



Separation of the isopropanol-water azeotropic mixture using ionic liquids



Elenitsa Boli, Elpianna Dimou, Epaminondas Voutsas*

Laboratory of Thermodynamics and Transport Phenomena, School of Chemical Engineering, National Technical University of Athens, 9, Heroon Polytechniou Str., Zografou Campus, 15780 Athens, Greece

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ABSTRACT

Vapor-liquid equilibrium (VLE) measurements of the isopropanol-water-ionic liquid ternary mixtures were performed using an ebulliometer at 101.3 kPa. The ionic liquids (ILs) synthesized and examined as entrainers for breaking the azeotrope of the isopropanol-water mixture are: 2-hydroxyethylammonium formate (2HEAF), 2-hydroxyethylammonium acetate (2HEAA) and 2-hydroxyethylammonium butyrate (2HEAB). Three initial IL (entrainer) concentrations in the feed solution were examined in the VLE experiments: $\approx 9\%$, $\approx 14.5\%$ and $\approx 19.2\%$ w/w. It is shown that the introduction of the entrainers to the isopropanol-water system results in an increase of the relative volatility leading to the successful elimination of the azeotropic point. The relative volatilities decrease with increasing the alkyl chain length of the anion of the IL, following the order: $2HEAB < 2HEAA < 2HEAF$. Dynamic viscosities of the ionic liquids were measured in the temperature range from 293.15 to 363.15 K. Finally, thermodynamic modeling of the isopropanol-water-IL mixtures was performed with the UNIQUAC and NRTL models, and the results for both models were found to be in good agreement with the experimental data.

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1. Introduction

Separation of mixtures is a topic of great practical and industrial interest. Special attention has been paid for the separation of azeotropic or close boiling-point mixtures since they are particularly challenging and their separation can be highly energy and capital intensive. Isopropanol is a basic chemical material and solvent widely used in chemical and pharmaceutical industries thus its recovery from waste solvent stream is an important issue worthy of detail study [1]. Isopropanol (propan-2-ol) is known to form a homogeneous minimum boiling azeotrope with water at atmospheric pressure at 0.68 mol fraction of isopropanol and 353.1 K [2]. Therefore, a high-purity isopropanol product over its azeotropic composition cannot be obtained through conventional atmospheric distillation. Many separation methods have been proposed to separate the azeotropic mixture such as azeotropic distillation [3–6], pervaporation [7–16], liquid-liquid extraction [17,18] and extractive distillation [19–24].

Over the last decade, the scientific community has been paying more attention to novel 'green' technologies, due to the increasing

concern about environmental issues, as well as the establishment of new regulations. On these grounds, Ionic Liquids (ILs) have been widely proposed in the literature as entrainers for the separation of azeotropic mixtures. ILs show a number of advantages over the organic solvents and salts that are traditionally used to separate the azeotropic mixture such as non-volatility, non-flammability, high chemical and thermal stability, convenient recycling and tailorable nature. Their tunability allows the design of ILs with desired properties and their use to perform separations of widely varied nature. A large number of research work exist in the literature where ILs have been investigated as possible entrainers for the separation of aqueous alcohol systems [24–33], alcohol-ester systems [34–37] and alcohol-ketone systems [38]. Isopropanol-water-IL mixtures have been also studied and experimental data have shown that it is thermodynamically possible to obtain anhydrous isopropanol using ILs. To the best of our knowledge, most of this work has been focused on imidazolium based ionic liquids [19–24,39–42].

In this work, a new class of biodegradable ethanolamine-based protic ionic liquids (PILs) [33], are investigated as entrainers for the separation of isopropanol-water azeotropic mixture. The effect of 2-hydroxyethylammonium formate (2HEAF), 2-hydroxyethylammonium acetate (2HEAA), and 2-

* Corresponding author.

E-mail address: evoutsas@chemeng.ntua.gr (E. Voutsas).

hydroxyethylammonium butyrate (2HEAB) PILs in the separation of isopropanol–water mixture was studied through isobaric vapor–liquid equilibrium measurements at 101.3 kPa. All the PILs were used in three different concentrations ($\approx 9\%$, $\approx 14.5\%$ and $\approx 19.2\%$ w/w). Furthermore, the isopropanol–water–PIL systems were successfully modelled using the UNIQUAC and NRTL activity coefficient equations. Dynamic viscosities of the ILs studied in this work were measured in the temperature range from 293.15 to 363.15 K, and the experimental data were correlated with the Vogel–Fulcher–Tammann (VFT) equation.

2. Materials and methods

2.1. Materials

Propan-2-ol (analytical reagent grade), water (HPLC gradient grade), Aqualine™ Titrant 5 and solvent for the Karl-Fischer titration as well as ethanolamine were purchased from Fisher Scientific. Formic acid 99+% and glacial acetic acid 99+% were purchased from Chem-Lab. Butyric acid was purchased from FERAK. 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 and can be found in the Supporting Information (Figs. S1–S3).

2.2. Synthesis and characterization of ionic liquids

Hydroxyl ammonium-based protic ILs (see Fig. 1) were prepared by direct neutralization of ethanolamine with different carboxylic acid as described in details in a previous publication [33].

