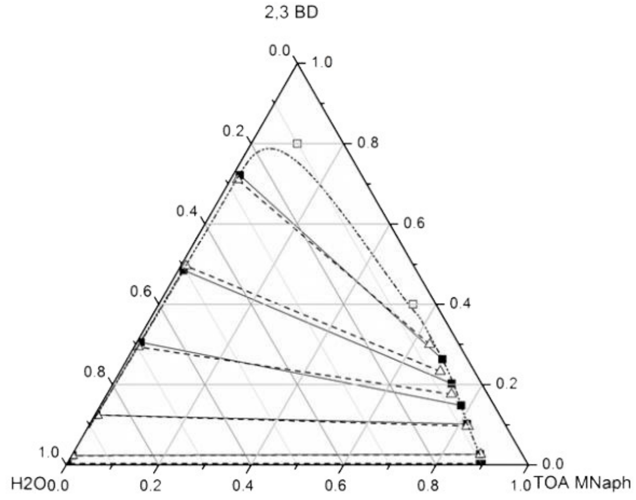


(b) 333.15 K

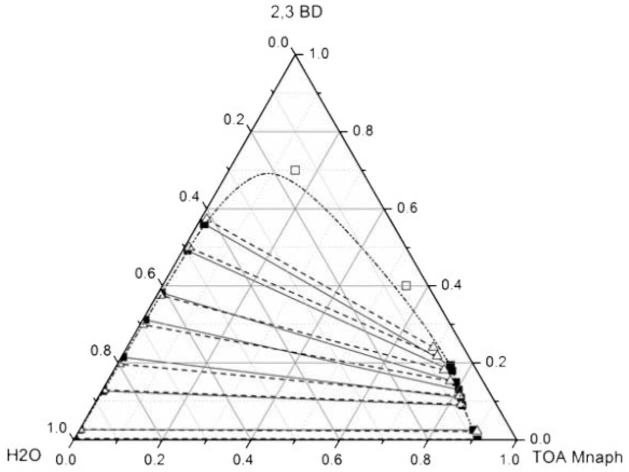


(c) 353.15 K

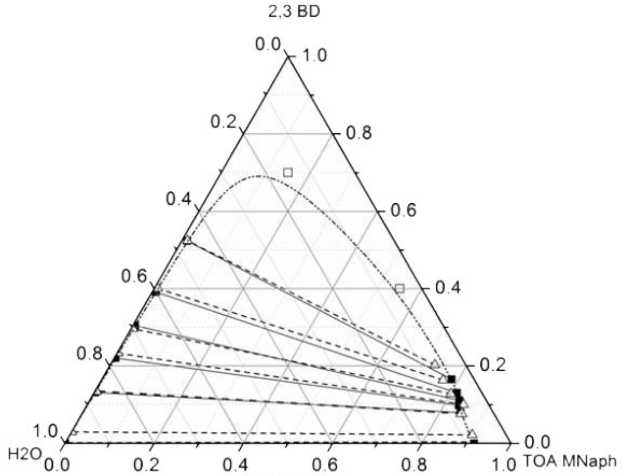
Figure 4-9. Ternary liquid-liquid equilibrium diagrams in mass fraction for the system [TOA MNaph] +2,3-BD + Water. Experimental data (■ —) and NRTL model (Δ ---), experimental single phase (□) and binodal curve trend (-··).



(a) 313.15 K



(b) 333.15 K



(c) 353.2 K

Figure 4-10. Ternary liquid-liquid equilibrium diagrams in mass fraction for the system [TOA MNaph] + 2,3-BD + Water. Experimental data (■ —),UNIQUAC model (Δ ---), experimental data single phase (□) and binodal curve trend (-··).

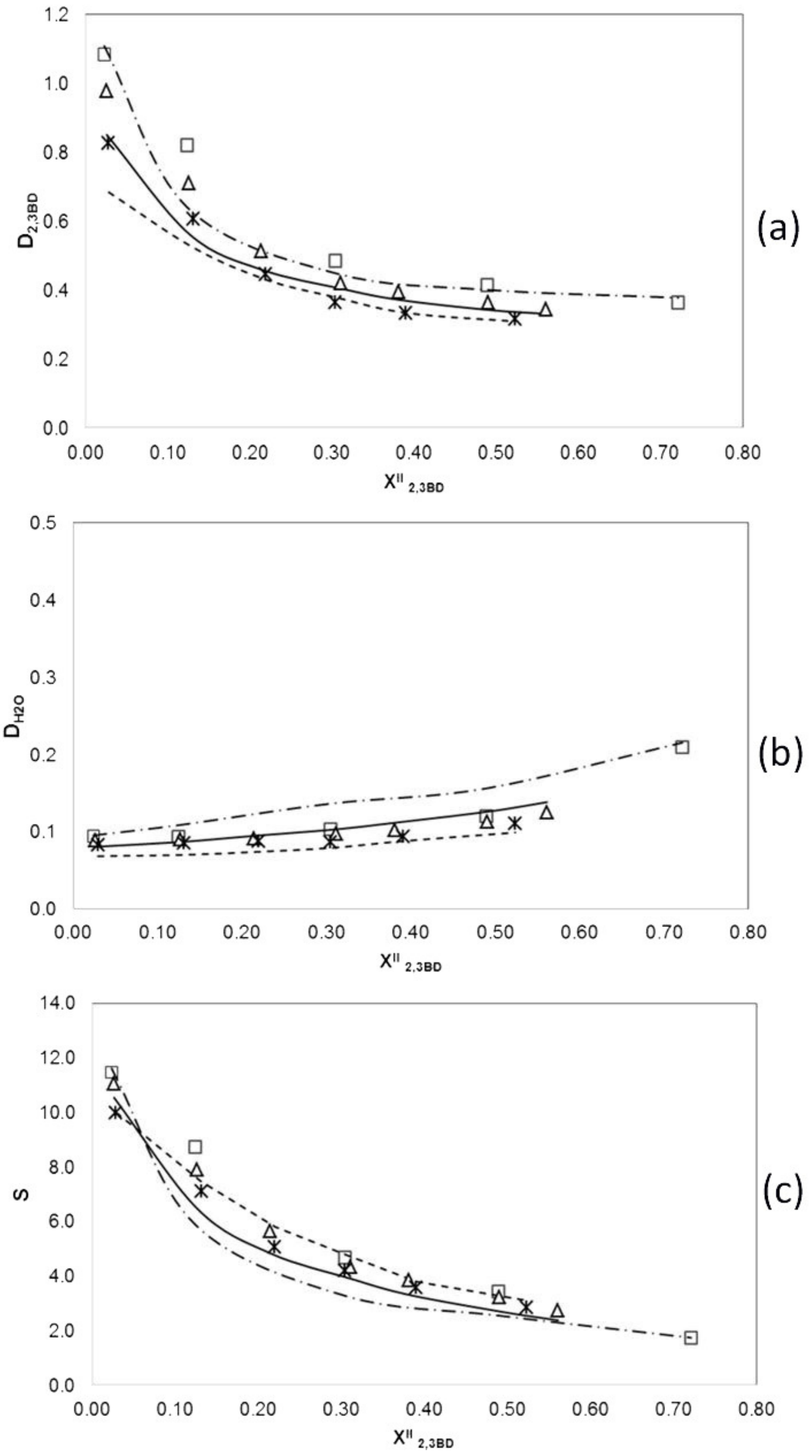


Figure 4-11. Distribution coefficient of 2,3-BD (a), distribution coefficient of water (b), and selectivity (c).Experimental data and NRTL model at 313.2 K (□) exp, (–· –·) NRTL ; 333.2 K (Δ) exp, (—) NRTL and 353.2 K (*) exp, (---) NRTL.

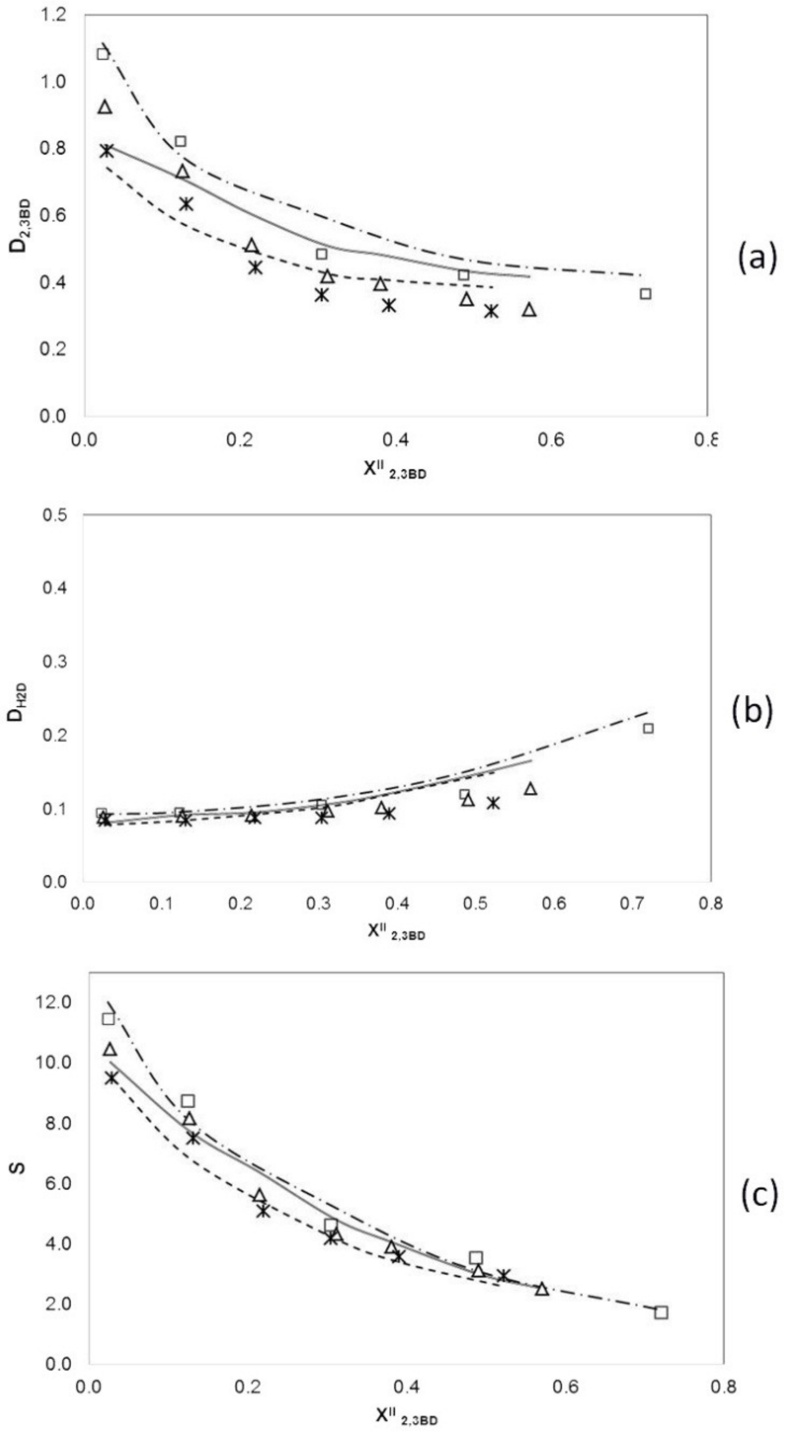


Figure 4-12. Distribution coefficient of 2,3-BD (a), distribution coefficient of water (b), and selectivity (c).Experimental data and UNIQUAC model at. 313.2 K (□) exp, (─· ─·) UNIQUAC ; 333.2 K (Δ) exp, (—) UNIQUAC and 353.2 K (*) exp, (---) UNIQUAC.

After evaluating the extraction of three different glycols (mono ethylene glycol, propylene glycol, and 2,3-butanediol) using [TOA MNaph] as solvent, it was found that the more hydrophobic the glycol (2,3 BD > PG > MEG), the higher the distribution coefficient and the selectivity. In the case of MEG and PG the highest values were D = 0.36 and 0.85 and S= 3.31 and 8.20 respectively [1,2].

Both NRTL and UNIQUAC models give a good correlation with the experimental data, therefore they can be used to develop conceptual process design for the extraction of glycols from aqueous streams. The goodness of the fit was determined with root mean square deviation (RMSD), according to equation 10.

$$RMSD = \sqrt{\frac{\sum_{k=1}^{N}\sum_{i=1}^{C}\sum_{l=I}^{II}\left(x_{\exp}^{l} - x_{calc}^{l}\right)^2}{2NC}} x100\% \qquad (4.10)$$

where, N is the number of experiments and C is the number of components in the system and $x_{\exp}^{l}, x_{calc}^{l}$ are the experimental and predicted compositions (in mass fraction) for the component i for the kth experiment in the phase *l*. The RMSD values obtained for the NRTL and the UNIQUAC models for MEG were 1.34% and 0.89%, for PG 1.51% and1.20% and for 2,3-BD were 1.54% and 1.88%.

4.5 Conclusions

In this work ternary liquid-liquid equilibrium data was reported for three different glycols (MEG, PG and 2,3-BD) at three different temperatures (313.2, 333.2 and 353.2) K. Two well-known thermodynamic models for activity coefficient NRTL and UNIQUAC were used to correlate the experimental data. The results showed that the experimental data was satisfactory correlated by the models, RMSD values between 1.88 % and 0.89 %. Therefore both thermodynamic models can be used to develop a process design for the extraction of glycols from diluted aqueous solutions. It was concluded from the ternary diagrams that under the studied conditions, the MEG system always contains two liquid phases, and that the distribution of MEG shows a beneficial behavior for liquid-liquid extraction, because the D_{MEG} increases with decreasing x_{II}^{MEG}. Furthermore, it was found that at higher glycols concentrations, the leaching of the IL to the raffinate phase could not be neglected. For the system PG and 2,3-BD a type I ternary phase behavior was observed. In all cases the highest distribution obtained with [TOA MNaph] was at 313.2 K and at low glycol concentrations. This IL present a good balance between the distribution coefficient and selectivity , which is one of the main advantages compared to the reported conventional solvent , making [TOA MNaph] a promising solvent for the extraction of glycols.

4.6 References

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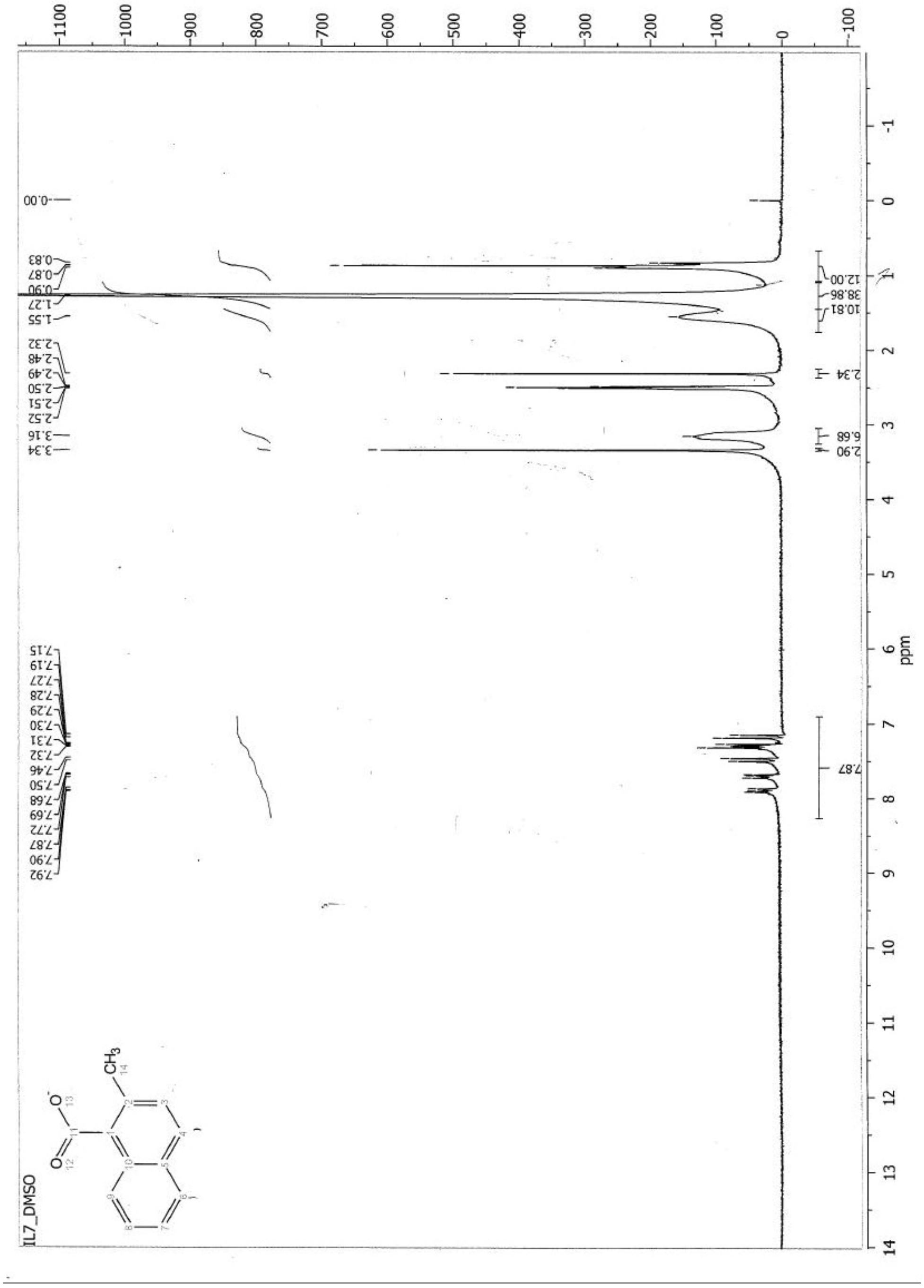
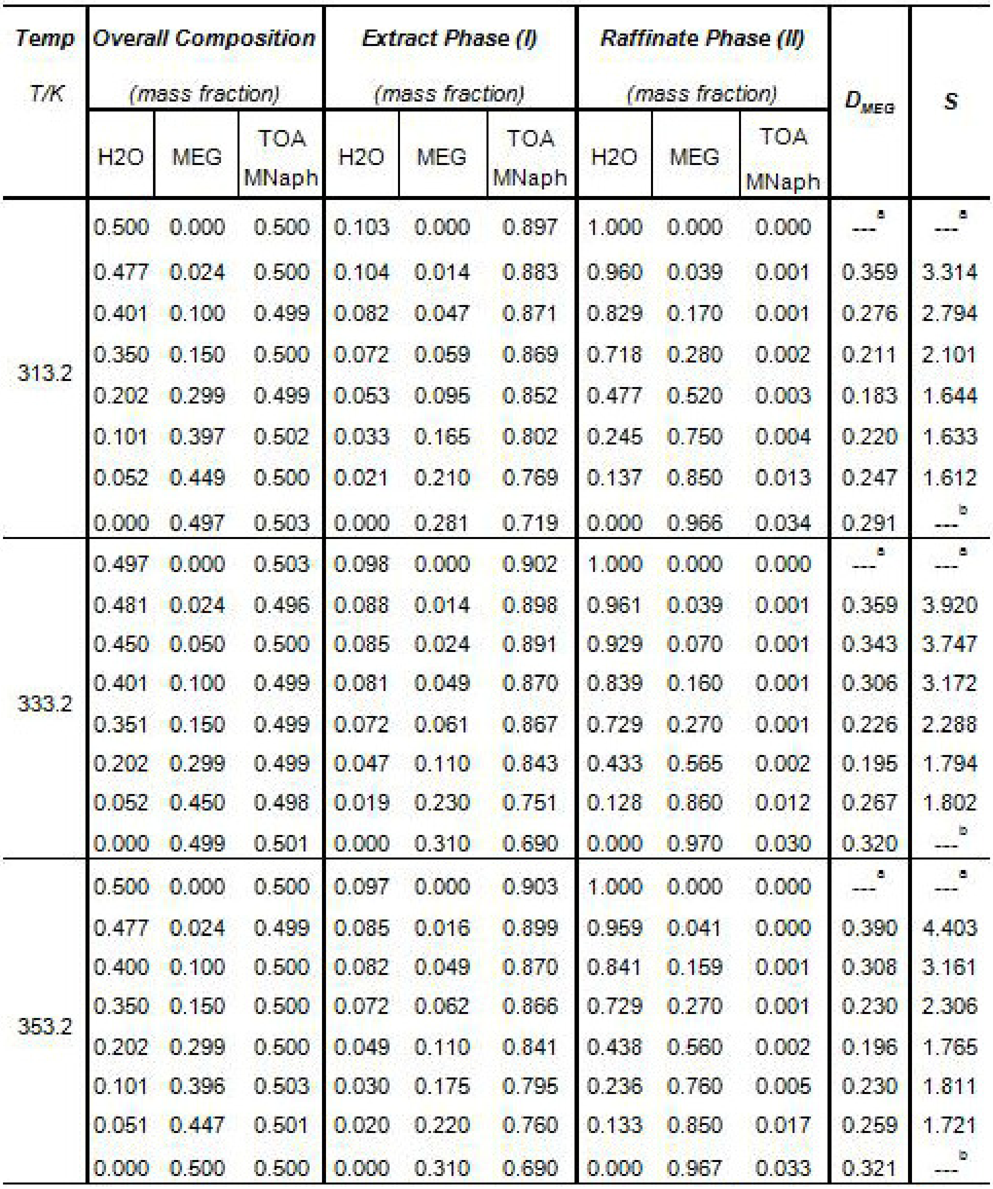
Appendix A

Proton H^1 NMR spectrum for Tetraoctyl ammonium methyl Naphtoate[TOA MNaph].



