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Ionic-Liquid Based Separation of Azeotropic Mixtures

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A methodology for the screening of ionic liquids (ILs) as entrainers for ILs-based separation processes in binary aqueous azeotropic systems (e.g., water + ethanol and water + isopropanol) is presented. Ionic liquids as entrainers were first screened based on a combination of criteria such as stability, toxicity, and environmental impacts of the ILs. A Hildebrand solubility parameter group contribution model for ILs is highlighted to screen the miscibility of the ILs with the target solute component which was considered as a key target property to further screen the candidates from the previous step. The best candidates for aqueous systems were selected for final evaluation as follows: 1-ethyl-3-methylimidazolium ethylsulfate [C_2MIM][$EtSO_4$], 1-ethyl-3-methylimidazolium acetate [C_2MIM][Ac], 1-ethyl-3-methylimidazolium dicyanamide [C_2MIM][$N(CN)_2$], and 1,3-dimethylimidazolium dimethyl phosphate [C_1MIM][DMP]. For the final evaluation, the best candidates for aqueous systems were used as entrainers, and then the vapor-liquid equilibrium (VLE) of the ternary systems containing ILs was predicted by the Non Random Two Liquids (NRTL) model to confirm the breaking of the azeotrope. Based on minimum concentration of the ILs required to break the given azeotrope, the best ILs as entrainers for water + ethanol and water + isopropanol azeotropic mixtures were [C_1MIM][DMP] and [C_2MIM][$N(CN)_2$], respectively.

1. Introduction

Separation of azeotropic mixture is a challenging task in various petrochemical and/or biochemical processes. An azeotrope can be either homogeneous, containing completely miscible mixtures in a single phase, or heterogeneous, composed of two liquid phases. Approximately 90 % of all azeotropic mixtures are homogeneous (Lide, 2000). One example of the azeotropic system in the green biofuel process is the purification of the bioethanol feed which is needed to be purified to obtain a purity up to 99-99.8 %w (Kiss et al., 2013) Separation of these mixtures cannot be done by a simple distillation. There are several potential processes used for azeotropic separation: extractive distillation, azeotropic distillation, pressure swing distillation, liquid–liquid extraction, adsorption, and membranes (Pereiro et al., 2012). The most general separation process for the azeotropic mixtures is the extractive distillation. This technique involves with the addition of a new heavy chemical compound, namely an entrainer, to remove one of the components in the azeotrope, thus altering the relative volatility of the mixture (Pereiro et al., 2012). Volatile organic solvents are commonly used as conventional entrainers in extractive distillation; however, there are a lot of disadvantages as they produce volatile organic compound (VOC) emissions and require high energy consumption (Li et al., 2009).

With an increasing concern about environmental issues, in addition to the new principles of green chemistry, ionic liquids as “green solvents” or “designer solvents” have recently become attractive replacement options for many conventional organic solvents used in extractive distillation owing to their many unique structures and properties along with non-volatility, non-flammability, thermal and chemical stability, high dissolvability as well as their high efficiency in altering the relative volatility of the azeotropic mixtures (Li et al., 2009). As “designer solvents,” the chemical and physical properties of ILs are able to tune or tailor for use in a multitude of specific applications by an optimal design or selection of the cation, anion, and cation alkyl chain length (Pereiro et al., 2012). Hence, ILs can be fine-tuned with specific properties to perform as an excellent entrainer properties used in the extractive distillation processes and

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help reduce energy consumption and environmental impact as compared to conventional organic solvents (Seiler et al., 2004).

The main problem with designing or selecting ILs as an entrainer is the tremendous number of variations of cation and anion combinations (Holbrey and Seddon, 1999). It is too time-consuming and too cost-intensive to conduct experiments. Predictive thermodynamic property models and methodology/tools for screening optimal ILs entrainers clearly show a reduction in experimental time and optimization of the energy consumption for azeotropic separation.

The purpose of this research is to improve the methodology and Hildebrand solubility parameter group contribution (GC) model for the screening of ILs as entrainers for ILs-based separation processes in various homogeneous binary aqueous azeotropic systems (e.g., water + alcohols). Group contribution method is widely used to estimate the properties of pure components based on the structure of their molecules (Gani et al., 2005) including some complicated compounds like vegetable oils, biodiesel (Cunico et al., 2013) and ionic liquids (Roughton et al., 2012).

