



Separation of the ethanol/water azeotropic mixture using ionic liquids and deep eutectic solvents



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ABSTRACT

Two ethanolamine-based ionic liquids (ILs) and two choline chloride-based deep eutectic solvents (DESs) were synthesized and evaluated as entrainers for the separation of the ethanol/water azeotropic mixture. Isobaric vapor-liquid equilibrium data of the ternary system ethanol/water/IL or DES were measured using an ebulliometer at 101.3 kPa. The ILs examined were 2-hydroxy ethylammonium acetate and 2-hydroxy ethylammonium hexanoate, while the DESs were choline chloride:urea (1:2) and choline chloride:triethylene glycol (1:3). In all cases, an increase of the relative volatility and, consequently, a displacement of the azeotropic point was observed. Depending on the entrainer, concentrations of about 5.5–9% (w/w) were adequate for the complete elimination of the azeotrope. Recoverability and biodegradation tests were carried out for all ILs and DESs. DESs were found to be biodegradable, while ILs exhibited lower biodegradation capacity than DESs. Furthermore, analysis with ¹H NMR proved that all entrainers can be recycled and reused. Finally, thermodynamic modeling of the ethanol/water/IL or DES mixtures was performed with the UNIQUAC and NRTL models. The results for both models were found to be in good agreement with the experimental data.

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1. Introduction

Increasing concern about environmental issues, as well as the establishment of new regulations, has directed the attention of the scientific community to novel processes based on “greener” technologies. In terms of biofuels, bioethanol is considered as the most promising alternative on short and medium terms due to its excellent properties as alternative biofuel. An important problem for biofuel industrial processes is the presence of azeotropic or close-boiling mixtures in their production, for example ethanol with water, since the separation is impossible by ordinary distillation. Several potential processes for separating azeotropes have come to light with extractive distillation being the most widely used process. The extractive distillation involves the addition in the system of a new heavy chemical compound (entrainer) which interacts with the components by altering their relative volatilities [1–3].

Ionic liquids (ILs) and Deep Eutectic Solvents (DESs) have been evaluated as entrainers for extractive distillation [4–7], due to their unique thermophysical properties. ILs are molten salts, consisting of large asymmetric organic cations and organic or inorganic anions. The low symmetry, high vibrational freedom and charge delocalization of the ions composing an IL reduce the stability of the crystalline phases, and thus their melting temperatures [8]. Many areas of application for ILs, except for use as entrainers, have been studied [9–11]. DESs are now widely acknowledged as a new class of Ionic Liquid analogues because they share many characteristics and physico-chemical properties with ILs (low vapor pressure, viscosity, density, conductivity, etc.). They can be often found in literature as “Low Transition Temperatures Mixtures”, (LTTMs) [12] and are composed of two or three cheap, renewable and safe components, which are capable to self-associate through hydrogen bonding interactions, to form a eutectic mixture with a melting point lower than that of each individual component [13]. The liquid state of the DES is achieved through freezing point depression, whereby hydrogen-bonding interactions between an anion and a hydrogen bond donor (HBD) are more energetically

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List of symbols

| | |
|----------------------------|--|
| p | Pressure |
| T | Temperature |
| \hat{f}_i^V, \hat{f}_i^L | Fugacity of component i in the vapor and liquid phase |
| y_i, x_i | Molar composition of component i in the vapor and liquid phase |
| $\hat{\varphi}_i^V$ | Fugacity coefficient of component i in the vapor phase |
| φ_i^S | Fugacity coefficient of component i in its saturation state |
| p_i^S | Vapor pressure of component i |
| PE_i | Poynting effect of component i |
| v_i^S | Saturated molar volume of component i |
| γ_i | Activity coefficient of component i |
| α_{12} | Relative volatility of component 1 with respect to component 2 |
| $\frac{\Delta u_{ij}}{R}$ | Binary interaction parameter of the UNIQUAC model |
| $\frac{\Delta g_{ij}}{R}$ | Binary interaction parameter of the NRTL model |

Acronyms

| | |
|--------|------------------------------------|
| IL(s) | Ionic liquid(s) |
| DES(s) | Deep eutectic solvent(s) |
| HBD | Hydrogen bond donor |
| VLE | Vapor-liquid equilibrium |
| NMR | Nuclear magnetic resonance |
| BOD | Biochemical oxygen demand |
| CBOD | Carbonaceous BOD |
| UCBOD | Ultimate carbonaceous BOD |
| NP | Number of experimental data points |

Superscript

| | |
|------|--------------------|
| exp | Experimental value |
| calc | Calculated value |

Subscript

| | |
|----------|-------------------------------------|
| IL-free | Ethanol/water pseudo-binary mixture |
| DES-free | Ethanol/water pseudo-binary mixture |

avored relative to the lattice energies of the pure constituents [14]. DESs were first reported in 2003 and since then, they have been studied in different areas of applications such as: electrochemistry, organic synthesis, biodiesel processing and catalytic reactions [13–17]. Among the unique properties of ILs and DESs, such as negligible vapor pressure, wide liquid range, good thermal stability, non-flammability and high dissolvability, the most important is that their physico-chemical properties can be tuned by proper selection of cation and anion in the case of ILs or HBD in the case of DESs (“designer solvents”). Furthermore, their use as entrainers in extractive distillation can overcome the handling problem associated with the use of solid salts due to the wide liquid range they exhibit. In addition, ionic liquids have been studied lately in process simulations [18].