Appendix B

Experimental liquid-liquid equilibrium data (mass fraction) for [TOA MNaph] +MEG+ Water at different temperatures. [C]



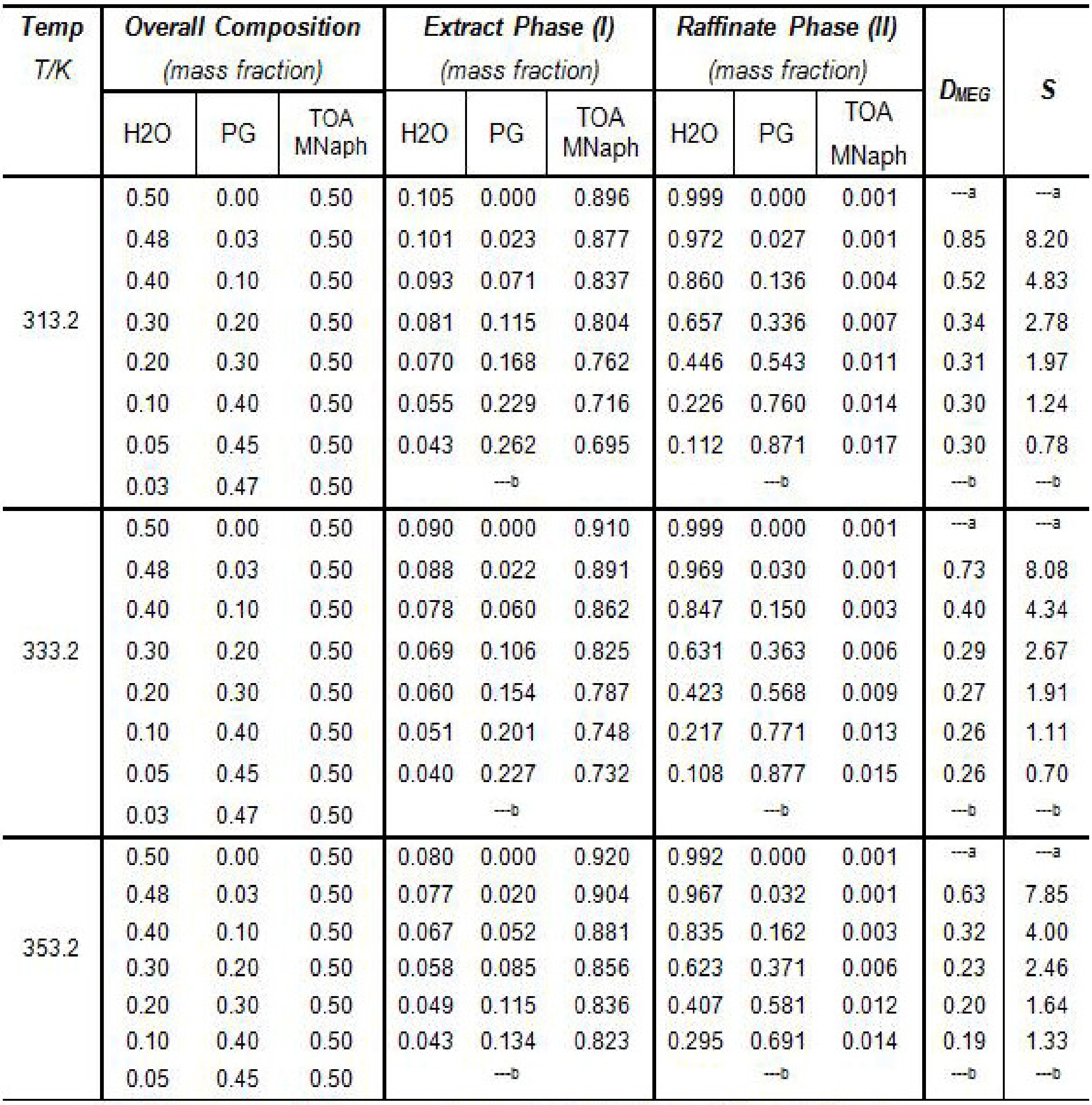
Temp *T/K*	*Overall Composition* *(mass fraction)*			*Extract Phase (I)* *(mass fraction)*			*Raffinate Phase (II)* *(mass fraction)*			D_{MEG}	*S*
	H2O	MEG	TOA MNaph	H2O	MEG	TOA MNaph	H2O	MEG	TOA MNaph		
313.2	0.500	0.000	0.500	0.103	0.000	0.897	1.000	0.000	0.000	---[a]	---[a]
	0.477	0.024	0.500	0.104	0.014	0.883	0.960	0.039	0.001	0.359	3.314
	0.401	0.100	0.499	0.082	0.047	0.871	0.829	0.170	0.001	0.276	2.794
	0.350	0.150	0.500	0.072	0.059	0.869	0.718	0.280	0.002	0.211	2.101
	0.202	0.299	0.499	0.053	0.095	0.852	0.477	0.520	0.003	0.183	1.644
	0.101	0.397	0.502	0.033	0.165	0.802	0.245	0.750	0.004	0.220	1.633
	0.052	0.449	0.500	0.021	0.210	0.769	0.137	0.850	0.013	0.247	1.612
	0.000	0.497	0.503	0.000	0.281	0.719	0.000	0.966	0.034	0.291	---[b]
333.2	0.497	0.000	0.503	0.098	0.000	0.902	1.000	0.000	0.000	---[a]	---[a]
	0.481	0.024	0.496	0.088	0.014	0.898	0.961	0.039	0.001	0.359	3.920
	0.450	0.050	0.500	0.085	0.024	0.891	0.929	0.070	0.001	0.343	3.747
	0.401	0.100	0.499	0.081	0.049	0.870	0.839	0.160	0.001	0.306	3.172
	0.351	0.150	0.499	0.072	0.061	0.867	0.729	0.270	0.001	0.226	2.288
	0.202	0.299	0.499	0.047	0.110	0.843	0.433	0.565	0.002	0.195	1.794
	0.052	0.450	0.498	0.019	0.230	0.751	0.128	0.860	0.012	0.267	1.802
	0.000	0.499	0.501	0.000	0.310	0.690	0.000	0.970	0.030	0.320	---[b]
353.2	0.500	0.000	0.500	0.097	0.000	0.903	1.000	0.000	0.000	---[a]	---[a]
	0.477	0.024	0.499	0.085	0.016	0.899	0.959	0.041	0.000	0.390	4.403
	0.400	0.100	0.500	0.082	0.049	0.870	0.841	0.159	0.001	0.308	3.161
	0.350	0.150	0.500	0.072	0.062	0.866	0.729	0.270	0.001	0.230	2.306
	0.202	0.299	0.500	0.049	0.110	0.841	0.438	0.560	0.002	0.196	1.765
	0.101	0.396	0.503	0.030	0.175	0.795	0.236	0.760	0.005	0.230	1.811
	0.051	0.447	0.501	0.020	0.220	0.760	0.133	0.850	0.017	0.259	1.721
	0.000	0.500	0.500	0.000	0.310	0.690	0.000	0.967	0.033	0.321	---[b]

[a] since there was no MEG present in these experiments, the distribution coefficient of MEG and selectivity could not be calculated.

[b] since there was no water present in these experiments, the selectivity could not be calculated.

[c] standard uncertainties : σ(T) = 0.1, σ(MEG) = 0.003, σ(H2O) = 0.005, σ(TOA MNaph) = 0.002.

Experimental liquid-liquid equilibrium data (mass fraction) for [TOA MNaph] + PG +Water at 313.2, 333.2 and 353.2 K. [C]



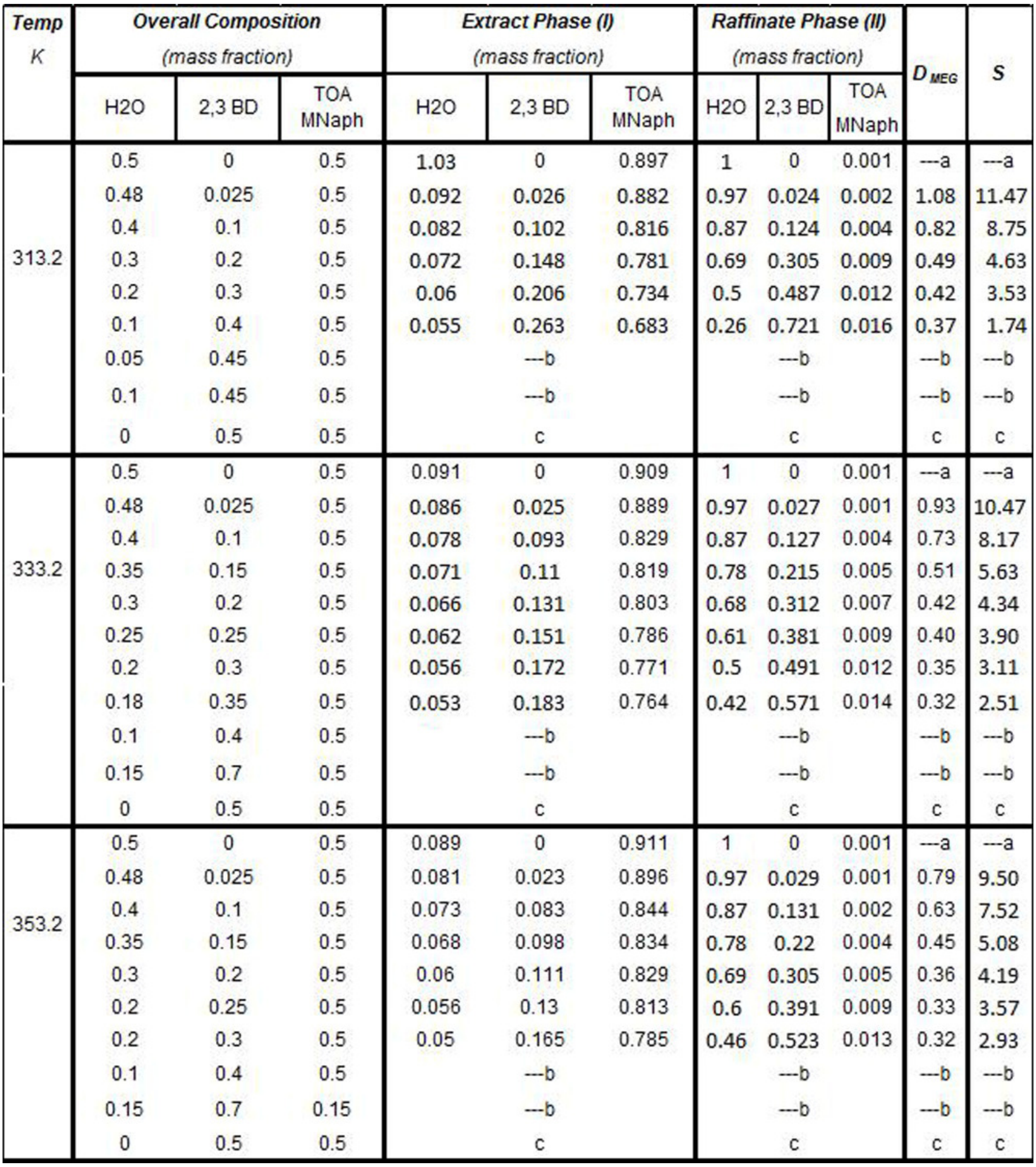
Temp *T/K*	**Overall Composition** *(mass fraction)*			**Extract Phase (I)** *(mass fraction)*			**Raffinate Phase (II)** *(mass fraction)*			D_{MEG}	**S**
	H2O	PG	TOA MNaph	H2O	PG	TOA MNaph	H2O	PG	TOA MNaph		
313.2	0.50	0.00	0.50	0.105	0.000	0.896	0.999	0.000	0.001	—[a]	—[a]
	0.48	0.03	0.50	0.101	0.023	0.877	0.972	0.027	0.001	0.85	8.20
	0.40	0.10	0.50	0.093	0.071	0.837	0.860	0.136	0.004	0.52	4.83
	0.30	0.20	0.50	0.081	0.115	0.804	0.657	0.336	0.007	0.34	2.78
	0.20	0.30	0.50	0.070	0.168	0.762	0.446	0.543	0.011	0.31	1.97
	0.10	0.40	0.50	0.055	0.229	0.716	0.226	0.760	0.014	0.30	1.24
	0.05	0.45	0.50	0.043	0.262	0.695	0.112	0.871	0.017	0.30	0.78
	0.03	0.47	0.50		—[b]			—[b]		—[b]	—[b]
333.2	0.50	0.00	0.50	0.090	0.000	0.910	0.999	0.000	0.001	—[a]	—[a]
	0.48	0.03	0.50	0.088	0.022	0.891	0.969	0.030	0.001	0.73	8.08
	0.40	0.10	0.50	0.078	0.060	0.862	0.847	0.150	0.003	0.40	4.34
	0.30	0.20	0.50	0.069	0.106	0.825	0.631	0.363	0.006	0.29	2.67
	0.20	0.30	0.50	0.060	0.154	0.787	0.423	0.568	0.009	0.27	1.91
	0.10	0.40	0.50	0.051	0.201	0.748	0.217	0.771	0.013	0.26	1.11
	0.05	0.45	0.50	0.040	0.227	0.732	0.108	0.877	0.015	0.26	0.70
	0.03	0.47	0.50		—[b]			—[b]		—[b]	—[b]
353.2	0.50	0.00	0.50	0.080	0.000	0.920	0.992	0.000	0.001	—[a]	—[a]
	0.48	0.03	0.50	0.077	0.020	0.904	0.967	0.032	0.001	0.63	7.85
	0.40	0.10	0.50	0.067	0.052	0.881	0.835	0.162	0.003	0.32	4.00
	0.30	0.20	0.50	0.058	0.085	0.856	0.623	0.371	0.006	0.23	2.46
	0.20	0.30	0.50	0.049	0.115	0.836	0.407	0.581	0.012	0.20	1.64
	0.10	0.40	0.50	0.043	0.134	0.823	0.295	0.691	0.014	0.19	1.33
	0.05	0.45	0.50		—[b]			—[b]		—[b]	—[b]

[a] no PG was present in these experiments, the distribution coefficient of PG and selectivity could not be calculated.

[b] a single phase was observed

[c] standard uncertainties σ(T)=0.1, σ(MEG)=0.001, σ(H2O)=0.005, σ(TOA MNAph)=0.002.

Experimental binary and ternary equilibrium data (mass fraction) for [TOA MNaph] + 2,3-BD + Water at 313.2, 333,2, and 353.2 K. [d]



Temp K	Overall Composition (mass fraction)			Extract Phase (I) (mass fraction)			Raffinate Phase (II) (mass fraction)			D_{MEG}	S
	H2O	2,3 BD	TOA MNaph	H2O	2,3 BD	TOA MNaph	H2O	2,3 BD	TOA MNaph		
313.2	0.5	0	0.5	1.03	0	0.897	1	0	0.001	---a	---a
	0.48	0.025	0.5	0.092	0.026	0.882	0.97	0.024	0.002	1.08	11.47
	0.4	0.1	0.5	0.082	0.102	0.816	0.87	0.124	0.004	0.82	8.75
	0.3	0.2	0.5	0.072	0.148	0.781	0.69	0.305	0.009	0.49	4.63
	0.2	0.3	0.5	0.06	0.206	0.734	0.5	0.487	0.012	0.42	3.53
	0.1	0.4	0.5	0.055	0.263	0.683	0.26	0.721	0.016	0.37	1.74
	0.05	0.45	0.5		---b			---b		---b	---b
	0.1	0.45	0.5		---b			---b		---b	---b
	0	0.5	0.5		c			c		c	c
333.2	0.5	0	0.5	0.091	0	0.909	1	0	0.001	---a	---a
	0.48	0.025	0.5	0.086	0.025	0.889	0.97	0.027	0.001	0.93	10.47
	0.4	0.1	0.5	0.078	0.093	0.829	0.87	0.127	0.004	0.73	8.17
	0.35	0.15	0.5	0.071	0.11	0.819	0.78	0.215	0.005	0.51	5.63
	0.3	0.2	0.5	0.066	0.131	0.803	0.68	0.312	0.007	0.42	4.34
	0.25	0.25	0.5	0.062	0.151	0.786	0.61	0.381	0.009	0.40	3.90
	0.2	0.3	0.5	0.056	0.172	0.771	0.5	0.491	0.012	0.35	3.11
	0.18	0.35	0.5	0.053	0.183	0.764	0.42	0.571	0.014	0.32	2.51
	0.1	0.4	0.5		---b			---b		---b	---b
	0.15	0.7	0.5		---b			---b		---b	---b
	0	0.5	0.5		c			c		c	c
353.2	0.5	0	0.5	0.089	0	0.911	1	0	0.001	---a	---a
	0.48	0.025	0.5	0.081	0.023	0.896	0.97	0.029	0.001	0.79	9.50
	0.4	0.1	0.5	0.073	0.083	0.844	0.87	0.131	0.002	0.63	7.52
	0.35	0.15	0.5	0.068	0.098	0.834	0.78	0.22	0.004	0.45	5.08
	0.3	0.2	0.5	0.06	0.111	0.829	0.69	0.305	0.005	0.36	4.19
	0.2	0.25	0.5	0.056	0.13	0.813	0.6	0.391	0.009	0.33	3.57
	0.2	0.3	0.5	0.05	0.165	0.785	0.46	0.523	0.013	0.32	2.93
	0.1	0.4	0.5		---b			---b		---b	---b
	0.15	0.7	0.15		---b			---b		---b	---b
	0	0.5	0.5		c			c		c	c

[a] no 2,3-BD was present in these experiments, therefore distribution coefficient of 2,3-BD and selectivity could not be calculated.

[b] a single phase was observed.

[c] for binary 2,3-BD and [TOA MNaph] several experiments were done, but for all concentration ratios, a single phase was observed.

[d] standard uncertainties σ(T)=0.1, σ(MEG)=0.001, σ(H2O)=0.005, σ([TOA MNaph])=0.003

Chapter 5.