2. Methodology

A methodology for the screening of ILs as entrainers for ILs-based separation processes in various homogeneous binary azeotropic mixtures has been developed. The methodology of this work consisted of three main steps. The overall methodology is presented in Figure 1. Step1 is dedicated to the stability of the ILs by considering their chemical stability (hydrolysis) and thermal stability (thermal decomposition). The information about the stability of the ILs is collected from a literature search. Step 2 is dedicated to the miscibility of the ILs and the target solute component. From this step the best candidates (no more than 5 ILs) are selected. Step 3 is dedicated to finding the minimum concentration of the ILs where the given azeotrope is broken, the NRTL model is employed to predict the VLE of the ternary systems containing selected ILs by using Integrated Computer Aided System, ICAS - utility toolbox (Gani, 2006). Finally, the best ILs as entrainers are obtained.

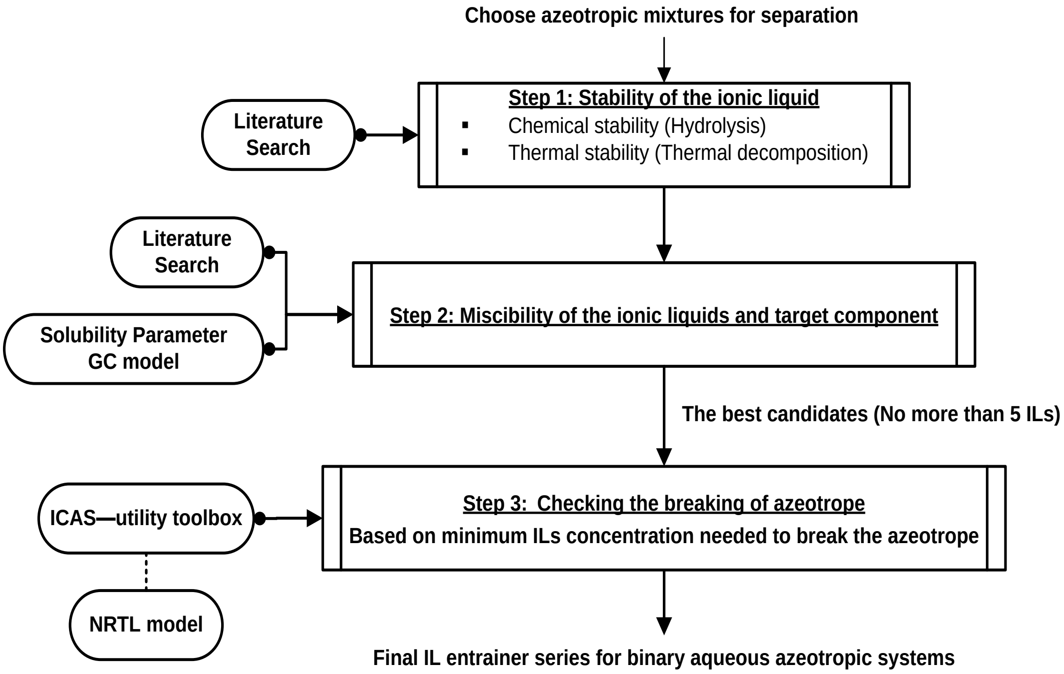


Figure 1: Overall methodology for screening of ILs as entrainers for ILs-based separation processes in binary aqueous azeotropic systems

3. Hildebrand solubility parameter GC model

The Hildebrand solubility parameter (δ_i) is defined as the square root of the cohesive energy density (c_{ii}) (Barton, 1991), as illustrated in Eq(1), which is the ratio of the enthalpy of vaporization (Δh_{vap}) to the molar volume (v_i). To indicate the miscibility of the ILs with the target solute component, δ_i is commonly used.

$$\delta_i = c_{ii}^{1/2} = \left(\frac{\Delta h_{vap} - RT}{v_1}\right)^{\frac{1}{2}} \tag{1}$$

Roughton et al. (2012) proposed a linear group contribution solubility parameter model for ILs (δ_{IL}) as shown in Eq(2). The ILs were defined into three groups consisted of alkyl chain groups, cation groups, and anion groups.

$$\delta_{IL} = \delta^{C}_{Alkylchain} + \delta^{C}_{Cation} + \delta^{C}_{Anion} = \sum\nolimits_{Alkylchain} n_i C_i + \sum\nolimits_{Cation} n_j C_j + \sum\nolimits_{Anion} n_k C_k + b \tag{2}$$

Where, subscripts i, j, and k represent alkyl chain groups, cation groups, and anion groups, respectively. The number of groups of type i is n_i, C_i is the contribution of group i to the overall solubility parameter value, and b is a constant value.