The objective of this study is the experimental evaluation of ILs and DESs as entrainers in the separation of the azeotropic ethanol/water mixture. The ILs examined were 2-hydroxy ethylammonium acetate and 2-hydroxy ethylammonium hexanoate, while the DESs were choline chloride:urea (1:2) and choline chloride:triethylene glycol (1:3). The chemical structure of ILs and DESs are illustrated in Fig. 1.

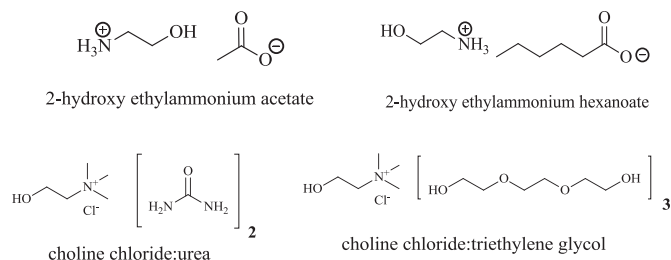


Fig. 1. Structures of the ionic liquids and deep eutectic solvents examined in this study.

Isobaric vapor-liquid equilibrium (VLE) measurements at 101.3 kPa and three different entrainer concentrations, 5%, 10% and 15% (w/w), have been performed. Furthermore, the VLE data were successfully modelled using the UNIQUAC and NRTL activity coefficient equations. The ILs and DESs synthesized in this study were also investigated for their recoverability and biodegradability.

2. Materials and methods

2.1. Materials

Ethanol (analytical reagent grade), water (HPLC gradient grade) as well as Aqualine™ Titrant 5 and solvent for the Karl Fischer titration were purchased from Fischer Scientific. Ethanolamine analytical grade was purchased from SERVA. Choline chloride 98 + % and hexanoic acid 98 + % were purchased from Alfa Aesar. From Alfa Aesar were also purchased acetic acid 98 + % and triethylene glycol 99%. All reagents were used without additional purification. The source and purities of the chemicals used are listed in Table 1. ¹H NMR spectra (300 MHz) were recorded on a Varian Gemini 2000 300 MHz spectrometer.

2.2. Synthesis and characterization of deep eutectic solvents and ionic liquids

2.2.1. Deep eutectic solvents

Choline chloride (ChCl), urea and triethylene glycol (TEG) were dried under vacuum for at least 3 h before use.

2.2.1.1. ChCl:urea. ChCl (0.14 mol, 20 g) and urea (0.28 mol, 16.8 g) were mixed under continuous and vigorous stirring at 70 °C for 30 min, under an inert atmosphere. The resulting colorless liquid was dried under reduced pressure for 5 h at 40 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm): 5.44 (s, 8H, 2(-NH₂)₂), 3.78–3.85 (m, 2H, HO-CH₂), 3.41 (t, 2H, $J = 5.1$ Hz, -N-CH₂), 3.12 (s, 9H, (-CH₃)₃).

2.2.1.2. ChCl:TEG. ChCl (0.06 mol, 8 g) and TEG (0.180 mol, 27.0 g) were mixed under continuous and vigorous stirring at 70 °C for 3.5 h, under an inert atmosphere. The resulting colorless liquid was dried under reduced pressure for 5 h at 40 °C.

¹H NMR (300 MHz, DMSO-*d*₆) δ (ppm): 4.59 (brs, 7H, -OH) 3.84–3.79 (m, 2H, OH-CH₂), 3.50 (s, 12H, 3(OH-CH₂)₂), 3.47 (d, 12H, $J = 6$ Hz, 3(O-CH₂)₂), 3.41 (d, 12H, $J = 6$ Hz, 3(O-CH₂)₂), 3.38 (d, 2H, $J = 3$ Hz, CH₂-N), 3.11 (s, 9H, (-CH₃)₃).

2.2.2. Ionic liquids

Hydroxyl ammonium ILs were prepared by neutralization of a carboxylic acid with ethanolamine as described in our previous work for analogous compounds [19]. Ethanolamine (0.5 mol, 30.2 mL) was placed in a two necked round-bottomed flask equipped with a reflux condenser and a dropping funnel. The flask

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