Conceptual Process Design and Economic Analysis of Liquid-Liquid Extraction using Ionic Liquids for the Recovery of Glycols from Aqueous Streams[1]

[1]the content of this chapter was submitted as:
L.Y. Garcia-Chavez, B. Schuur, A. B. de Haan (2012)
Conceptual Process Design and Economic Analysis of a Process based on liquid-liquid extraction for the Recovery of Glycols from Aqueous Streams.
Industrial &Engineering Chemistry Research

Abstract

The recovery of mono ethylene glycol (MEG) and 1,2-Propylene glycol (PG) from aqueous streams via liquid liquid extraction (LLE) using a tailor made ionic liquid [TOA MNaph] is evaluated as an alternative technology to conventional triple effect evaporation of water. In this chapter the conceptual process designs for the purification of aqueous MEG from petrochemical feedstock and the recovery of PG from fermentation broths using both separation technologies are presented. The results show that LLE technology offers high energy savings, around 94% for MEG production (from petrochemical feedstock) and 54% for the PG (from fermentation broth) process compared to triple effect distillation. The economic evaluation shows that at current crude oil prices (€70-95/barrel) the LLE for MEG production is not a suitable option. This holds particularly for the production of MEG via fermentation. In the case of PG, even though the capital investment of the LLE process is double for the solvent extraction technology, the extraction process is beneficial in terms of total annual costs for the recovery of PG (plant capacity < 100 kton/year and glycol feed concentrations <10 % wt),due to the higher distribution coefficient and selectivity of PG comparted to MEG.

5.1 Introduction

Separations of diluted high boiling polar compounds from aqueous streams are energy intensive processes. [1] The purifications of mono ethylene glycol (MEG) and 1,2 propanediol, also known as propylene glycol (PG) from their aqueous solutions belong to these energy intensive separations. Both glycols are important chemicals within the food, cosmetic and pharmaceutical industry.[2-3] The variety of its applications includes uses as direct food additive, as emulsifier and as humectant agent in personal care products, and as carrier in pharmaceuticals. [2] It is also employed as anti-freeze, industrial coolant and aircraft deicing fluid, and as plasticizer. [4] For these two glycols, the purification is conventionally done by multiple effect evaporation or distillation, where typically large amounts of water need to be evaporated. The high heat of evaporation of water (2260 kJ/kg) and the high boiling points of the glycols (470.3 K for MEG and 460.6 K for PG (1,2 propanediol) make these processes very energy intensive.[2,3]

Liquid-liquid extraction with organic solvents (e.g. aliphatic alcohols, terpineol and phosphates) has been studied as an alternative to recover glycols from aqueous stream. However, these extraction solvents have been reported as insufficiently effective because of the low distribution of the polar glycols into the conventional solvent [5,8]. In an attempt to open opportunities for liquid-liquid extraction, we studied ionic liquids as potential solvents for separation of these polar solutes from their aqueous solutions. [6,9,10] Ionic liquids are popular in a range of fields, [11, 13] because of the ability to tailor their physico-chemical properties by variation of the chemical structure of either the cation or the anion. By tailoring the properties through both experimental and molecular modeling studies on different solvents, [6] we found several ILs performing significantly better than traditional solvents (in terms of distribution coefficients of the glycols and selectivity over water), that a more detailed conceptual process evaluation study is justified. Tetraethyl ammonium 2-methyl-1-naphtoate [TOA MNaph] was selected for this study as one of the most promising solvents for extraction of MEG [6], propylene glycol [14], 1,2 butanediol [15] and butanol. [9]

In this Chapter, the process descriptions for the production of MEG and PG using conventional multiple effect distillation and liquid liquid extraction using [TOA MNaph] as solvent are presented. The process modeling approach and considerations are explained, as well as the input for the calculation of the capital and operational expenditures (OPEX and CAPEX) and the total annual cost (TAC). These parameters were used to compare the two different processes for MEG and PG recovery from aqueous streams.

5.2 Processes Descriptions and Specifications

5.2.1 Conventional MEG production process

MEG is typically produced by an exothermic neutral non-catalytic hydrolysis reaction (pH 6-10) carried out in a tubular reactor in the presence of a large excess of water (molar ratio 1:22) at high temperatures and pressures (463.15-473.15 K and 20-30 bar) to achieve a high selectivity 89-91%. The large excess of water in the reaction is used to minimize byproduct formation (e.g. diethylene glycol (DEG), triethylene glycol (TEG), and higher oligomers).[16] As a result, the reaction product typically contains only 20 %wt MEG and 1% of byproducts, and as much as 79 % wt water. The water is then removed from the mixture by triple effect distillation. The first effect operates at the reaction pressure of typically 22 bar and is reboiled with high pressure steam. The second effect operates at lower pressure (10 bar) and driven by the overhead vapor of the first effect. The third stage operates at 5 bar, the overhead vapor is normally exported to other units in the ethylene oxide plant. The evaporated water is recovered as condensate and recycled back to the glycol reaction. After the distillation sequence, the glycol-water mixture containing 90 % wt MEG is sent to a series of vacuum distillation towers to remove the DEG, TEG, and higher oligomers. In the overall process the high energy demand is due to the evaporation of water (multiple effect distillation). The general scheme is presented in figure 5-1.[3-17]

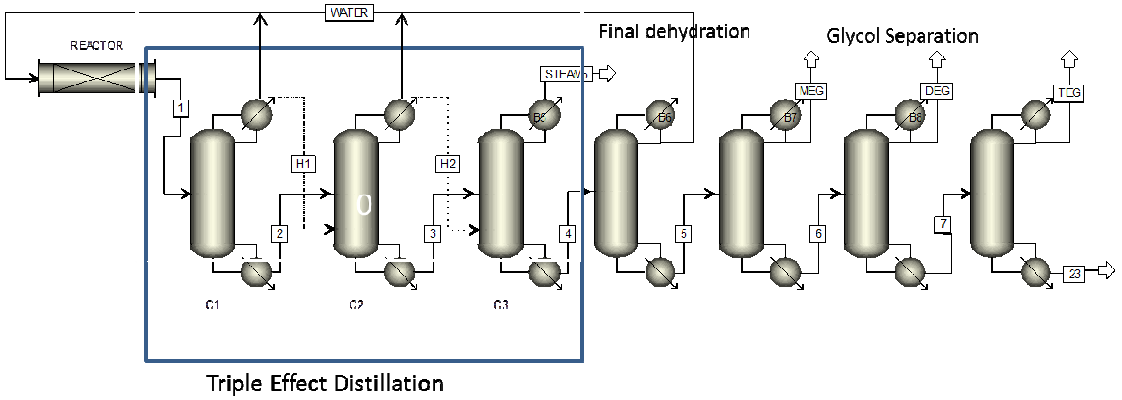


Figure 5-1. Conventional MEG production process scheme.

5.2.2 Conventional PG production process

The PG production process is based on the microbial production through direct fermentation of sugars (a renewable feedstock) using *clostridium thermosaccharolyticum* [18]. The microbiological process has a low yield and the concentration of PG in the fermentation broth is only around 1-10 % wt [19] The rest is water and other fermentation products like ethanol and organic acids. As in the case of MEG, triple effect distillation is used to recover the PG.[1] The evaporation of water is done in three columns at different pressures (1.0, 0.7 and 0.04 bar). A schematic block diagram of the conventional production of PG using multi-effect distillation is presented in figure 5-2.[3]

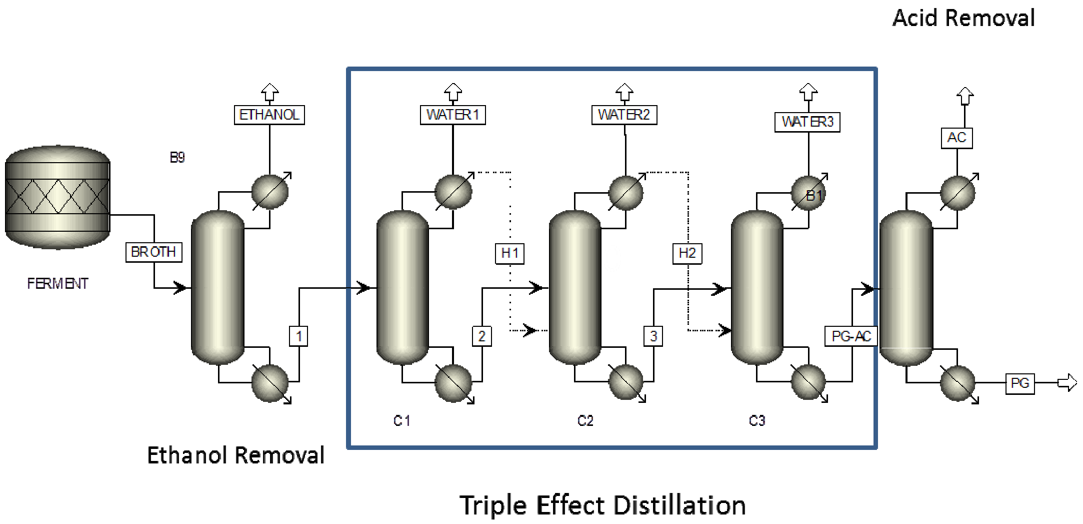


Figure 5-2. Conventional PG production process scheme.

5.2.3 Liquid-Liquid Extraction using TOA MNaph for recovery of MEG.

The liquid-liquid extraction process for the recovery of MEG (presented in figure 5-3), includes an extraction column that operates at 323.15K and 1 bar, in which the feed is counter currently brought into contact with [TOA MNaph]. The extract stream leaving the extraction column contains co-extracted water, MEG, and the solvent. Recovery of the extract stream involves a double effect distillation (columns at 1.0 and 0.2 bar) to separate the co-extracted water (over the top) from the MEG and solvent (bottom). This configuration was selected over a single distillation to minimize the energy demand. Because of the negligible vapor pressure of the IL, the MEG can be recovered from the solvent by simple evaporation instead of distillation. However, a double evaporation system operating at very low pressures (10 mbar and 1 mbar) is required to recycle the IL with a high purity (0.14 %wt) while keeping the temperature below 440.2 K. Higher temperatures are not allowed to avoid the degradation of [TOA MNaph] (more details on solvent purity and process configuration are presented in section 5.2). Although [TOA MNaph] is a hydrophobic ionic liquid with a low solubility in water (around 0.1%wt) [14], the loss of ionic liquid into the raffinate must be avoided due to the high cost of the solvent. The ionic liquid has to be recovered and sent back to the extraction process, which is done using a second extraction system where the IL is extracted into hexane, a non-polar solvent commonly used in industry.[20] The IL can be removed from the hexane using an evaporator. In the LLE process for MEG recovery, due to the high temperature and pressure of the stream coming from the reactor, a lot of energy consumption reduction is possible by heat integration (dashed lines in figure 5-3). The main energy consuming operation is the heating up of the solvent stream leaving the extraction to evaporate water and MEG The energy from the hot stream leaving the reactor is used to supply the energy to evaporate the MEG and the recycle IL hot stream (at 423.1) is used to preheat the extract phase before entering the distillation column to remove the co-extracted water.

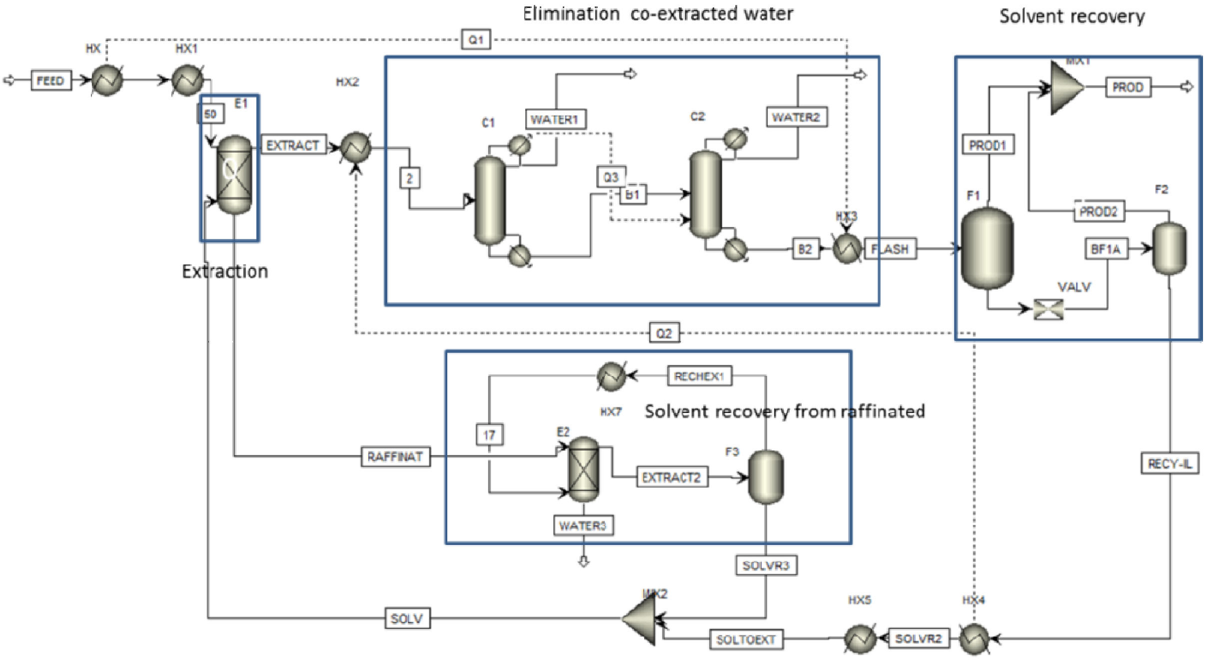


Figure 5-3. Process scheme for the LLE of MEG using [TOA MNaph].

5.2.4 Liquid-Liquid Extraction using TOA MNaph for PG recovery.

The LLE process for the recovery of PG is similar to the MEG extraction process, though operational pressures and temperatures differ. The process scheme of the LLE for PG is presented in figure 5-4. In the PG case the extraction column operates at 313.15 K and 1 bar (considering that the feed coming from the fermentation process is around this temperature and pressure). The co-extracted water is also removed using a double effect distillation as in the MEG process, and the PG –IL separation is done by evaporation of PG. In this case only one evaporator under vacuum (at 10 mbar and 438.15 K) is needed to reach the desired purity of 0.14 % wt in the recycled IL, This is expected because even though PG has a higher molecular weight than MEG, the structural isomer used in this study 1,2 propanediol has a lower boiling point (460.6 K) than MEG (470.3 K). The recovery of the IL from the raffinate stream is also done using LLE with hexane as solvent. The heat integration in the PG extraction process (dashed lines figure 5-4) is slightly different from the scheme proposed for MEG. The main difference is that the feed stream temperature for the PG process is at 313.15 K, therefore it cannot be used to provide heat in other parts of the process. Only the recycle IL stream (at 438.15 K) can be used to preheat the extract phase after the extraction and to cover part of the reboiler heat duty of the first distillation column used to evaporate the co-extracted water.

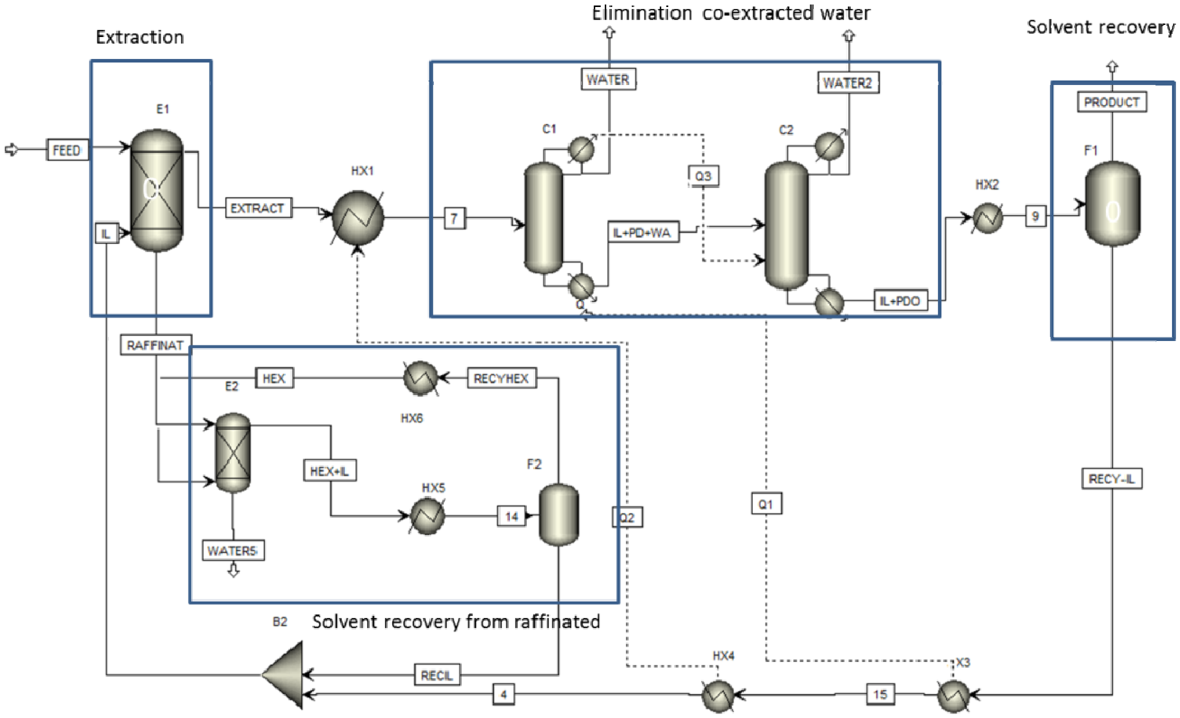


Figure 5-4. Process scheme for the LLE of PG using [TOA MNaph].

5.3 Process Simulation

Three different processes for the recovery of MEG and PG were simulated in Aspen Plus®, two scenarios for MEG and one for PG. The two scenarios for MEG differ in capacity and MEG concentration. The first MEG process has a capacity of 450 kton/year (90% wt pure MEG leaving the plant, from a feed of 20 %wt MEG in water) with the feed stream at high temperature and pressure (473 K and 22 bar). The plant capacity of 450 kton/year was chosen based on a medium size MEG plants [3]. For the second MEG process (90% wt pure MEG leaving the plant, from a feed of 10 %wt MEG in water), it was assumed that the feed is coming from fermentation (at 313 K and 1 bar) and because typical microbial production plants operate at around 100 kton/year of product, [21] this capacity was taken. For the PG process the simulation was also done for a 100 kton/year PG plant. A product purity of 99% was assumed, because in the conventional process after the triple effect distillation (in vacuum) water free PG is obtained. The PG concentration in the feed was set to 10 % wt. In the simulation, the presence of byproducts (DEG and TEG in the case of MEG production and ethanol for PG production) was not considered. For all scenarios an annual running time of 8000 hr was assumed equivalent to 56,250 kg/hr for the 450 kton/year plant and 12,500 kg/hr for the100 kton/year plant. For all three scenarios, the maximum glycol concentration in the raffinate and in the evaporated water is 1%wt glycol. With this specification the water can be reused in the reactor or fermentor without increasing the content of byproducts or affecting the process.

5.3.1 Thermodynamic Model and required properties

The equilibrium based processes have been simulated in Aspen Plus making use of the non- random two-liquid (NRTL) thermodynamic model to describe the phase equilibria. For the simulation of the triple effect evaporation process, the binary interaction parameters for the glycols and water were available in the Aspen Plus data base. For the simulation of the liquid-liquid extraction processes with TOA MNaph, the binary interaction parameters were obtained from experimental data by regression using the Aspen Regression tool, as discussed in Chapter 4. [9-14]

The binary interaction parameters for the glycol-water-IL systems are presented in table 5-1.

Table 5-1 Binary interaction parameter for NRTL model for glycol-IL-water systems. [9-14]

	H_2O / Glycol (i) / (j)		**H_2O / [TOA MNaph] (i) / (j)**		**Glycol / [TOA MNaph] (i) / (j)**	
	MEG	PG	MEG	PG	MEG	PG
a_{ij}	2.295	1.319	14.101	3.920	5.291	6.183
a_{ji}	-0.848	-5.198	-16.064	6.195	13.990	1.015
b_{ij}	338.796	189.05	-1414.56	1537.69	-200.688	477.41
b_{ji}	617.606	2036.33	6497.79	-1774.70	3732.64	-997.19
α_{ij}	0.73	0.843	0.36	0.393	0.57	0.246

The ionic liquid used in this process simulation is not available in the data bank of Aspen Plus. Therefore, in order to develop the conceptual designs, it was necessary to introduce some properties of [TOA MNaph] in the simulator Aspen Plus ®, these properties are presented in table 5-2.

Table 5-2. General properties of [TOAMNaph].