In this work, δ_i has been extended from the work done by Roughton et al. (2012). The experimental solubility parameter values of the 39 different ionic liquids at 298.15 K were utilized for the extension of the Hildebrand solubility parameter GC model (Marciniak, 2010, Marciniak, 2011, Weerachanchai et al., 2012, Yoo et al., 2012). It is assumed that the solubility parameters are similar at all different temperatures.

4. Results and discussion

4.1 Extended Hildebrand solubility parameter group contribution

Ionic liquids can be broken down into 5 alkyl chains, 8 cations, and 20 anions, and are used to explain the ILs in the data series. The contribution parameters existing in the molecule of ILs are given in Table 1. A plot between the experimental data and the predicted solubility parameters for ILs, calculated from Eq(2) along with the Hildebrand solubility parameter GC (Table 1), shows a high accuracy with 0.319 %AARD (percent Average Absolute Relative Deviation). The maximum relative deviation observed was 3.29 $MPa^{1/2}$. For instance, 1-ethyl-3-methylimidazolium tetrafluoroborate, $[C_2mim][BF_4]$, consists of 2 CH_3 groups (i), 1 CH_2 group (i), 1 imidazolium [Im] cation group (j) , and 1 tetrafluoroborate $[BF_4]$ anion group (k). By using Eq(2) and Table 1, the solubility parameter of $[C_2mim][BF_4]$ is 32.07 $MPa^{1/2}$.

4.2 Screening of ILs as entrainers for ILs-based separation processes

The proposed methodology (as illustrated in Figure 1) has been evaluated through two case studies: water + ethanol and water + isopropanol.

4.2.1 Stability of the ionic liquid (Step-1)

With regard to environmental stability, hydrolytic stability, and thermal stability of ILs are considered first. From the literature search, the hydrolytic or chemical stability of the ILs strongly depends on the anions of the ILs. Halogen containing anions of the ILs such as $[AlCl_4]^-$, $[PF_6]^-$, and $[BF_4]^-$ are normally found. The habitation of the halogen atoms in anions can form the toxic and corrosive hydrofluoric acid (HF) or hydrochloric acid (HCl) into the environment (Sowmiah et al., 2009). Freire et al. (2009) indicated that the ILs based on tetrafluoroborate $[PF_6]^-$ and hexafluorohoshate $[BF_4]^-$ anions are able to hydrolyse in water, and at high temperatures these anions lead to the formation of HF—an extremely toxic and corrosive compound. Therefore, the halogen containing ILs are avoided in the screening of the entrainers. In terms of thermal stability of ILs, the decomposition temperature (Td) commonly depends on the type of the cation. For instance, the imidazolium-based cation of the ILs seem to have better thermal stability than the pyridinium-based and tetraalkylammonium-based cation (Lazzús, 2012). Therefore, the suitable ILs as entrainers should consist of imidazolium-based cations and non-halogen containing anions with respect to the stability of ILs.

4.2.2. Miscibility of the ionic liquid and target component (Step-2)

The miscibility of the ILs and water as the target component is shown in Table 2. The miscibility of the ILs in water was obtained from literature (Pereiro et al., 2012) and the solubility parameters of the ILs were calculated from the Hildebrand solubility parameter GC model (Eq(2)). To avoid phase splitting of liquid mixtures, the best suitable entrainers should have a solubility parameter close to or similar to the solubility parameter of water as the target component and should be completely miscible with water. For water as the target component, the solubility parameter of water is 48 $MPa^{1/2}$ (Barton, 1991). The closest ILs are 1-

ethyl-3-methylimidazolium tetrafluoroborate, [C$_2$mim][BF$_4$] (δ_{IL}= 32.07 MPa$^{1/2}$) and 1-butyl-3-methylimidazolium tetrafluoroborate, [C$_4$mim][BF$_4$] (δ_{IL}= 31.60 MPa$^{1/2}$). However, due to the stability limitation, these two ILs can hydrolyse in water and cause the formation of HF. Hence, they are not suitable as entrainers. The criteria for screening suitable ILs are 1) non-halogen containing anions, and 2) completely miscible with water. Finally, four ionic liquids, which are 1-ethyl-3-methylimidazolium ethylsulfate [C$_2$MIM][EtSO$_4$], 1,3-dimethylimidazolium dimethyl phosphate [C$_1$MIM][DMP], 1-ethyl-3-methylimidazolium dicyanamide [C$_2$MIM][N(CN)$_2$], and 1-ethyl-3-methylimidazolium acetate [C$_2$MIM][Ac], were selected as best candidates for the aqueous azeotropic systems.