Ethanolamine was placed in a round-bottomed flask equipped with a pressure equalizing dropping funnel. The flask was mounted in an ice bath due to the highly exothermic nature of the acid–base reaction. Increased heat could lead to dehydration of the salt to the corresponding amide. Equimolar amount of the appropriate carboxylic acid was added drop wise to the flask under nitrogen atmosphere and vigorous stirring using a magnetic stirrer. Stirring was continued for 24 h at room temperature in order to obtain a viscous clear liquid. All the synthesized ILs were dried for 4 h at 60 °C in vacuum before use.

2-hydroxyethylammonium formate (2HEAF): Prepared following the General Procedure. IL₁ was obtained as a light-yellow liquid. ^1H NMR (300 MHz, DMSO-*d*₆, 26 °C) δ /ppm: 8.41 (1H, s, HCOO^-), 7.41 (4H, br s, $-\text{NH}_3^+$ and $-\text{OH}$), 3.56 (2H, t, $J = 5.1$ Hz, $-\text{CH}_2\text{OH}$), 2.81 (2H, t, $J = 5.1$ Hz, $\text{CH}_2-\text{NH}_3^+$).

2-hydroxyethylammonium acetate (2HEAA): Prepared following the General Procedure. IL₂ was obtained as an orange liquid. ^1H NMR (300 MHz, DMSO-*d*₆, 26 °C): δ /ppm 5.08 (4H, br s, $-\text{NH}_3^+$ and $-\text{OH}$), 3.44 (2H, t, $J = 5.5$ Hz, $-\text{CH}_2\text{OH}$), 2.67 (2H, t, $J = 5.5$ Hz, $-\text{CH}_2\text{NH}_3^+$), 1.77 (3H, s, $-\text{CH}_3$).

2-hydroxyethylammonium butyrate (2HEAB): Prepared following the General Procedure. IL₃ was obtained as an orange liquid. ^1H NMR (300 MHz, DMSO-*d*₆, 26 °C) δ /ppm: 6.01 (4H, br s, $-\text{NH}_3^+$ and $-\text{OH}$), 3.47 (2H, t, $J = 5.4$ Hz, $-\text{CH}_2\text{OH}$), 2.70 (2H, t, $J = 5.4$ Hz, $-\text{CH}_2\text{NH}_3^+$), 2.00 (2H, t, $J = 7.2$ Hz, $-\text{OOCCH}_2-$), 1.52–1.40 (2H, m, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 0.85 (3H, t, $J = 7.3$ Hz, $-\text{CH}_3$).

2.3. Apparatus and procedures

2.3.1. Viscosity measurements

Measurements of dynamic viscosity of the studied ionic liquids

Table 1
Materials description.

Chemical name	Source	Mole fraction purity	Purification method	Analysis method
2-propanol	Fisher Scientific	Analytical grade	None	–
Water	Fisher Scientific	HPLC gradient grade	None	–
Aqualine™ Titrant 5 and solvent for Karl-Fischer titration	Fisher Scientific	–	None	–
Ethanolamine	Fisher Scientific	Analytical grade	None	–
Formic acid	Chem-Lab	99+%	None	–
Acetic acid (glacial)	Chem-Lab	99+%	None	–
Butyric acid	FERAK	99+%	None	–
2-hydroxyethylammonium formate (2HEAF)	synthesis	99+%	In vacuo evaporation	^1H NMR ^a spectroscopy
2-hydroxyethylammonium acetate (2HEAA)	synthesis	99+%	In vacuo evaporation	^1H NMR ^a spectroscopy
2-hydroxyethylammonium butyrate (2HEAB)	synthesis	99+%	In vacuo evaporation	^1H NMR ^a spectroscopy

^a Nuclear Magnetic Resonance.

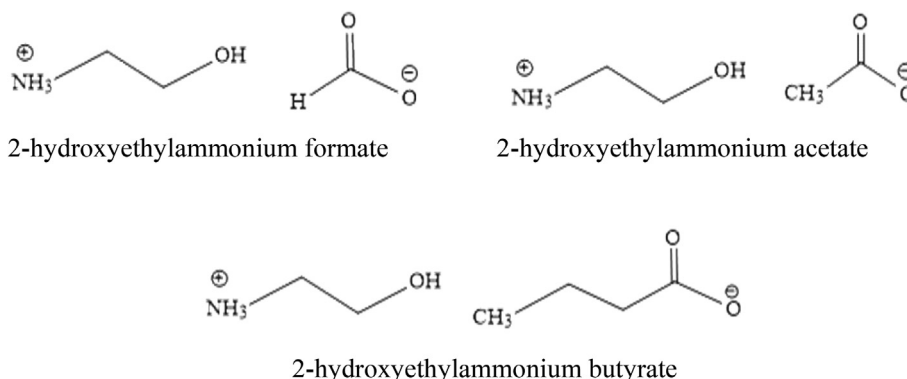


Fig. 1. Structures of the ionic liquids examined in this study.

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