Properties [TOA MNaph]	
Critical volume (cm3/mol)	2431.8
Critical temperature (K)	1696.7
Critical pressure (bar)	6.96
Critical compressibility factor	0.12
Acentric factor-ω	0.3251
Boiling temperature (K)	1334.0
Density (g/cm^3)	0.897
Molecular weight (g/mol)	652.09
Heat capacity (J/mol K)	1505.79

The critical properties of the IL were calculated using the group contribution method as reported by Valderrama and co-workers. [22] The heat capacity of the IL was experimentally determined by differential scanning calorimetric following the methodology reported by Diedrichs. [23] The thermal stability of the IL was measured using thermo gravimetrical analysis (TGA), and it was found that above 440 K the compound starts to decompose.

5.3.2 Simulation of unit operations

The process designs include three separation unit operations, extraction, distillation and evaporation. These unit operations were simulated using the Extract, RadFrac and Flash modules of Aspen Plus®, respectively. The equilibrium stage model was used to simulate the MED and the LLE processes, this type of model is based on the MESH (Material and Equilibrium- Summation, and Heat balance). The RadFrac model was used in combination with Newton's algorithm to simulate the distillation colums.[24,25]

5.3.3 Simulation of Distillation Columns

Standard shortcut methods such as Underwood and Fenske equations have been used for first estimations in the Aspen simulations. For the distillation columns, the minimum reflux ratio and the minimum number of stages were estimated using the Underwood (equation 5.1) and Fenske (equation 5.2) equations, respectively.[26]

$$R_{min} = \frac{\frac{x_D}{x_F} - \alpha_{AB}\frac{1-x_D}{1-x_F}}{\alpha_{AB}-1} \qquad (5.1)$$

$$N_{min} = \frac{ln\left[\frac{\left(\frac{x_D}{1-x_D}\right)}{\left(\frac{x_B}{1-x_B}\right)}\right]}{\ln \alpha_{AB}} \qquad (5.2)$$

Where α_{AB} is the relative volatility between the heavy and light component and it is defined by the following equation:

$$\alpha_{AB} = \frac{y_i/x_i}{y_j/x_j} = \frac{\gamma_i P_i^o}{\gamma_i P_j^o} \qquad (5.3)$$

Where, y and x are the mole fractions of the components in the vapor and liquid phases, respectively. γ_i is the liquid phase activity coefficient, P^o is the vapor pressure. The activity coefficients can be estimated from the thermodynamic models and the vapor pressure from the Antoine equation.[24] The Antoine parameters were obtained from Aspen Plus database. For the IL, which has a negligible vapor pressure, the Antoine equation must lead us to a very small value for the vapor pressure, therefore the Antoine parameter were defined as A= -5 N/m^2 and B= -1000 N/m^2, this assumption was already used for Hansmeier and coworkers with systems containing IL.[27]

Simulation of Extraction Columns

The minimum solvent to feed rate that would be necessary to obtain the separation in an extraction column with infinite amount of equilibrium stages can be estimated according to equation 5.4:

$$\left(\frac{S}{F}\right)_{min} = \frac{X_{in}-X_{out}}{Y_{out}-Y_{in}} \qquad (5.4)$$

Where S is the solvent flow, F the feed flow and x_{in} is the mass fraction of the solute in the feed, x_{out} is the mass fraction of the solute in the raffinate, y_{in} is the mass fraction of the solute in the entering solvent and y_{out} is the mass of the solute in the extractant phase. As a good estimation of the optimal solvent to feed ratio as suggested by King, is a value between $1.15 < S/F_{min} < 2$, in this work we have selected 1.5. [1] The calculated solvent to feed rates for both glycols using [TOA MNaph] are presented in table 5-3.

Table 5-3. Parameters for liquid liquid extraction process.

Parameter	Process 1-MEG Feed 20%wt	Process 2-MEG Feed 10%wt	Process 3-PG Feed 10%wt
D_i	0.306	0.359	0.65
Selectivity	3.1	3.9	7.08
$(S/F)_{opt}$	4.9	4.19	2.31

(a) process specification based on equation 5.4.

Regarding the second extraction column, where the IL is recovered from the raffinate phase, the binary interaction parameters for the system TOA MNaph +H2O + hexane are not available. Therefore in the simulation the distribution coefficient of ionic liquid needs to be estimated from the experimental solubility data of ionic liquid in water (0.1 %wt at 333.15 K), assuming that only this mass fraction of IL will go to the aqueous phase and the rest to organic phase. Based on the aqueous solubility of the IL, the distribution coefficient of the IL into hexane will be 10^3mass based. This distribution coefficient is introduced in Aspen Plus using the KLL correlation equation. The solvent to feed ratio is calculated to be 0.001 using equation 5.4. However, in reality it is not feasible to have such low solvent flow in an extraction column, thus a solvent to feed ratio of 0.01 was taken.

5.4 Economic Evaluation

5.4.1 Operational Expenditures (OPEX) Calculation

The calculation of the cost of high and low pressure steam (per 1000 kg of stream), as function of the fuel price was done based on several assumptions, including the fuel type (price and energy content), the enthalpy difference between the saturated steam at the desired pressure and the feed water (ΔH, kJ/kg) and the efficiency of the heating system (n), as expressed in equation 5.5. [29]

$$\text{Steam Cost} = \frac{\text{Fuel Price (eur/kg)}}{\text{Fuel Energy Content (kJ /kg)}} \text{ x } \Delta H \left(\frac{\text{kJ}}{\text{kg}}\right) \text{ x } \frac{100}{\text{n}} \text{ x } 1000 \qquad (5.5)$$

The type of fuel considered in this evaluation was distillated fuel oil N.-4 with a combustion efficiency of 86%, and feed water stream at 343.15 K. The crude oil price was varied between € 50-200/ barrel, considering that in the last year the price per barrel has fluctuated between €70-95/barrel in the last year and higher increments can be expected in the following years due to fossil fuels depletion.[115] The price of cooling water was taken as € 0.03 /m^3, this value was obtained from Aspen Economic Analyzer.

5.4.2 Capital Expenditures (CAPEX) Calculation

The CAPEX estimation was done through the “percentage of delivered equipment method”, the accuracy of this method is ± 20-30% range.[31] In this method different direct and indirect costs are estimated as percentage of the equipment cost. Aspen Process Analysis was used to calculate equipment dimension and estimate the free-on-board (FOB) purchase of equipment. The diameter and the column heights of the distillation columns and evaporators were calculated in Aspen Plus. The purchase costs of pumps were not taken in account. Stainless steel was specified as material in reboilers, tanks, and internals to avoid iron contamination in the final product.[3] The total solvent investment was calculated from the total solvent hold up in the process. The solvent price was set to € 20/kg, this assumption was taken considering that this is the price for ILs already implemented at industrial scale.[32]

5.4.3 Total Annual Cost (TAC)

To compare the two different alternatives for the separation of the glycols from water streams (liquid-liquid extraction and triple effect evaporation), without involving sales revenues of products, the total annualized cost (TAC) was calculated, using the operational and capital expenditures (equation 5.6). [31]

$$\mathrm{TAC} = \mathrm{OPEX} + \mathrm{i}_{\mathrm{min}}(\mathrm{CAPEX}) \qquad (5.6)$$

A reasonable return of investment (i_{min}) of 0.3 is taken, which is generally applied for moderate risk projects.[31]

5.5 Results and Discussion

5.5.1 Triple effect evaporation

The multiple effect distillation for the three processes is very similar. However, because the feed stream condition and product purities are not the same, different process conditions were used, as mentioned in sections 2.1 and 2.2, for process 1 and process 3, respectively. For process 2, the pressure in the columns was fixed at 1, 0.5 and 0.2 bar. For process 2 and 3 a heat exchanger was required to heat up the feed to saturated liquid. The operating specifications for the different processes are presented in Table 5-4.

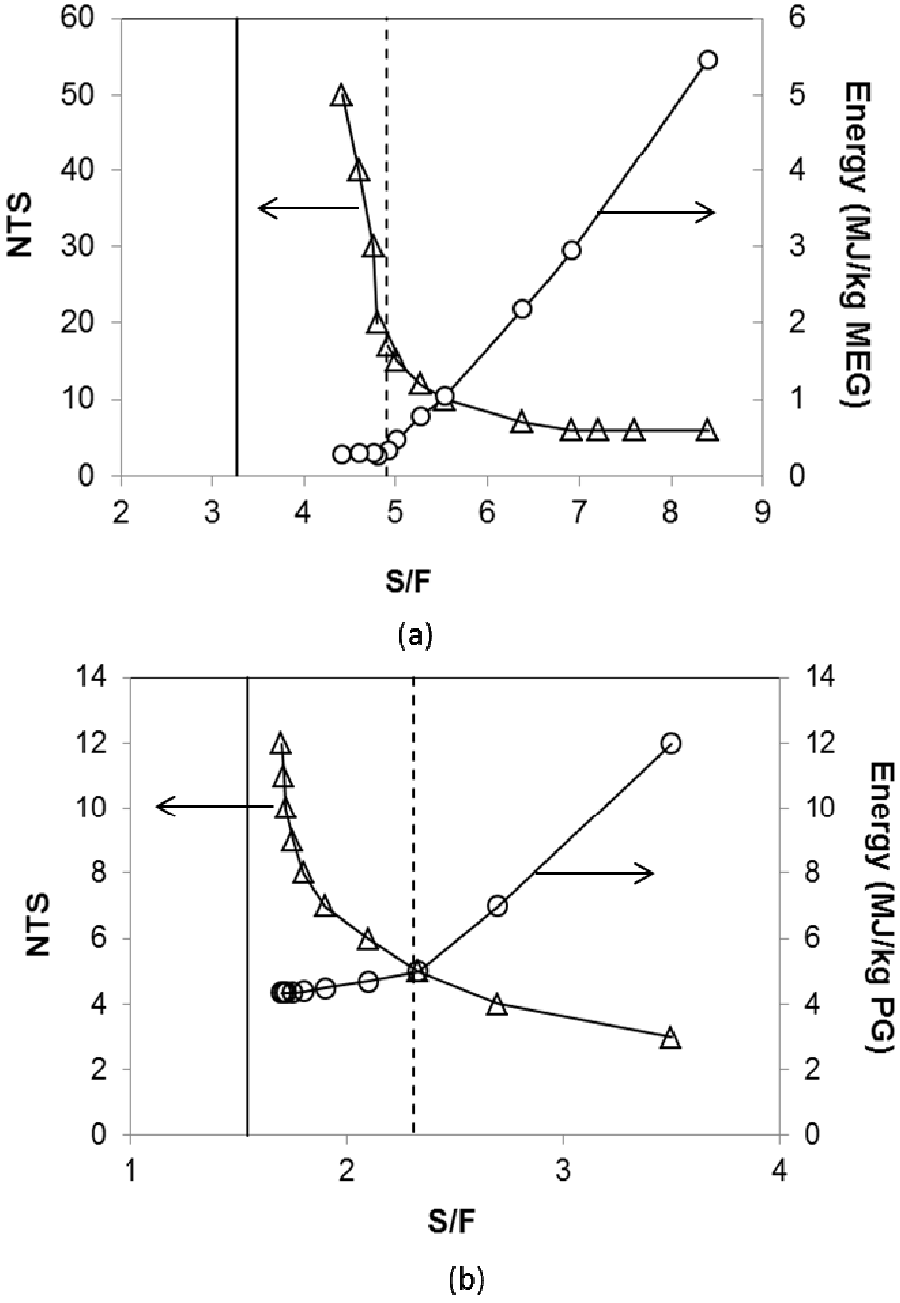
Table 5-4. Operating specifications for distillation columns in the simulation of the conventional process.

Parameter	Process 1-MEG Feed 20%wt	Process 2-MEG Feed 10%wt	Process 3-PG Feed 10%wt
Reflux Ratio[a] (R)			
C1	0.17	0.13	0.05
C2	0.15	0.10	0.04
C3	0.14	0.09	0.014
Number stages[b](N)			
C1	4	4	4
C2	4	4	4
C3	4	4	5

(a)Reflux ratio R= 1.2* Rmin, (b)Number of stages N=1.5*Nmin

5.5.2 Extraction column optimization.

In figure 5-5, the optimizations of these parameters for the extraction columns are presented. The required NTS (left y-axis) and the energy demand (right y-axis) with respect to the minimum and actual solvent to feed ratio are presented for Process 1 (MEG) and Process 3 (PG) in figures 5-5a and 5-5b respectively. For MEG extraction, the simulation result was that 17 theoretical stages will be required to reach the specification of 1% wt of MEG in the raffinate at S/F = 4.8 and lower energy demand. For the PG case, the calculated optimum conditions are S/F=1.71 was and NTS= 9. The PG extraction column process requires less solvent and number of stages, which is originated from the higher distribution coefficient and selectivity of PG towards [TOA MNaph] compared to MEG.



(a)

(b)

Figure 5-5. Determination of the required equilibrium stages and optimal solvent to feed ratio meet the extraction specifications (1%wt glycol in raffinate) and reduce energy demand. (a) Process 1-MEG (b) Process 3 –PG.

5.5.3 Ionic Liquid Recovery.

The main challenge when using solvent extraction technology is to recover the solvent with the proper purity to recycle it back into the extraction column and still reach the extraction column specification regarding the raffinate glycol concentration (1%wt glycol). The solvent purity depends on the operating conditions (temperature and pressure) of the final evaporation step, where the glycol is removed from the IL. The main constraint is the degradation temperature of the IL (440.2 K), therefore very low pressures are required (10 mbar and 1 mbar) in the evaporator. For the separation of the PG-IL, a single evaporator at 10 mbar and 438.15 K was sufficient to get a recycle IL with only 0.02%wt PG and meet the specification in extraction column. In the case of MEG recovery, as is shown in figure 5- 6, a single evaporation requires very high temperatures (up to 530.2 K) to produce high purity recycle IL (left y-axis) that allows to reach the specification of 1%wt of MEG in the raffinate phase (right y-axis).

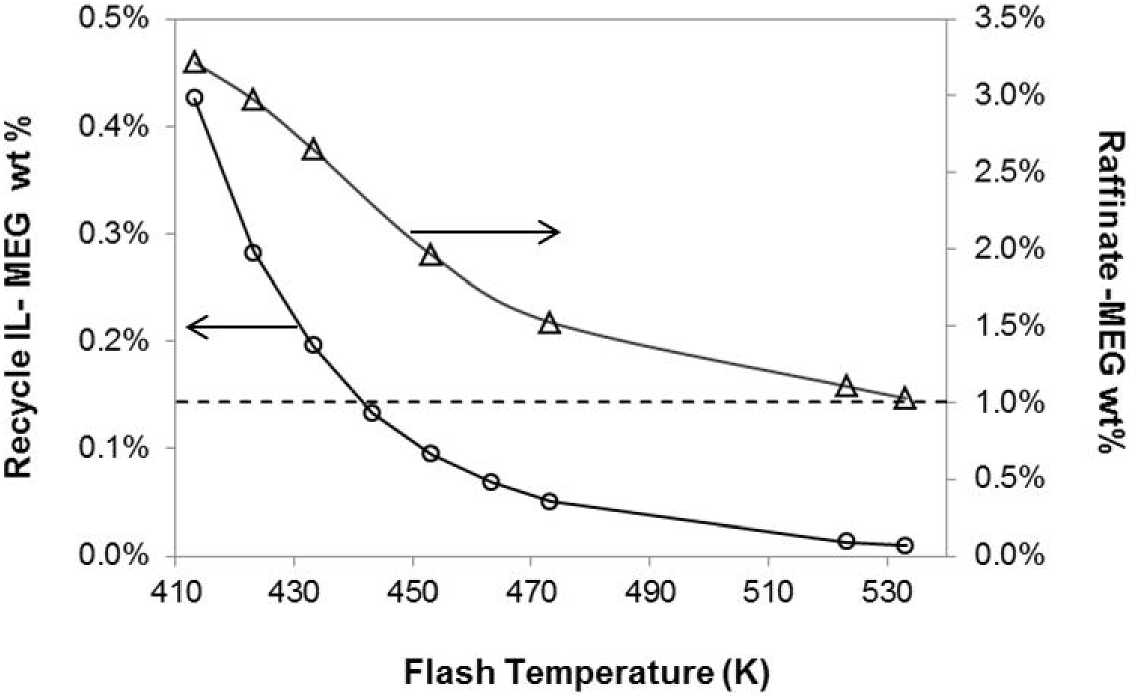


Figure 5-6. Effect of temperature in single evaporator (10 mbar) on IL recovery, MEG content in the recycled solvent and raffinate phase (Δ ,MEG %wt raffinate), (O ,MEG %wt recycled IL), (--- 1%wt, raffinate specification).

To operate the evaporator at 530.2 K has two disadvantages, the degradation of the IL and the increase of energy demand in the process. In figure 5-7, the effect of evaporator temperature in the raffinate phase (left y-axis) and influence of the energy demand in the process (right y-axis) are presented. From this figure we can see that extraction column specification of 1% MEG in the raffinate using a single evaporator is not feasible. A different configuration, based on two consecutive evaporators operating at 10 mbar and 1 mbar and 423.15Kwas proposed for the solvent recovery. From figure 5-7 (black circle), we can see that with the double evaporator system, the raffinate specification can be reached without thermal degradation of IL and at lower energy demand.

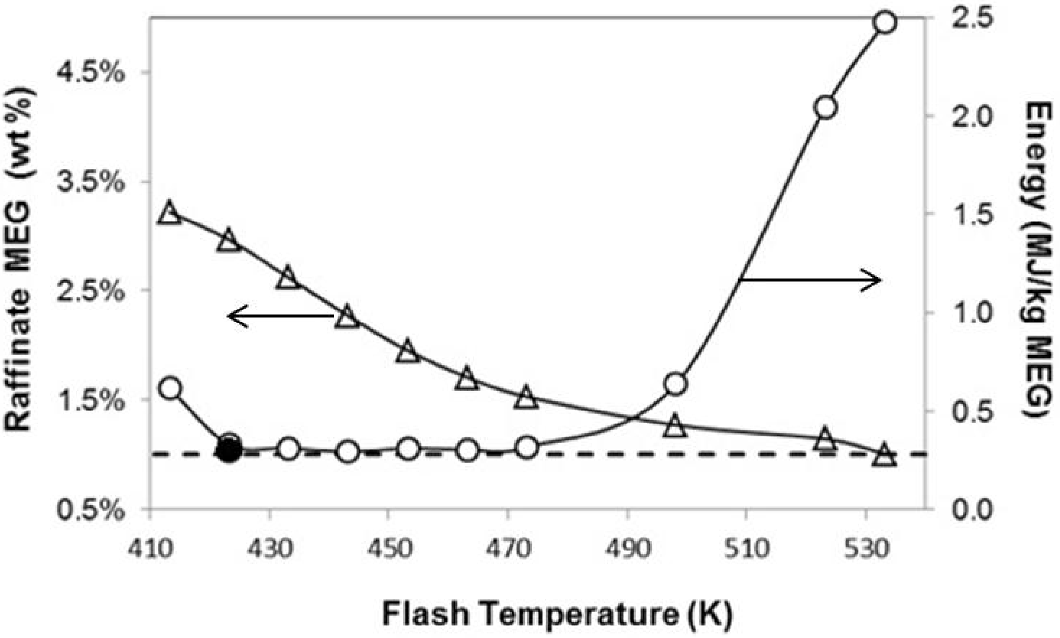


Figure 5-7. Effect of the evaporator temperature in the MEG content in the raffinate and process energy requirement (-Δ- , MEG %wt), (-O- , energy), (--- 1%wt, raffinate specification), (●, double evaporator at 10 and 1mbar)

5.5.4 Process comparison - Energy demand

Figure 5-8, shows the comparison of the energy requirements for the multiple effect distillation (MED) and solvent extraction (LLE) technology for the three different scenarios. The energy demand for the MED process is mainly due to the reboiler heat duties and in the case of the fermentation process (process 1 and 2) also a heat exchanger for preheating of the feed stream is considered. In principle, in the LLE process is very energy demanding, most of the energy is used in the solvent heating (which has a high heat capacity), and to evaporate the co-extracted water and the glycol. Without heat integration the energy demand is 10.28 MJ/kg MEG, 17.95 MJ/kg MEG and 9.34 MJ/kg PG for process 1, 2 and 3 respectively, which indeed is higher than for the conventional technology. Nevertheless, for MEG process 1, significant energy savings are possible through heat integration (see figure 5-3), especially with the MEG feed stream coming from the reactor at high temperature (495.15K). For this process changing from MED to LLE technology, represents energy savings of 94%. In the case of MEG recovery, presented in process 2, changing from a MED to LLE technology only 8% of energy saving is possible, because the opportunity for heat integration is lower than in process 1 and because the amount of heat required to heat up the solvent and to evaporate the co-extracted water is high (due to the low selectivity and distribution coefficient). For the PG process (process 3) the energy saving is around 54%. When comparing the fermentation processes, (process 2 and 3) we see the strong dependency of the energy demand on the glycol distribution coefficient and selectivity.