Table 1: Extended GC values of the ILs for the Hildebrand solubility parameter GC model

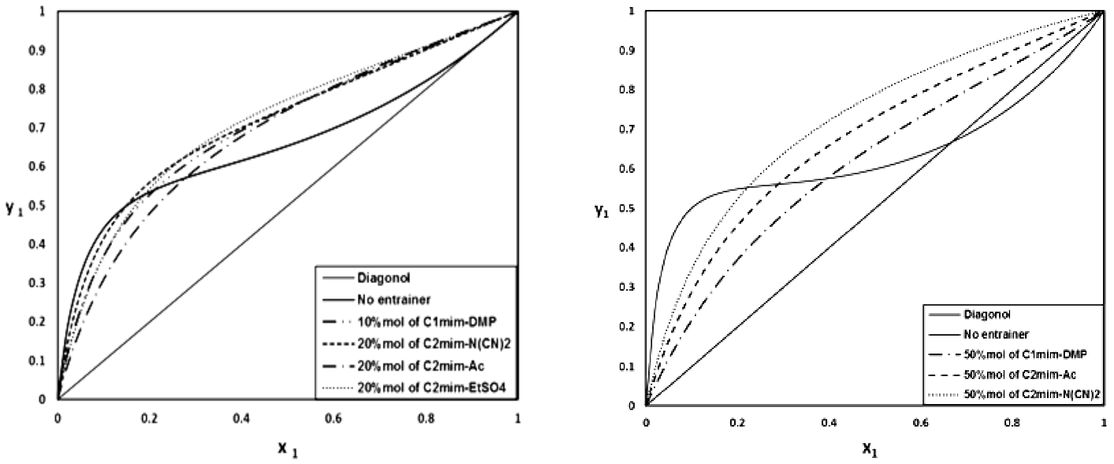
	Ionic Liquid group	Contribution [MPa$^{1/2}$]
Alkyl chain group (i)	CH$_3$	1.28
	CH$_2$	-0.24
	CH	-0.04
	CH$_2$O	-2.22
	OH	3.04
Cation groups (j)	Imidazolium [Im]$^+$	5.14
	Pyridinium [Py]$^+$	4.95
	Pyrrolidonium [Pyr]$^+$	5.31
	Phosphonium [P]$^+$	-0.05
	Sulfonium [S]$^+$	-0.79
	Piperidinium [Pip]$^+$	2.84
	Ammonium [A]$^+$	3.32
	Isoquinolinium [Isoq]$^+$	4.16
Anion groups (k)	Trifluoroacetate [CF$_3$COO]$^-$	0.62
	Thiocyanide [SCN]$^-$	0.25
	Trifluormethanesulfonate [CF$_3$SO$_3$]$^-$	-1.81
	2-(2-Methoxyethoxy)ethyl sulfate [MDEGSO$_4$]$^-$	0.33
	Octylsulfat [OcSO$_4$]$^-$	0.33
	Tosylate [TOS]$^-$	-1.22
	Bis(trifluoromethylsulfonyl)imide [Tf$_2$N]$^-$	1.24
	Dimethyl phosphate [DMP]$^-$	1.9
	Diethyl phosphate [DEP]$^-$	1.01
	Tetrafluoroborate [BF$_4$]$^-$	7.13
	Hexafluorophosphate [PF$_6$]$^-$	4.61
	Chloride [Cl]$^-$	-0.33
	Acetate [Ac]$^-$	0.22
	Dicyanamide [N(CN)$_2$]$^-$	0.9
	Nitrate [NO$_3$]$^-$	3.32
	Methylsulfate [MeSO$_4$]$^-$	1.18
	Ethylsulfate [EtSO$_4$]$^-$	-0.49
	Tetracyanoborate [TCB]$^-$	0.96
	Trifluorotris(perfluoroethyl)phosphate [FAP]$^-$	0.24
	Hexafluoroantimonate [SbF$_6$]$^-$	7.03
Constant value	b	17.48