The PG process has an important advantage regarding capital expenditures because the higher distribution coefficient and selectivity and smaller equipment like, heat exchanger (compared to process 1) and also evaporators (for the IL recovery) are required. Therefore the economic evaluation considering both operational and capital expenditures is needed.

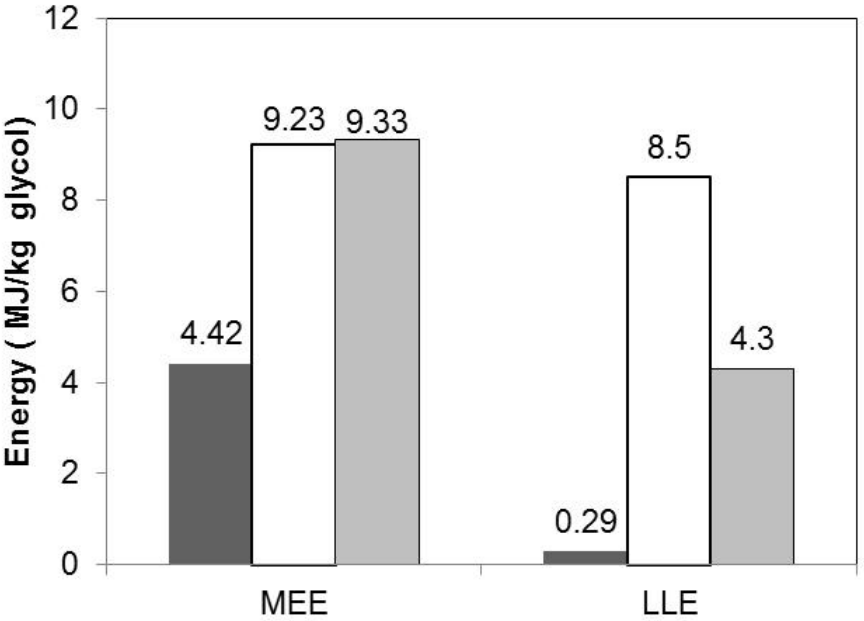


Figure 5-8. Energy requirement for multiple effect evaporation and liquid liquid extraction for different glycol production processes. (dark grey, Process 1-MEG), (white , Process 2-MEG), (light grey, Process 3-PG) .

5.5.5 CAPEX and TAC calculation

The calculation of the operational and capital expenditures was done as explained in sections 4.1 and 4.2, respectively. The detailed results regarding CAPEX estimation for the three different scenarios and the two different technologies (MED and LEE) are presented in table 5-5. From this table we can see that for MEG case, the capital investment for both technologies MED and LLE is around 50% higher for the larger plant capacity (scenario1) which is expected because larger equipment is required to accommodate the higher capacity. For plants with similar capacity (scenarios 2 and 3), the CAPEX for MED technology is comparable. For LLE technology, it was found that the ionic liquid investment represents between 17% and 27 % of the total CAPEX for the different scenarios and that between 50% - 60% of the equipment cost is spend on heat integration equipment (heat exchangers). The lowest CAPEX for the LLE technology is obtained for the recovery of PG (process 3). This is related to the higher distribution coefficient and selectivity of the IL towards PG and in consequence a lower solvent to feed ratio and smaller equipment sizes are required. The CAPEX of the propylene glycol LLE technology is around 34% lower compared to process 2. As the OPEX changes as function of the crude oil price (equation 5.5) the final cost comparison will be done using the total annual cost (TAC). In Figure 5-9, we can see how the oil price affects the TAC of the two different technologies (MED and LLE). The crossing point between the MED (solid lines) and LLE lines (dashed lines) indicates the fuel price at which the LLE technology could be a better option than MED, mainly because the OPEX will be high enough to compensate the increased CAPEX. In figure 5-9a, the comparison of the TAC for the MEG recovery cases are presented. Considering that in the last year the price of crude oil has fluctuated between €70-95 per barrel, we can say that currently the LLE process for MEG production is not a suitable option. This holds particularly for the MEG fermentation option (process 2, 100 kton/year and 10% MEG) because the energy demand of the LLE process is comparable to the conventional process and the CAPEX is much higher. For process 1, feed streams of 20 % wt of MEG (coming from petrochemical process), the oil price needs to reach at least €170/barrel to equal the MED technology. In contrast, as shown in figure 5-9b, the LLE technology for PG production (process 3) seems to be a feasible process at the current oil prices. This can be expected because the distribution coefficient and selectivity of [TOA MNaph] towards PG is higher than for MEG, which provides advantages regarding the CAPEX and also the energy demand because less water will be co-extracted during the extraction.

TABLE 5-5. CAPEX for the different processes and scenarios to recover glycols from aqueous streams.

Components	**Percentage***	**Process 1-MEG 450kton Feed 20%wt.**		**Process 2-MEG 100kton Feed 10%wt.**		**Process 3-MEG 100kton Feed 10%wt.**	
		MED (M€)	LEE (M€)	MED (M€)	LEE (M€)	MED (M€)	LEE (M€)
Delivered Equipment	0.10	3.32	10.73	2.11	4.51	2.25	3.85
Facilities Installation and Services	2.60	8.65	27.88	5.42	11.73	5.83	10.01
Total direct cost		11.97	38.61	7.53	16.24	8.08	13.86
Engineering and supervision	0.33	1.10	3.54	0.70	1.49	0.74	1.27
Construction Expenses	0.41	1.36	4.40	0.87	1.85	0.92	1.58
Legal Expenses	0.04	0.13	0.43	0.08	0.18	0.09	0.15
Contractor’s Fee	0.22	0.73	2.36	0.46	0.99	0.49	0.85
Contingency	0.44	1.46	4.72	0.93	1.98	0.99	1.69
Total Indirect Cost	1.44	4.78	15.44	3.04	6.49	3.23	5.54
Solvent Cost	20€/KG	---	20.89	---	9.53	---	3.96
FIXED CAPITAL INVESTMENT		**16.75**	**74.94**	**10.57**	**32.26**	**11.31**	**23.36**

*Average values for a fluid processing plant

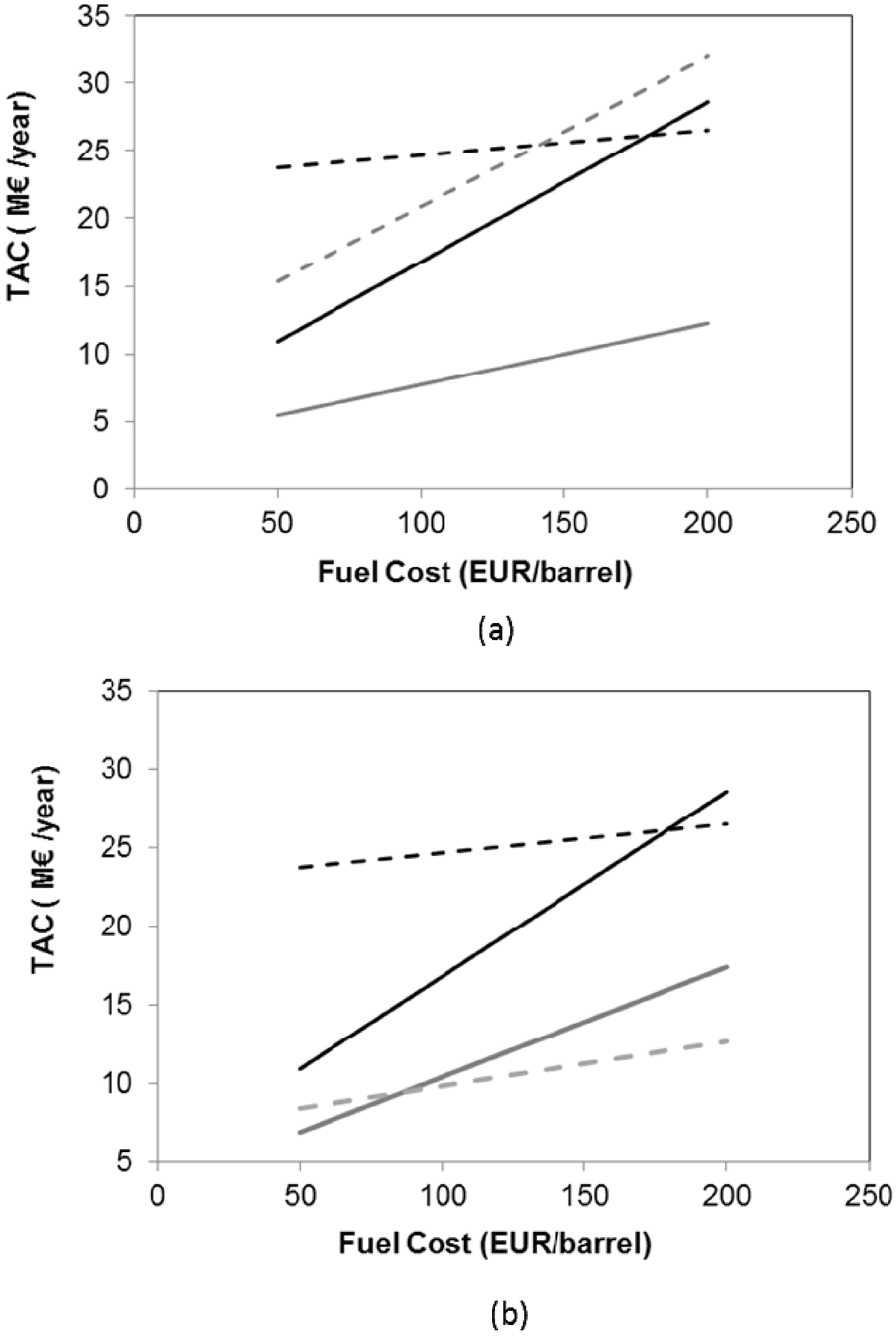


Figure 5-9. Process comparison based on the total annualized cost. (a) MEG cases (—, process 1 MED), (---, process 1 LLE),(— , process 2 MED), (---, process 2 LLE) (b) (— , process 3 MED), (---, process 3 LEE) (—, process 1 MED), (---, process 1 LEE).

5.6 Conclusions

A process comparison for the production of MEG and PG with two different technologies, conventional triple effect distillation (MED) and solvent extraction (LLE) using [TOA MNaph] was investigated. The results showed that the LLE alternative could provide energy savings between 94% (for MEG 20%wt from the petrochemical process) and 54% (for PG 10%wt from a fermentation process) in energy consumption compared to MED. Regarding CAPEX, the conventional technology is always preferable because less equipment is required. The capital investment for the LLE technology increases due to the solvent cost, the equipment in solvent recovery section and the additional heat exchangers required for the heat integration in the process. The purification of PG (process 3) has the lowest CAPEX because a lower solvent to feed ratio is required compared to MEG extraction. According to TAC analysis at the current crude oil prices, the purification of PG from fermentation broth via LLE could be an advantageous technology to replace MED. For the MEG production we can say that currently the LLE process is not a suitable option. This holds particularly for the MEG fermentation option (process 2), while for the MEG from petrochemical feedstock (process 1) a significant increase in crude oil prices is required before the use of LLE technology can become feasible.

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Chapter 6.

Bio-butanol Recovery Using Non-Fluorinated Task Specific Ionic Liquids (TSILs)[1]

[1] the content of this chapter was previously published as:
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Industrial &Engineering Chemistry Research

Abstract

Bio-butanol has received major attention as alternative for and additive to fossil fuels. Bio-butanol produced via fermentation, is hampered by low butanol concentrations in the fermentation broth. An efficient separation process is required to make bio-butanol production economically viable. In this work, liquid-liquid extraction of butanol from water, employing non-fluorinated task-specific ionic liquids (TSILs) has been evaluated against distillation and extraction with conventional solvents. Experimental data for the equilibrium distribution ratios of butanol and water were used in a conceptual process design study to find the most promising solvent. The results show that the IL with the best distribution coefficient and very high selectivity was [TOA MNaph] (D_{BuOH}=21, S=274), performing much better than the benchmark solvent oleyl alcohol (D_{BuOH}=3.42, S=192). The conceptual design study showed that butanol extraction with [TOA MNaph] requires 73% less energy than in conventional distillation (5.65 MJ/kg BuOH vs 21.3 MJ/kg for distillation). [1]

6.1 Introduction

Important fuels and chemicals like ethanol and butanol can be produced from biomass, e.g. through fermentation of corn or lignocellulose.[2,3] These bio-based chemicals provide a new, sustainable alternative to fossil fuel and fossil oil based chemicals. Although ethanol is currently the most used biofuel, several properties of butanol, like the higher energy density, the lower vapor pressure, less flammability (hence, a more stable combustion) and hydrophobicity are leading to a growing interest in butanol over ethanol.[4] Butanol is produced from biomass via batch or pseudo-continuous fermentation processes. The traditional process for butanol production is the Acetone–Butanol–Ethanol (ABE) fermentation.[5] In this process acetone, ethanol, butanol and some carboxylic acids like acetic acid and butyric acid are produced. Of these products, butanol is the main inhibitory metabolite, since concentrations higher than 1.5% wt can retard and even stop the growth of the microorganisms and therefore the process.[6] Important improvements are reported to increase the tolerance level of the bacteria up to 16 wt % ethanol but only around 3 wt % for butanol.[7] Therefore in this study we will evaluate only on the extraction of butanol.

In order to exploit the fermentative production of butanol, the main challenge is to find an economical route for butanol recovery. Purification of butanol is difficult, mainly due to its high boiling point and very low concentration (0.5 to 2.0 wt %) in the aqueous product streams.[5] Distillation is the conventional process for butanol purification and it is classified as an energy intensive process due to the high amount of water that is present in the fermentation broth. Even though it is not necessary to evaporate all the water, due to the presence of the butanol-water heterogeneous azeotrope that induces the formation of two liquid phases, and allows a significant concentration of butanol (around 7 %wt in the aqueous phase)[3], still more than one distillation column is needed. Therefore avoiding the conventional couple distillation systems may result in large energy savings.[8]

An approach to increase the butanol productivity could be the use of an extractive fermentation system, in which the butanol can be removed from the broth by in situ liquid– liquid extraction (LLE).[9,10] LLE is identified as an alternative with high potential to effectively recover polar products from aqueous streams with less energy cost.[33] For effective use of LLE, a good solvent with high affinity for butanol combined with low water co-extraction is required. Because the heat of evaporation of butanol (706 kJ/kg)[12] is lower compared to the heat of evaporation of water (2443 kJ/kg)[12], extracting butanol with a higher boiling point solvent is recommended, especially for the recovery section, where the solvent needs to be separated from the butanol and recycled back to the extraction step. A solvent with low boiling point will evaporate together with the butanol stream, causing solvent losses. Another required property of an extractive agent to be used in a fermentation system, is the non-toxicity towards the microorganisms, because this could suppress the microbiological activity in the process. However, in this study this remains unstudied and we are particularly focus in properties like solvent capacity and selectivity for butanol.

Several authors have undertaken important attempts to find suitable solvents[10, 13,14] and oleyl alcohol (OA) has become the solvent of choice for extractive fermentation, because it is non-toxic and it has a high selectivity for butanol. The distribution coefficients of butanol and water (equation 6.1 and 6.2) are the primary parameters that affect the performance of the different solvents. The distribution coefficients are given as the ratio of the equilibrium weight fraction, in the aqueous raffinate phase, x, and in the extract phase, y. The ratio of the distribution coefficients is the selectivity as given by equation 6.3.

$$D_{BuOH} = \frac{y^{BuOH}}{x^{BuOH}} \qquad (6.1)$$

$$D_{H2O} = \frac{y^{H2O}}{x^{H2O}} \qquad (6.2)$$

$$S_{BuOH} = \frac{D^{BuOH}}{D^{H2O}} \qquad (6.3)$$

Ionic liquids (ILs) have been studied as potential solvents for different applications, including the LLE of alcohols from aqueous streams.[4,15-19] ILs are defined as salts with low melting points, by definition below 373.15 K,[20-22] however they have wide liquid ranges, as large as 473.15−573.15 K, which contrast with the reduced liquid range for many common organic fluids.[23] Important properties include their non-volatility, non-flammability, and thermal stability (sometimes up to 673.15 K).[23,24] By changing the combination of cation and anion, the physical and chemical properties can be tailored,[25,26] allowing solvent design aiming at a high preference for butanol over water. Nevertheless this tailoring step is not simple, and additional effort in research is needed. Meinersma et al.[27] reported that ILs can be used to replace conventional solvents for the extraction of aromatics, but the selection of a suitable IL requires investigation because only a small number of ILs are able to combine higher distribution coefficients and selectivities compared to conventional solvents.

The most common cations in ILs bear a ring structure like imidazolium, pyridinium or pyrrolidinium salts, however tetralkyl ammonium and tetralkyl phosphonium cations can have desirable properties like a low density.[25,26] Tailoring another, very important parameter, the hydrophobicity, may be done by choosing the right anion. It has been reported that anions can greatly affect the hydrophobic or hydrophilic behaviour.[15,25] For example, anions like hexafluorophosphate PF_6 [28] and bis(triflouromethylsulfonyl)imide NTf_2 are immiscible with water and have low viscosities.[25-29] Additionally to that, increasing the length of the alkyl lateral chain(s) in the cation can also decrease the affinity to water.[26]

Fadeev and Meagher[16] studied the recovery of butanol from dilute aqueous solutions using octyl and butyl methylimidazolium (OMIM and BMIM) cations in combination with the PF_6 anion. They found that these ILs could suppress the biological activity in the fermentation process. An additional study was performed by Ha and co-workers,[18] who also evaluated imidazolium based ILs with tetrafluoroborate BF_4, PF_6, and NTf_2 anions for the extraction of butanol from aqueous solutions. The results of the two studies demonstrated that for all anions the distribution coefficient and selectivity are lower than the reported value for oleyl alcohol.[16, 18] The main drawback of BF_4 and PF_6 anions according to Swatloski[28] and Huddleston [15] is that in contact with aqueous streams the anions go into a slow hydrolysis, inducing the formation of hazardous hydrofluoric acid (HF) making their use and recycling complicated.[15,28] More stable fluorous hydrophobic anions like NTf_2 and tris(pentafluoroethyl)trifluorophosphate FAP exist, and were also investigated by several authors.[17,18,30,31] Changing from NTf_2 to FAP improved the selectivity from around 100 to 300, but resulted in a very low distribution coefficient[17] (less than 0.5) meaning that the amount of solvent required for the process will be high. On top of that, FAP ionic liquids are expensive, because of their difficult synthesis and the use of expensive raw materials.[31]

Another attempt to improve the IL distribution and selectivity for butanol was reported by Górak and Santangelo,[17] who used ILs functionalized with an OH-group attached to imidazolium, pyridinium and phosphonium cations, in order to enhance the extraction of butanol. It was clearly demonstrated that the presence of the OH-group increases the capability of hydrogen bonding in the IL, causing an increase in the distribution coefficient of butanol. Although high distribution coefficients can be reached with functionalized ionic liquids, the selectivity is affected due to an increase in water co-extraction. Additional research has been done by Merck KGaA and Dortmund University (Górak and co-workers)[32] to evaluate anions like tetracyanoborate TCB and tricyanomethide TCM [33]. These

ILs report a slightly higher distribution coefficient than oleyl alcohol.[32, 33] Recently, a research performed by Cascon [34] showed that ILs like tetrahexylammonium dihexylsulfosuccinate [THA DHSS] and tetradecyl(trihexyl)phosphonium dicyamide [Ph3t DCN] have strong affinity for butanol, therefore very high distribution coefficients are reported 7.99 and 7.49 g/g, respectively. These ILs have a higher distribution coefficient than fluorinated, TCB and TCM ILs. Several authors agree that the difference in distribution coefficient can be attributed to the higher capacity for H-bonding between the anion and the butanol[35-37]. Unfortunately no selectivity is reported for [THA DHSS] and [Ph3t DCN] to compare with previously reported ILs. Figure 1, maps some of the reported values for the butanol distribution coefficient and selectivity for different ILs for a feed composition of 1wt% of butanol in comparison with the reference solvent OA. The lines in Figure 1 indicate the reference distribution and selectivity.

As we can see in Figure 6-1, most of the ILs reported so far are not significantly better than oleyl alcohol for both distribution coefficient and selectivity. However, the solvent capacity could be improved, because the distribution coefficient of 3.3 g/g [17] is relatively low, leading to high solvent to feed ratios, and large equipment. Here we describe our studies aiming at alternative solvents, specifically TSILs that are able to combine better distribution coefficient and selectivity towards butanol compared to OA. In this study we also evaluate how these parameters will affect the LLE process in terms the energy demand and solvent requirement. Figure 6-2 displays the chemical structures of the ILs that we evaluated in this study. Next to the recently information reported by Cascon[34], the selection of TSIL that we propose is based on the knowledge that phosphonium and ammonium ILs with long alkyl chains could provide the desired hydrophobic behavior and higher affinity to polar compounds than imidazolium and pyridinium cations [19,32,33] . In addition to that, we also want to evaluate hydrogen bond capacity of a long chain carboxylate anion. Solvents like oleyl alcohol and 1-hexyl-3-methylimidazoliumbis(trifluoromethylsulfonyl) imide were used as the reference solvents to validate our experimental technique.

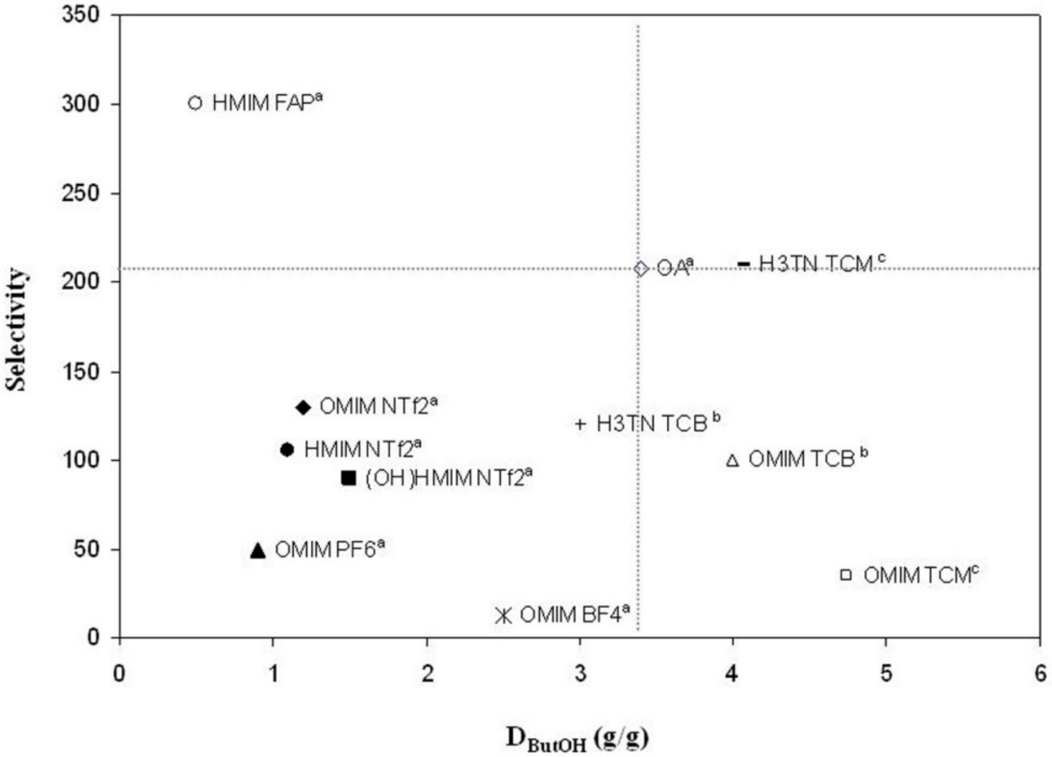
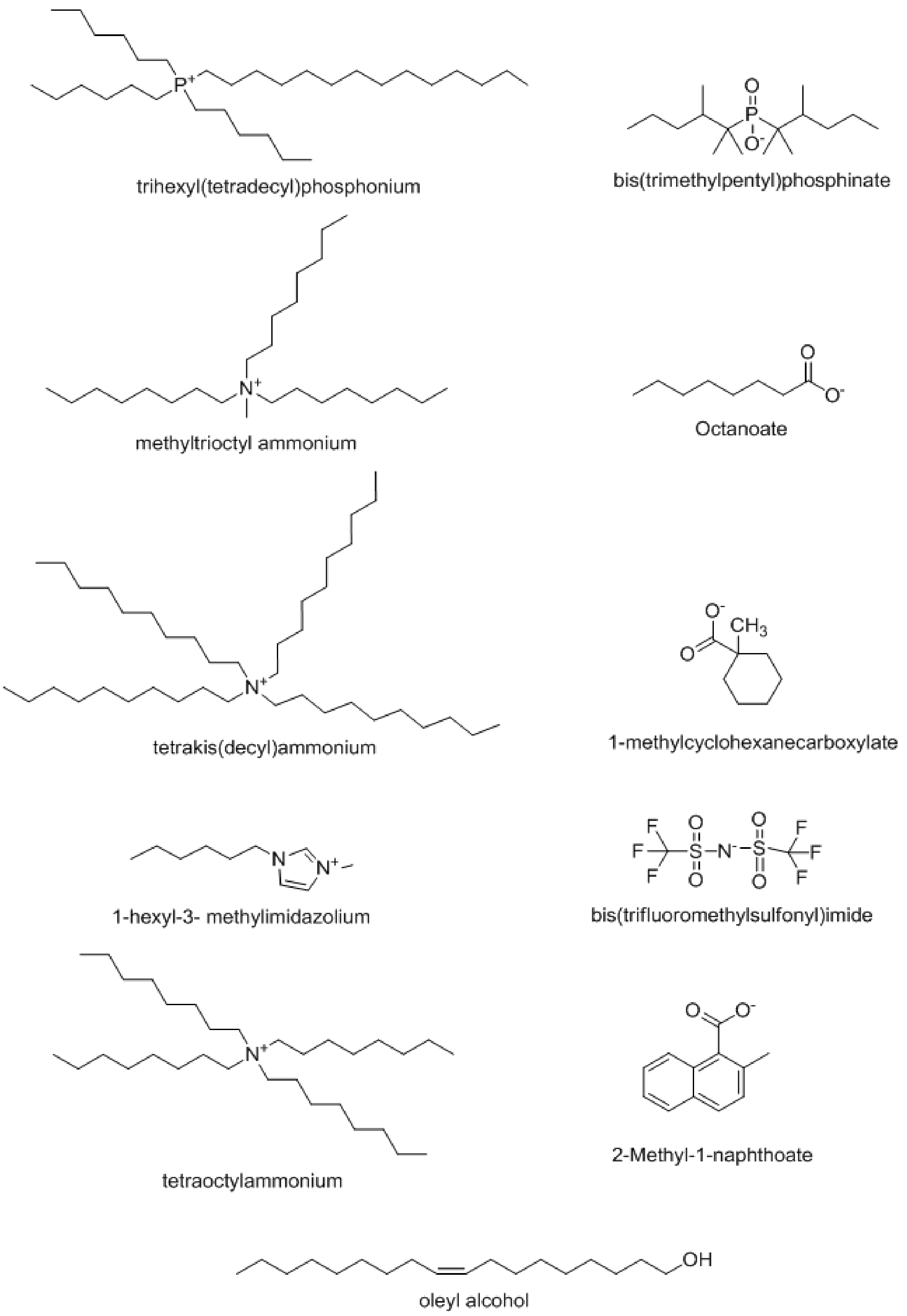


Figure 6-1. Reported distribution coefficient and selectivity for butanol extraction with hydrophobic ILs and reference solvent oleyl alcohol (OA). [a] data from ref [17], [b] data from ref [33], [c]data from ref [32]



trihexyl(tetradecyl)phosphonium

bis(trimethylpentyl)phosphinate

methyltrioctyl ammonium

Octanoate

tetrakis(decyl)ammonium

1-methylcyclohexanecarboxylate

1-hexyl-3- methylimidazolium

bis(trifluoromethylsulfonyl)imide

tetraoctylammonium

2-Methyl-1-naphthoate

oleyl alcohol

Figure 6-2 Task Specific Ionic Liquids (and oleyl alcohol as reference solvent) tested in this study.

6.2 Experimental Section

6.2.1 Materials

1-Butanol (purity 99.9 %) was purchased from Sigma-Aldrich; oleyl alcohol (purity 85 %) was provided by ABCR GmbH; α-terpineol (purity ≥99 %) and 1-hexyl-3-methylimidazolium bis(triofluoromethylsulfonyl) imide [HMIM NTf_2] (purity ≥99 %) were supplied by Merck. 1-methyl trioctyl ammonium octanoate [MTOA Oct] (purity ≥95 %) was supplied by Iolitec, tetradecyl(trihexyl)phosphonium bis 2,4,4 –trimethylpentyl-phosphinate [Cyphos 104® trademark] was provided by CYTEC. All chemicals were used without further purification. Tetrakis(decyl)ammonium hydroxide solution (10% in methanol) and 1-methyl-1-cyclohexane carboxylic acid provided by Sigma-Aldrich were used to synthesize tetrakis(decyl)ammonium 1-methyl-1-cyclohexanoate [TDA MCH]. Tetraoctylammonium hydroxide solution (20% in methanol) and 2-methyl-1-naphthoic acid was supplied by Sigma-Aldrich for the synthesis of tetraoctylammonium 2-methyl-1-naphtoate [TOA MNaph].

6.2.2 Ionic Liquid Synthesis

The reaction to synthesize TDA MCH is an acid-base reaction. In a 100 mL round bottom flask equipped with a reflux condenser and magnetic stirrer, 1.735 g ($13.54x10^{-3}$ mol) of 1-methyl-1-cyclohexane carboxylic acid diluted in methanol (10 mL) was combined with 80.72 g tetrakis(decyl)ammonium hydroxide solution 10% in methanol,($13.6x10^{-3}$mol of the hydroxide) by slow addition of the hydroxide solution at room temperature. The reaction was carried out at 343.15 K for 2 hours, and afterwards the formed water and the methanol were removed using a rotavapor (VWR RV 10 digital) at 283.15 K and 200 mbar for 6 h. The product was characterized using ^{1}H-NMR on a Varian 200 MHz NMR spectrometer. ^{1}H-NMR (DMSO-d_6): 3.32 (m, 14H), 3.15 (d, 4H), 1.86 (m, 1H), 1.53 (m, 8H), 1.23 (m, 52H), 1.10 (m, 3H), 1.04 (m, 3H), 0.84 (t, 12H). [TOA MNaph] was synthesized following the same procedure, mixing 1.86g (0.01 mol) of 2-methyl naphthoic acid with 24.2 g (0.01 mol) of tetraoctylammonium hydroxide. The NMR results for [TOA MNaph] Yield: (97%) ^{1}H-NMR (DMSO-d_6): 7.9-7.46 (3H,m),7.31-7.15(2H,m), 3.34 (s,2H), 3.16 (m,8H), 2.5 (s,2H), 1.55 (m,10H),1.27

(m, 38H), 0.85 (m, 12H). The purity of the ILs was at least 95%, checked by ^{1}H-NMR, the major impurity was the starting material tetraoctyl ammonium hydroxide proven to be present in < 1% (based on the 2.2 ppm signal).

6.2.3 Liquid-liquid Extraction Experiments

Aqueous butanol solutions were prepared by dissolving 1.0 wt % 1-butanol in distilled water. Extraction experiments were carried out by combining equal masses of the aqueous phase (5 g) with of the organic solvent phase in a glass cell equipped with a mantle and two sampling ports. The temperature was controlled at 298.15K using a water bath (Julabo F-25-MW). The system was stirred (800 rpm) for 20 hours. Afterwards the phases were allowed to settle for 1 hour, (preliminary experiments were done with settling times between 30 min and 4 hours to study the time required for complete phase separation) after which samples from both phases were taken through the sample ports (the lower one of them was always below the interface to collect from the bottom phase). All experiments were done in duplo.

6.2.4 Analytical Methods

Analysis of the butanol content in both the aqueous and the organic phase was done by gas chromatography. The GC was equipped with a Nukol Fused silica capillary column of 15 m of length and 0.53 μm diameter, and a flame ionization detector. The oven was kept isothermally at 363.15 K for 9 minutes. A special liner, (split injector cup design) and an uncoated capillary pre-column was used to prevent contamination with the IL, a commonly applied method for GC analysis of systems containing ILs. The liner was changed every 50 injections, and the column washed with ethanol every after the injection of extractant phase samples. The injector and detector temperatures were fixed at 523.15 K. Quantitative analysis (0.01% accuracy) was enabled using ethanol as internal standard. The water content in the organic phase was determined by volumetric Karl Fisher titration using a Metrohm 795 KF (accuracy 0.05%). The IL concentration in the aqueous phase was assumed to be negligible, and in the organic phase was calculated by difference.

6.3 Process Simulation

Conceptual process designs were simulated using Aspen Plus® software (Aspen Technologies, Inc., Cambridge, MA). The process design was based on a production capacity of 100 kton per annum of 99.9 wt% pure butanol, corresponding to 11,620 kg/h, assuming 358 production days per annum. The butanol composition was 1wt% in the feed, and 0.1wt% in the raffinate; the feed concentration was selected according to the reported values for the inhibition of the microbial cell growth (>10g/L) during fermentation, [18] the concentration in the raffinate was chosen to achieve at least 90% of recovery in extraction process . The design spec/vary feature of Aspen Plus was used to hold the product compositions by varying the feed flow rate. The Non-Random Two Liquid (NRTL) model was selected as the thermodynamic model to estimate physical properties and vapor liquid equilibrium in Aspen Plus. The NRTL model was chosen because it provided a good description of the vapor liquid equilibrium data for the butanol-water system reported by Gmehling and coworkers.[38] In addition the NRTL model has been reported as a suitable model for describing liquid-liquid equilibria and vapor liquid equilibria of polar systems involving ILs.[39] Because the properties of the ILs were not available in the database, the experimental values of D_{BuOH} and S_{BuOH} (Equations 1 and 3) were directly used in Aspen Plus for the extraction column through the KLL correlation. Additional IL properties like molecular weight and heat capacity were introduced manually. The heat capacity of the IL was calculated using the method reported by Crosthwaite based on the IL molecular weight.[40] The vapor pressures of the ILs were assumed to be negligible.

6.4 Results and Discussion

6.4.1 Experimental Determination of D and S

Using the experimental procedure described in section 2.3, LLE experiments were carried out with several solvents to determine the distribution coefficients of both butanol and water, and from that the selectivity was calculated (Equations 6.1 – 6.3). The experimentally obtained distributions are given in Table 6-1.

Table 6-1. Experimental results of the solvents evaluated in this study.

Solvent	$BuOH_{org}$	$H2O_{org}$	$BuOH_{aq}$	$H2O_{aq}$	D_{BuOH}	D_{H2O}	S
OA	0.0068	0.0176	0.0020	0.9980	3.42	0.02	194
HMIM NTf$_2$	0.0056	0.0092	0.0050	0.9950	1.11	0.01	120
Cyphos 104	0.0056	0.1680	0.0006	0.9994	9.21	0.17	55
MTOA Oct	0.0070	0.2300	0.0006	0.9994	11.29	0.23	49
TDA MCH	0.0075	0.0650	0.0009	0.9991	8.49	0.07	130
TOA MNaph	0.0095	0.0765	0.0005	0.9996	21.00	0.08	274

Next to some new ILs, also some ILs already reported in literature[17,18] and oleyl alcohol were measured as reference systems. The experimental results in this study for oleyl acohol were D_{BuOH}=3.42 and S=194, which is in very good agreement with the literature (D_{BuOH}= 3.33 and S=208).[17,34,41] Experimental validation for ILs was done with [HMIM NTf$_2$]. The experimental results were D_{BuOH}=1.11 and S=120 compared to the results reported by Górak and coworkers of D_{BuOH}=1.2 S=105 [17]. The differences in values are primary due to the analytical methods and purity of extractant used, as well as the assumption made by other authors that the volume of the organic and the aqueous phase does not change after reaching equilibrium, which may be not necessary true, especially because most of the solvents have a water content higher than 1 wt%. Considering the above given reasons it can be concluded that our experimental methodology is valid. Figure 6-3 displays an overview of the experimental results for the distribution coefficients and the selectivity that were obtained for all the solvents. The closed symbols correspond to the experimental values measured in this study and the open symbols, displayed for comparison, were taken from literature.

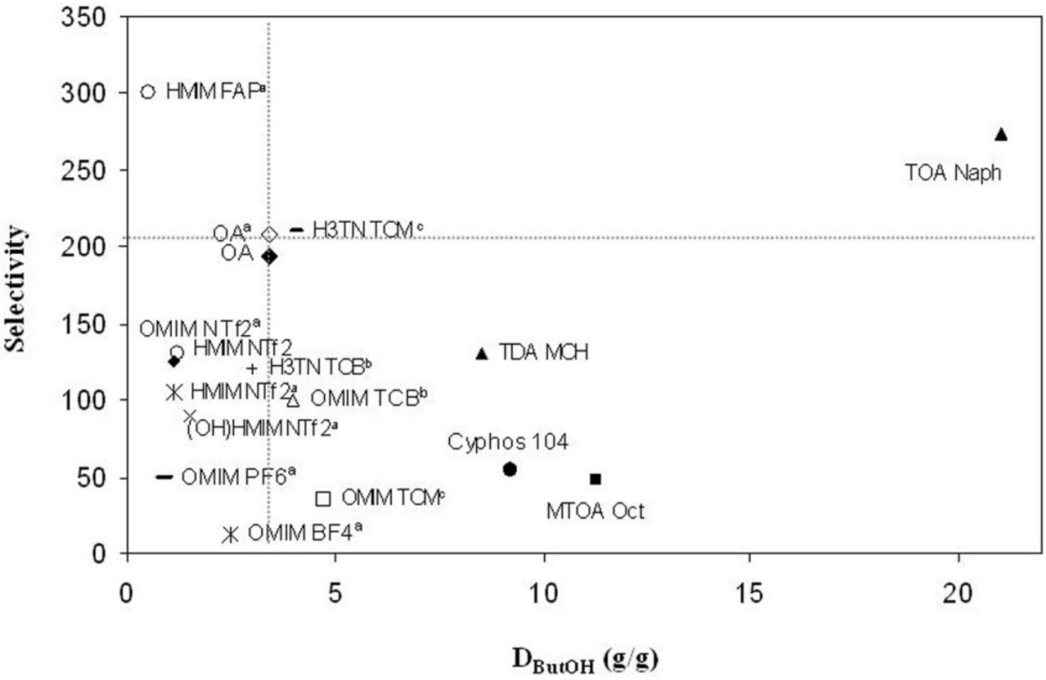


Figure 6-3. Butanol selectivity and distribution coefficient of different ionic liquids and oleyl alcohol as reference system. Closed symbols represent data from this study, those with superscripts [a] data from ref [17], [b] data from ref [33], [c] data from ref [32].