Table 2: The miscibility of the ILs and water as the target component in the miscible phase

Ionic Liquid	Ionic Liquid Name	δ_{IL}^{calc} [MPa$^{1/2}$]
C$_2$mim-BF$_4$	1-ethyl-3-methylimidazolium tetrafluoroborate	32.07
C$_4$mim-BF$_4$	1-butyl-3-methylimidazolium tetrafluoroborate	31.60
C$_1$mim-DMP	1,3-dimethylimidazolium dimethyl phosphate	27.08
C$_2$mim-N(CN)$_2$	1-ethyl-3-methylimidazolium dicyanamide	25.84
C$_4$mim-N(CN)$_2$	1-butyl-3-methylimidazolium dicyanamide	25.37
C$_2$mim-Ac	1-ethyl-3-methylimidazolium acetate	25.16
C$_2$mim-EtSO$_4$	1-ethyl-3-methylimidazolium ethylsulfate	24.45

4.3 Checking the breaking of azeotrope (Step 3)

The best candidates for aqueous systems from the previous step were used as entrainers. To confirm the breaking of the azeotrope, the VLE of the ternary systems with ILs were generated by using the binary parameters and non-random factor of the NRTL model taken from literature (Calvar et al., 2008, Hernández, 2013, Wang et al., 2010, Zhang et al., 2007, Zhao et al., 2006). Among the four selected ILs for ethanol + water azeotropic separation, [C_1MIM][DMP] requires the lowest concentration to break the azeotrope with 10 %mol of the entrainer (Figure 2a). For water + isopropanol azeotropic separation, 50 % mol of ILs was required to break the azeotrope for all four IL candidates. As illustrated in Figure 2b, [C_2MIM][N$(CN)_2$] demonstrates the best IL entrainer since it gives the highest curve on the x-y diagram, indicating the ease of IL-water separation as compared to other ILs. The chemical structure of the final selected candidate of the water + ethanol and the water + isopropanol azeotrope is illustrated in Figure 3 and Figure 4, respectively.



a) b)

Figure 2: The a) x–y diagram of water + ethanol and b) water + isopropanol at 1 atm for the different concentration of four best ILs candidates

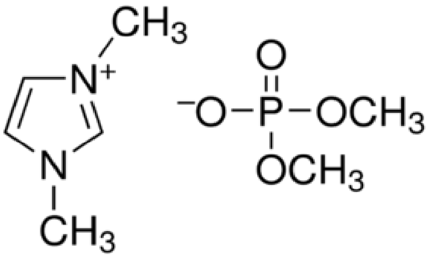


Figure 3: 1,3-dimethylimidazolium dimethyl phosphate ([C_1MIM][DMP]), the final entrainer for the separation of water + ethanol azeotrope

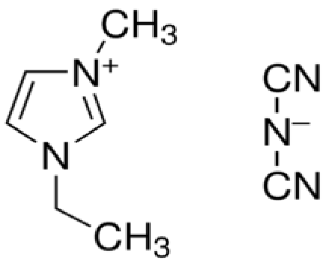


Figure 4: 1-ethyl-3-methylimidazolium dicyanamide *([C_2MIM][N$(CN)_2$]), the final selected entrainer for the separation of water + isopropanol azeotrope*

5. Conclusion

A methodology for the screening of ILs as entrainers for ILs-based separation processes in binary aqueous azeotropic systems (e.g., water + alcohols) was highlighted. The extended Hildebrand solubility parameter group contribution was presented to calculate the solubility parameter of the ILs as a key target property to screen ILs candidates. The VLE of the ternary systems containing ILs was predicted by NRTL model to confirm the breaking of the azeotrope, and to determine the minimum concentration of the ILs required to break the given azeotrope. For final evaluation, the best ILs entrainers for water + ethanol and water + isopropanol azeotropic mixtures were [C_1MIM][DMP] and [C_2MIM][N$(CN)_2$], respectively. The proposed methodology could be easily extended to other azeotropic systems. For future work, it is recommended to design and simulate the azeotropic separation processes (extractive distillation processes) using the proposed IL as entrainers to evaluate overall energy consumption of the ILs-based separation processes.

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