According to Figure 6-3, the TSILs tested in this study performed much better in terms of butanol distribution coefficient compared to oleyl alcohol, fluorinated ILs and to TCM and TCB anions. We can see that the distribution coefficients of Cyphos 104 (D_{BuOH}=9.2) and [MTOA Oct] (D_{BuOH}= 11.3), the first two ILs that we tested, are approximately three times higher than oleyl alcohol and around 30 % higher than the ILs reported by Cascon[34]. A high value of distribution coefficient could have a positive effect in the process because less solvent is required. In terms of selectivity, oleyl alcohol and fluorinated ILs performed better. This indicates that Cyphos 104 and [MTOA Oct] have the capability to extract more water, which could be a disadvantage in the LLE process because the co-extracted water needs to be removed from the butanol stream afterwards. Taking into account the structure of the [MTOA Oct] and Cyphos 104, the increase in butanol extraction and also in water co-extraction can be explained, mainly because the presence of the oxygen atoms in acetate and phosphinate groups increases the capability of hydrogen bonding in the ILs. The results are in agreement with the findings of Marták and Schlosser who reported that Cyphos 104 can effectively extract polar compounds like lactic acid from aqueous solution.[19]

Based on the interpretation of the results obtained with Cyphos 104 and [MTOA Oct], we decided to design a new IL with a tetra alkyl ammonium cation, and a cyclic aliphatic or aromatic carboxylate anion to combine the benefits of a high butanol distribution (provided by the carboxylate) with less water affinity (provided by a cyclic or aromatic structure in the anion and long aliphatic tails on the cation). As can be seen in Figure 6-3, these structural modifications of [TDA MCH] resulted in a better performance in terms of selectivity (S=130), while the distribution coefficient decreased only slightly (D_{BuOH}=8.5) as compared to Cyphos 104 and [MTOA Oct]. Furthermore, is important to point out that the modifications of [TOA MNaph], resulted in an outstanding performance of both selectivity and distribution coefficient (D_{BuOH}=21, S=274). For this IL, the selectivity improved around 30% and the distribution coefficient increased by factor six compared to the conventional OA. The main modification in [TOA MNAph] ionic liquid is the presence of naphthalene's structure, which is a non-polar polycyclic aromatic hydrocarbon, that could increase the hydrophobic behavior of the IL and affinity to BuOH . The increase of distribution coefficient and selectivity is important because it represents benefits in the LLE process in terms of energy demand and solvent requirement.

6.5 Conceptual Process Design

6.5.1 Conventional distillation process

A conventional distillation process, using the two-column system in conjunction with a decanter as suggested by Doherty and Malone[38] was simulated in Aspen Plus. Figure 6-4 shows the Aspen Plus flow sheet for this system. The two columns operate at a pressure of 0.5 atm, the overheads of both columns are connected to a single condenser, where due to the immiscibility gap of butanol and water a two liquid phase system is formed, and afterwards the liquid flows to a decanter in which the aqueous and the organic phase are separated. The aqueous phase returns to the top of C1 and the organic phase is sent to the top section of C2.

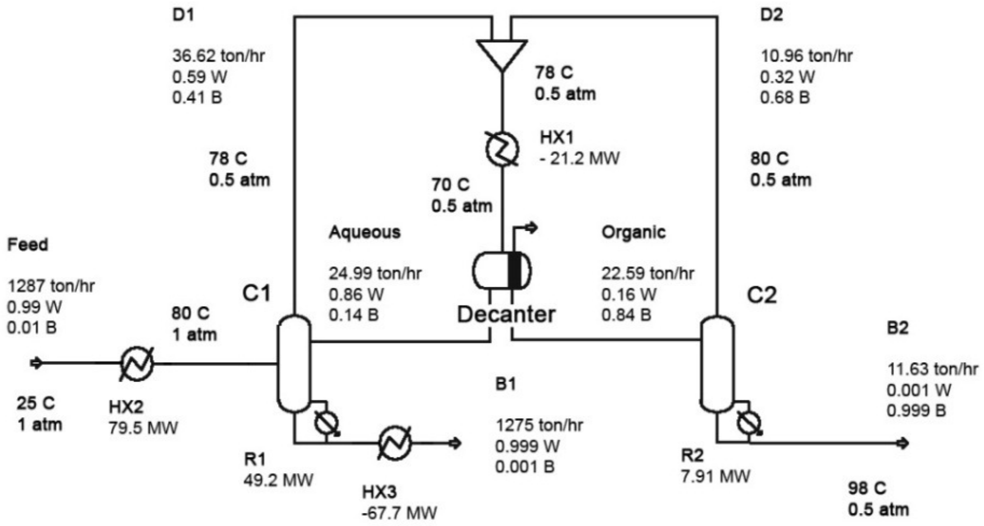


Figure 6-4. Aspen Plus flowsheet of the butanol /water distillation.

In this process, most of the energy is consumed in the reboilers (R1,R2), while also the heat exchanger HX2 requires energy. Using the excess energy from HX1 and HX3 through heat integration, the total energy consumption of this process could be reduced to 21.3 MJ/kg BuOH. A minimum temperature difference of 10 K between the streams is assumed for heat integration. A list of the net energy consuming units is given in Table 6-2.

Table 6-2. Net energy consuming units in for the distillation process (Figure 4).

Product Specification	Unit	Energy (MJ/kg BuOH)
Butanol 99.9 wt%. 11,628 kg/h	R1	15.2
	R2	2.45
	HX2	3.65
	Total	**21.3**

6.5.2 Liquid-Liquid Extraction Process

The conceptual design for the LLE process to recover butanol can be divided in three main units, the extraction, the solvent recovery and the butanol purification. As in the distillation process, specifications for the feed and the final product were 1 wt% butanol and 99.9 wt% of butanol respectively. The flow sheet of the process is depicted in Figure 6-5.

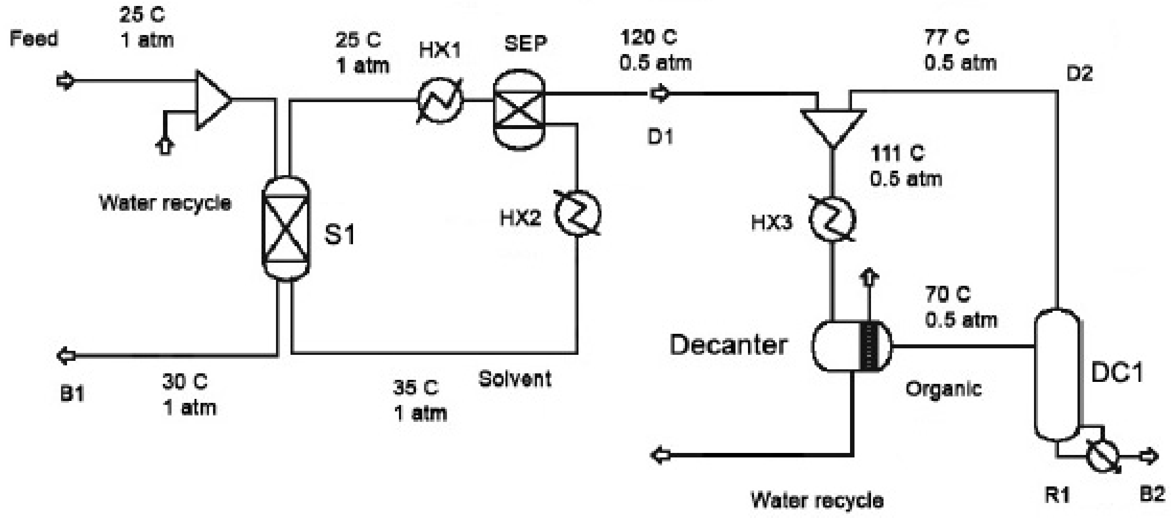


Figure 6-5. Aspen Plus flow sheet for LLE processes to separate butanol and water.

An important assumption is that the aqueous phase leaving the extraction column has a maximum butanol content of 0.1 wt%. This assumption was based on the idea to have an extraction operation where at least 90% of the butanol entering the process will be converted into the final product. After extraction, the solvent recovery section is placed. In this step the saturated solvent leaving S1 is heated up to 393.15K and transferred to a flash separator (SEP) at 0.5 atm to remove the butanol and the co-extracted water from the solvent. The solvent recovered from the flash separator is recycled to extraction column, while the overhead stream (D1) with high butanol concentration flows to a decanter where the temperature is lowered to 343.15 K and two phases are formed (water and butanol are not completely miscible at 343.15 K). The final step is the butanol purification; where the water is removed from the butanol phase by conventional distillation to reach the desired product purity.

The LLE process also has potential for heat integration, which is a very important step to make the process energetically feasible. Heating up of the solvent from room temperature to 393.15 K (in HX1) is energy intensive, and by heat integration with HX2 part of this energy can be recovered. Similar to the approach in the distillation process, a minimum temperature difference of 10 K between the streams is assumed for heat integration. Based on these assumptions and considerations, the energy demand is calculated by adding the energy requirements in the flash separator (SEP), heat exchangers HX1 and HX2 and of course in the reboiler (R2) in the distillation column. The resulting calculated energy demands for the conceptual LLE processes are tabulated in Table 6-3.

Table 6-3. Energy demand for LLE-based processes to obtain 11,628 kg/h butanol with 99.9% purity.

Unit	**Energy Demand (MJ/kg BuOH)**					
	Oleyl Alcohol	**HMIM NTf_2**	**Cyphos 104**	**MTOA Oct**	**TDA MCH**	**TOA MNaph**
SEP	2.33	3.37	8.02	10.50	3.34	2.63
R1	2.43	1.88	1.93	2.05	2.00	1.90
HX1	7.71	21.60	4.49	4.55	4.24	3.40
HX2	-6.35	-18.76	-2.43	-2.10	-3.09	-2.22
Total	**6.12**	**8.10**	**12.0**	**15.10**	**6.50**	**5.65**

From Table 6-3, it becomes clear that for solvents with low butanol distribution coefficients and high selectivity like oleyl alcohol and [HMIM NTf_2] the major energy demand in the LLE process originates from heating up the solvent in unit HX1 but also that a large amount of this energy can be recovered by heat integration with HX2. In the case of solvents with a high butanol distribution coefficient but low selectivity like [MTOA Oct] and Cyphos 104 the energy requirement is higher in the flash separator unit due to more water is presence in these IL phase. The main advantage of ILs with high selectivity as well as a high distribution coefficient is that the energy requirement in both the solvent heating unit HX1 and in the flash separation unit can be reduced.

Comparing the energy demand of the LLE processes listed in Table 6-3, it may be concluded that with respect to the 21.3 MJ/kg energy consumption of the conventional distillation, all LLE processes perform much better. Using ILs with a low selectivity, like Cyphos 104 and [MTOA Oct] will reduce the energy around 43 %, while solvents with a higher selectivity such as [TDA MCH] and [TOA MNaph] can reach up to 69% and 73% of energy savings respectively. The best IL tested in this study, [TOA MNaph] shows an energy consumption (operational costs) that is around 8% lower compared to the energy demand for the conventional solvent (OA). In order to visualize the trade off between the selectivity and the distribution coefficient for the energy demand in the LLE process, several simulations varying these two parameters were run with initial feed concentration and final product specifications constant. In addition, the solvent to feed ratio was calculated based on the butanol distribution coefficient. A theoretical IL was used in the simulations, assuming a molecular weight of 500g/mol and a heat capacity of 500 J/mol K, both based on reported values for ionic liquids.[40] The results from these simulations are shown in Figure 6-6.

The simulations show that the selectivity has an important influence on the total energy consumption, especially for solvents with a low butanol distribution coefficient, in which the high energy demand is due to the amount of solvent that needs to be heated in HX1. In Figure 6-6 it is clearly illustrated that for a given selectivity, there is no significant further reduction in the overall energy demand when $D_{BuOH} > 4$, which is mainly caused by the heat integration between HX1 and HX2 that reduces the benefits of increasing the distribution coefficient. This means that when considering only energy demand for process evaluation and within a process with a similar configuration for heat integration, a good solvent could be one with a D_{BuOH} of 4 or higher and further improvement in energy demand could be possible using a solvent with a selectivity higher than 250. However next to the operational cost generated by the energy demand, also capital expenditure is an important factor, therefore an estimation was made on the solvent to feed ratio (S/F), that can provide us an idea of the amount of solvent that will be required for the extraction compared to the amount of feed. The S/F ratio is an important factor because it affects the size of the equipment.

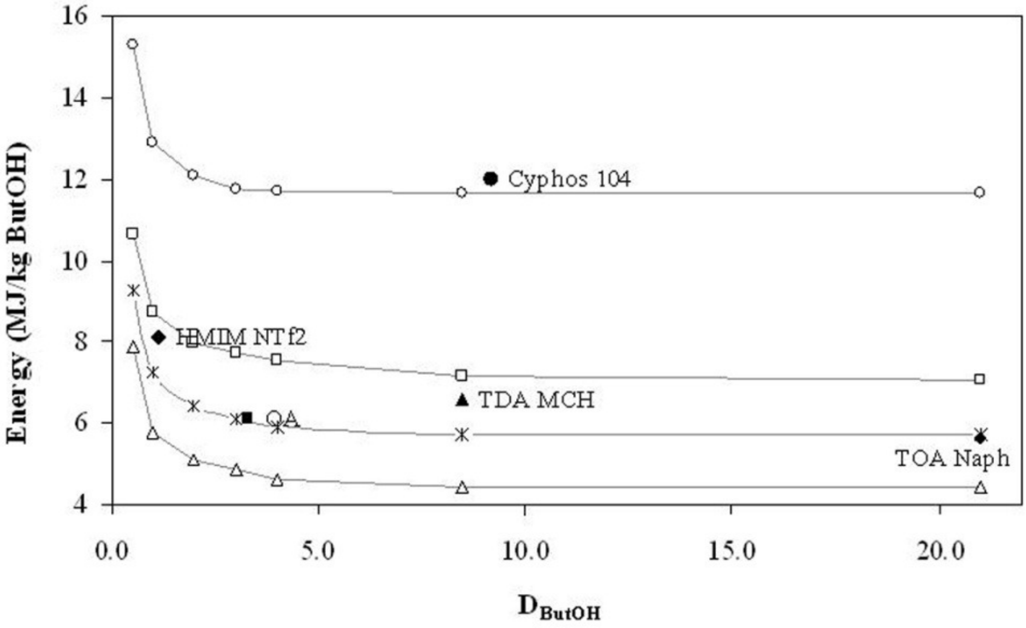


Figure 6-6. Energy requirement for a liquid-liquid extraction process with ILs having varying butanol distribution coefficient and selectivity. Symbols represent experimental values obtained in this study, lines correspond with Aspen plus simulations for hypothetic ILs with selectivities of 300 (-Δ-), 150 (-ж-), 100(-□-), and 50(-○-).

The solvent to feed (S/F) mass ratio was estimated as 1.5 times the minimum solvent to feed ratio, a common estimate for industrial processes.[38] Figure 6-7, shows the resulting S/F ratios for the different solvents tested in this study. Solvents with very high distribution coefficients like Cyphos 104, [MTOA Oct], [TDA MCH] and [TOA MNaph] report as expected a lower S/F ratio compared to OA and [HMIM NTf2]. Considering both the S/F ratio and the energy demand, the most promising performing TSIL evaluated in this study is [TOA MNaph].The chemical structure of [TOA MNaph] with a bicyclic aromatic carboxylic anion and the long aliphatic tails on the ammonium cation, provides high affinity for butanol together with a reduced affinity to water. As a result, this IL combines the benefits of a high distribution coefficient and selectivity. [TOA MNaph] selectivity (S=274) is higher than the selectivity of oleyl alcohol (S=194), leading to a reduction on the energy demand (6.12 MJ/kg BuOH of OA compared to the 5.65 MJ/kg BuOH of TOA MNaph). In addition, the high distribution coefficient of 21 for [TOA MNaph] has the advantage that the amount of solvent required for the LLE process will be around 6.3 times less that for OA, resulting in smaller equipment, and thus in lower capital cost.

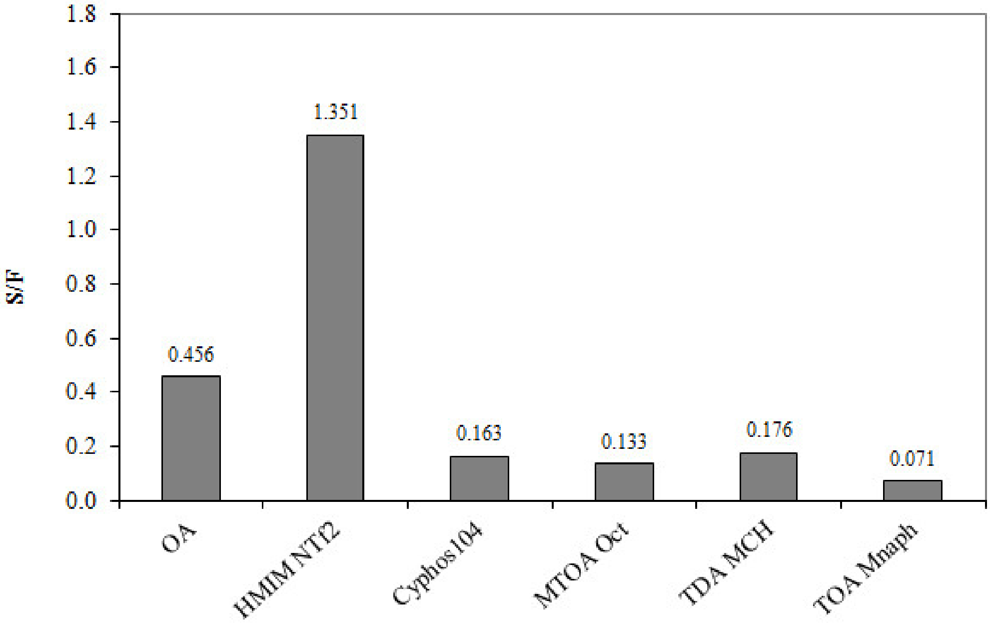


Figure 6-7. Solvent to feed mass ratio requirement for recovery of 1% (wt) BuOH in water using LLE with different solvents.

6.6 Conclusions

In this study, distribution coefficients of butanol and water (and thus also the selectivity) were experimentally determined for a range of TSILs to evaluate their potential for use in liquid-liquid extraction processes to recover bio-butanol. The experimental results were used in a conceptual process design to compare the energy demand for the solvents. It may be concluded that a trade off between the distribution coefficient and the selectivity is needed in order to reduce the energy consumption and the amount of solvent required in the LLE process. The best IL tested in this study was [TOA MNaph], which performs better than the benchmark solvent oleyl alcohol in terms of energy demand (5.65 MJ/kg BuOH vs 6.12 for oleyl alcohol). The six times higher butanol distribution coefficient of 21 for [TOA MNaph] results in a reduction of 6.3 times of the solvent to feed ratio, and thus reduces the capital costs largely. It is important to mention that a cost evaluation is still needed for the LLE technology. The capital cost analysis can help to detail the advantages of a solvent with a higher butanol distribution coefficient that can result in lower capital costs due to smaller equipment and less inventory. In addition more research is required to investigate the biocompatibility of these new TSILs towards microorganisms and to quantify the solvent losses due to its possible solubility in the aqueous streams.

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Chapter 7.

Conclusions and Recommendations

7.1 Extraction of polar compounds from aqueous streams

The main objective of this thesis was to investigate whether LLE (e.g. with reactive extraction or with task specific ionic liquids (IL)) could be a suitable technology to recover polar compounds from aqueous streams, and whether the solvent extraction technology could provide benefits in the operational and capital costs compared to the multiple effect distillation (the benchmark industrial process). Typical examples of polar aqueous mixtures were studied, i.e. low molecular weight diols, including mono ethylene glycol (MEG), 1,2 propanediol (PG), and 2,3-butanediol (2,3-BD), and an alcohol higher boiling than water, i.e. butanol (BuOH). These compounds were present in low concentrations in the feed (from 1 % up to 20 % wt) and needed to be concentrated to more than 90 %wt. The key conclusions from this thesis can be categorized in conclusions on solvent screening for MEG recovery from aqueous conclusions, applicability of the most promising solvent in other glycol and alcohol systems, and on process design and economy.

7.2 Solvent screening

In the search for a proper solvent, a wide range of conventional solvents (octanol, oleyl alcohol, 2-ethyl- hexanol, boronic acid derivatives) for recovery of glycols and alcohols have been investigated, [1,2] as well as commercially available ionic liquids that were previously reported for similar separations.[3] Next to an experimental evaluation of relevant solvent characteristics such as distribution coefficient and selectivity towards MEG, the quantum chemical based program COSMO-RS was used as a tool for solvent screening (Chapter 2), based on the qualitative analysis of the σ-profiles of solvents with known extraction characteristics by COSMO-RS, hypothetic ILs with tetraalkylamonium or phosphonium cations and carboxylates, phosphinates and boronates anions were identified on the basis of their σ-profiles as most promising solvents. On the basis of this COSMO-RS evaluation, 13 new ILs were synthesized and experimentally studied in extraction of MEG. These solvents performed very good compared to conventional solvents and commercially available ILs. Bicyclic aromatic anions like [MNaph] and [N_2B] in combination with long alkyl chains ammonium or phosphonium cations (as shown in figure 7-1) showed a good balance between a high distribution coefficient and selectivity (see Figure 7-2, this behavior could be explained by the strong hydrogen bond interaction between the solute and the carboxylate or boronate functionalities, which is caused by the high molecular surface of the anions in the electronegative region (reaching values up to + 4 e/nm^2). The hydrophobicity of the solvent is given by the long lateral chains attached to the cation and also by the presence of the bicyclic aromatic rings in the anion.

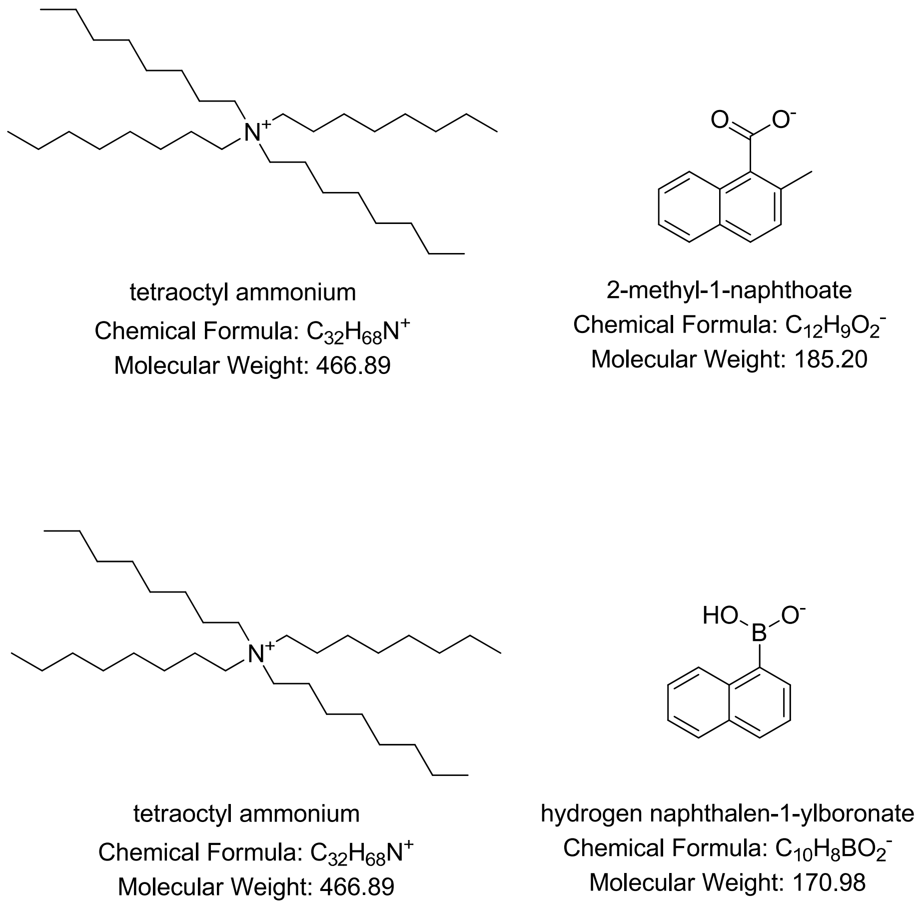

Figure 7-1. Best performing solvents [TOA MNaph] and [TOA N_2B] for MEG extraction.

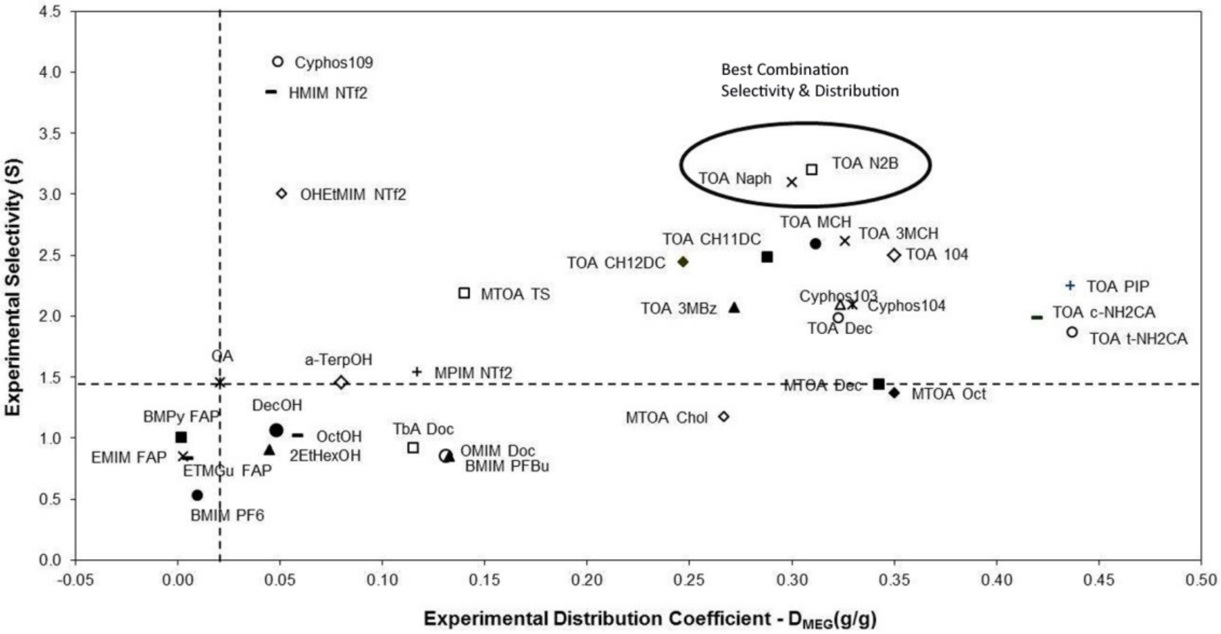

Figure 7-2. Distribution and selectivity for all investigated solvents. [TOA MNaph] (in the figure Naph) and [TOA N_2B] show the best combination of D and S.

7.3 Use of [TOA MNaph] for the recovery of other polar systems

[TOA MNaph] was selected for further research based on the aforementioned investigation on the MEG extraction performance, the lower cost of the anion as compared to [N_2B] and its easy synthesis. As the initial screening already showed that this ionic liquid offers a good balance between distribution coefficient and selectivity, this was studied much more extensively for a range of solutes. It was found that the more hydrophobic the solute (BuOH>2,3 BD > PG > MEG), the higher the distribution coefficient and the selectivity, the observed distributions were $D_{BuOH} = 21$, $D_{2,3\text{-}BD} = 1.08$, $D_{PG} = 0.85$, $D_{MEG} = 0.36$ and the selectivities $S_{BuOH}=274$, $S_{2,3\text{-}BD} = 11.47$, $S_{PG}= 8.20$, $S_{MEG}= 3.31$. In all cases and under varying conditions, [TOA MNaph] showed a combination of high solvent capacity and selectivity compare to conventional solvents (fatty alcohols) and commercially available ILs,[4-6] but in order to evaluate on the possible benefits of these solvents in solvent extraction technology, a conceptual process design including solvent recycling was developed and analyzed on energy requirements and technical feasibility.

7.4 Conceptual Process Design and estimation of energy consumption

In order to develop a conceptual process design of liquid-liquid extraction processes, proper thermodynamic descriptions of the liquid-liquid ternary systems (solute – water – solvent) are required. Most common, activity coefficient models such as NRTL or UNIQUAC [7] are applied, and in this work, these models have as well been applied. However, because the solvent was custom developed, the parameters for the thermodynamic models were not available, and Chapter 4 describes the thermodynamic modeling of the liquid-liquid systems. The conceptual process design for the extraction of MEG and PG (Chapter 5) was developed using Aspen Plus and the NRTL model that was developed in Chapter 4. The conceptual extraction process for the production of MEG and PG was compared with the conventional triple effect distillation (MED).

The conceptual modeling of the LLE process revealed that most of the energy is used in the recovery of the solvent which needs to be heated to evaporate the co-extracted water and the glycol. Because of the high heat capacity of the solvent, heat integration to recover the energy from the solvent was a necessity to reduce the energy demand in the extraction process. With heat integration, the energy demand of the LLE-process to recover MEG from the petrochemical process feedstock (20% wt MEG) can be reduced to 94% compared to the MED, this includes the recovery of the reaction and the solvent heat. For PG around 54% energy savings is feasible (for 10% wt PG from a fermentation process) by recovering the heat from the solvent recovery section. Although important energy saving are achieved a comparison on the capital expenditures is also required to conclude on the economic feasibility of the LLE technology. For the BuOH case (Chapter 6), the conceptual process design showed that [TOA MNaph], performs better than the benchmark solvent oleyl alcohol (OA) in terms of energy demand (5.65 MJ/kg BuOH vs 6.12 MJ/kg for oleyl alcohol). Even though no economic evaluation was made for this compound it is expected that the six times higher butanol distribution coefficient of 21 for [TOA MNaph] results in a reduction of 6.3 times of the solvent to feed ratio, and could reduce the capital costs largely compared to OA.

7.5 Economic Evaluation

Based on the conceptual processes that were developed to evaluate the energy consumption, economic evaluations including capital expenditure (CAPEX) and total annualized costs (TAC) were made for the recovery of MEG (from petrochemical and fermentation feed streams) and PG (from fermentation). With respect to the CAPEX, the conventional technology was found to be preferable over the liquid-liquid extraction for all three studied cases, because less equipment is required. Next to the additional equipment that is required for LLE technology, also the large inventory of expensive solvent increases the CAPEX significantly. The ionic liquid cost and heat integration equipment (heat exchangers) represent with 17-27% (for hypothetical solvent price of € 20/kg TOA MNaph), and 50-60% respectively important fractions of the overall CAPEX. Regarding the TAC for the MEG recovery, it can be concluded that at the current oil price level the LLE with IL is not an economic alternative for the conventional MED, particularly for the MEG fermentation option, despite the strong improvements in selectivity and distribution that were achieved in the work described in this thesis, a solvent with even higher selectivity and solvent capacity towards MEG is required to reduce the capital expenditures. Considering that in the last year the price of crude oil has fluctuated between €70-95 per barrel and as is shown in figure 7-3, the PG production from a fermentation process (process 3, where higher D and S were found) the LLE process with [TOA MNaph], looks more feasible to be implemented because the CAPEX is lower compared to MEG extraction from petrochemical feedstock due to less solvent amount and smaller equipment size are required and it could be an advantageous technology to replace MED when the crude oil price increases (at oil prices > 180 EUR/barrel).

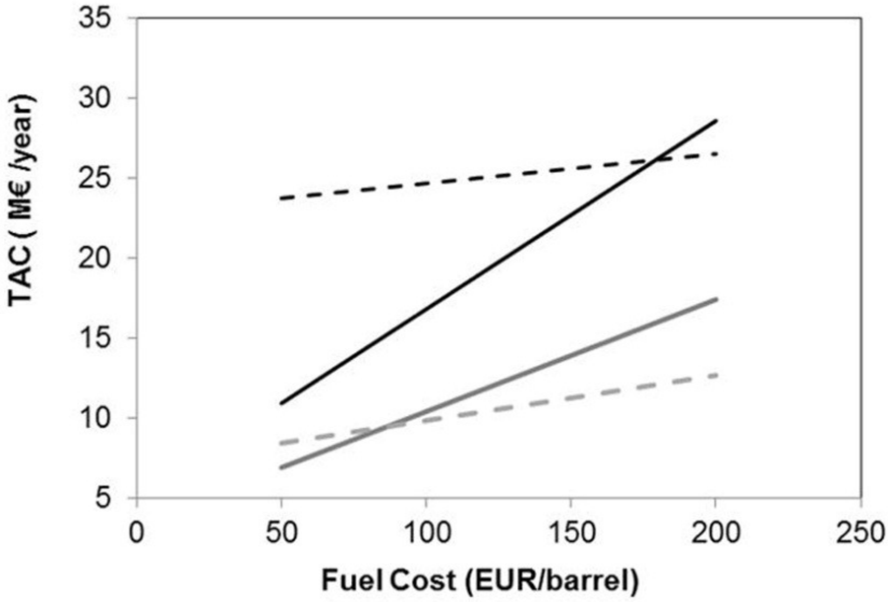

Figure 7-3. Process comparison based on the total annualized cost. (—, process 1 MEG, MED), (---, process 1 MEG, LEE) (— , process 3 PG, MED), (---, process 3 PG,LEE) .

7.6 Outlook and Recommendations

The feasibility of the LLE with IL is strongly dependent on the final glycol distribution coefficient and selectivity achieved and as the conceptual process design and economic evaluation showed, there are still challenges and improvements to extend the search of additional solvents (not limited to ionic liquids), especially for extremely polar compounds like MEG, which requires higher capacity and selectivity ($D_{MEG} > 0.36$ and $S > 3.31$ at $S/F = 1$, for an initial concentration of MEG of 20 wt% and 313.15 K) to reduce the energy for solvent heating and to reduce the equipment size and avoid CAPEX increment due to heat integration equipment. Previous simulations, showed that for MEG recovery values around $D > 3$ and $S>10$ are required to reduce the energy demand close to 50% without any heat integration. However, our experience regarding solvent screening for MEG recovery showed that getting a new solvent able to fulfill these requirements in solvent capacity and selectivity is a challenging task. Regarding the conceptual process design, although removal of glycol from the IL by means of the combination of double effect distillation and flash distillation seem to be possible, severe vacuum (10 and 1 mbar) and temperatures close to degradation temperature of [TOA MNaph] are required, it is advisable to study other options for the solvent recovery (such as nitrogen stripping), especially if the solvent is used for the extraction of compounds with higher boiling points. In order to improve the thermal stability of the IL, we also synthesized an IL with the same anion but a phosphonium cation (trihexyl(tetradecyl)phosphonium), [P^+ MNaph], because it has been reported that phosphonium bases IL are more thermally robust [8] than ammonium (as shown in Appendix C), in our evaluation for the extraction of MEG with [P^+ MNaph] we found than the D=0.31 and S=3.1 at 313.2 K and 20%wt MEG concentration , which is similar to values obtained with [TOA MNaph]. Additionally, more research is required to investigate the biocompatibility of [TOA MNaph] towards microorganisms to use this solvent for the recovery of products from fermentation broths. Finally, the most successful IL designed in this research can also be study and implemented in a process, where the IL be immobilized (solvent impregnated resins or membranes).The immobilization of the solvent could enhance mass transfer, and reduce solvent leaching in the aqueous phase and CAPEX due to solvent losses.

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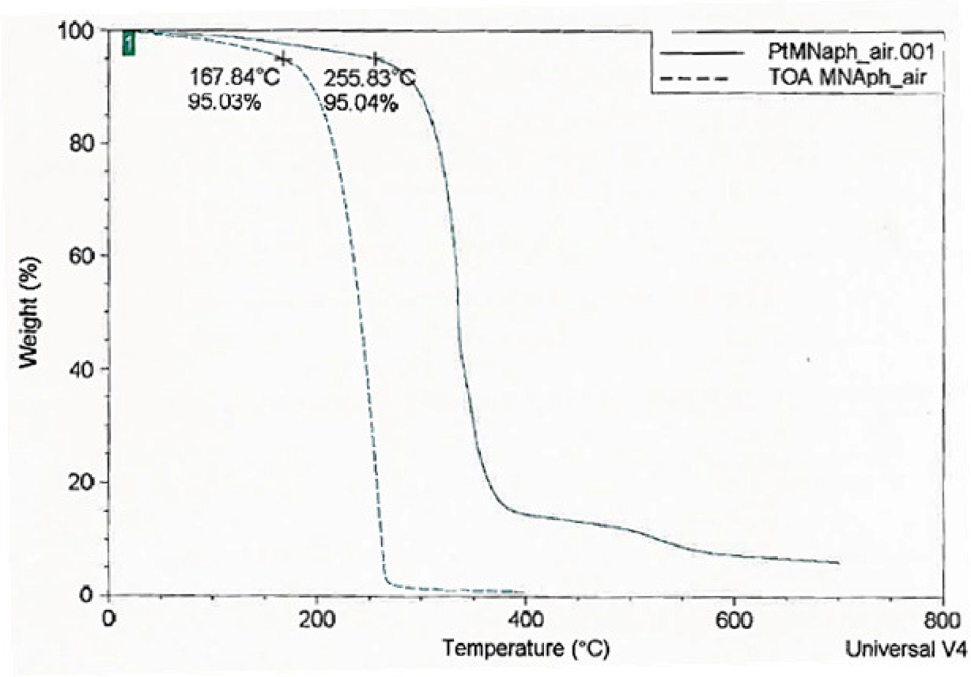
Appendix C

Thermogravimetrical Analysis (TGA) for the thermal degradation of Tetraoctyl ammonium methyl Naphtoate [TOA MNaph] and tetradecyl(trihexyl)phosphonium hydrogen [P+ MNaph].



Publication List

Journal Publications

Garcia-Chavez, L. Y.; Hermans, A. J.; Schuur, B.; de Haan, A. B., COSMO-RS assisted solvent screening for liquid-liquid extraction of mono ethylene glycol from aqueous streams. *Sep. Pur. Technol.* **2012**;

Garcia-Chavez, L. Y.; Schuur, B.; de Haan, A. B., Liquid-liquid equilibrium data for mono ethylene glycol extraction from water with the new ionic liquid Tetraoctyl Ammonium 2-Methyl-1-Naphtoate as solvent *J. Chem.Thermodynamics* **2012**

Garcia-Chavez, L. Y.; Shazad, M.; Schuur, B.; de Haan, A. B., Liquid-Liquid Equilibrium Data for the System Propylene Glycol +Water Tetraoctyl Ammonium 2-Methyl-1-Naphtoate for Recovery of Propylene Glycol from Aqueous Streams. *J. Chem. Thermodynamics* **2012**;

Garcia-Chavez, L. Y.; Garsia, C. M.; Schuur, B.; de Haan, A. B., Bio-butanol Recovery Using Non-Fluorinated Task Specific Ionic Liquids (TSILs). *Ind. Eng. Chem. Res.* **2012**.

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Garcia-Chavez, L. Y.; Garsia, C. M.; Schuur, B.; de Haan, A. B., Conceptual Process Design and Economic Analysis of Liquid-Liquid Extraction using Ionic Liquids for the Recovery of Glycols from Aqueous Streams. *Ind. Eng. Chem. Res.* **Submitted**

Oral Conference Presentation

Garcia- Chavez, L.Y.; Schuur B.; de Haan, A.B.Designer Solvent for Water Removal, DSTI Congress, Amersfoort, The Netherlands, September 2010.

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Curriculum Vitae

Lesly Garcia Chavez was born on 19 April 1980 in Morelos, Mexico. After finishing her Bachelor studies in Chemical Engineering in 2002 at the Universidad de las Americas-Puebla Mexico, she worked for two years in the Instituto de Investigaciones Electricas in the department of Thermal Processes in Morelos, Mexico. From 2005-2007 she studied a master in Chemical Engineering at the Universidad de Guanajuato in, Mexico. In April 2008 she started a PhD project at Eindhoven University of Technology in the Netherlands within the Process System Engineering group under the supervision of Prof. A.B. de Haan, focusing on the research topic “Designer Solvents for the Extraction of Glycols and Alcohols from Aqueous Streams”, of which the results are presented in this dissertation. Since April 2012 she is employed at Akzo Nobel Chemical B.V., Deventer in the Netherlands.