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Boiling point elevation of aqueous solutions of ionic liquids derived from diethanolamine base and carboxylic acids

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ABSTRACT

This work reports experimental data and mathematical modeling of the boiling-point elevation (BPE) of aqueous solutions of ionic liquids (IL) derived from diethanolamine (DEOA) of cationic base and acetic, propionic, butanoic and pentanoic acids. Experimental boiling points were obtained for solutions of the four ILs in different water mole fractions (0.32 to 1.00) and pressures (12.1 to 91.8) kPa. Since ILs are compounds with very low vapor pressure, BPE calculations were performed employing the isofugacity conditions of water in liquid and vapor phase, in which the NRTL model was used to take into account the non-ideality of these liquid mixtures. The proposed model presented a satisfactory agreement with the experimental data, with a Mean Absolute Error of T = 1.43 K between calculated and all experimental values.

1. Introduction

Despite the intrinsic importance of solvents, which are usually volatile organic compounds in chemical processes, they can present undesirable characteristics such as flammability and toxicity making their usage potentially dangerous and unhealthy. For this reason, recent years have been seen interest in the total or partial replacement of traditional solvents by others that are safer for process operations and avoid environmental impact caused by loss of volatile solvents [1,2]. In this context, ionic liquids (ILs) seem to be a promising alternative due to some of their peculiar thermophysical characteristics such as low vapor pressure, non-flammability and high polarity [3].

Ionic liquids (ILs) are liquid phases designed for ions and they have been extensively studied in the chemistry community [4]. A subset of ILs is the group of protic ionic liquids (PILs), which are easily produced from a combination of a Brønsted acid and a Brønsted base. PILs are distinguished from other ILs due to proton transfer from the acid to the base leading to the presence of proton-donor and proton-acceptor sites that can be used to assemble a hydrogen-bonded network [5]. This characteristic can be

determined for the thermophysical properties of mixtures of PILs with molecules that contain a strong electronegative atom.

(Vapor + liquid) phase equilibrium (VLE) has been studied for binary and pseudo-binary systems containing alkanolamine based {PILs + water + ethanol [6] + methanol [7,8]}. Shen et al. [7] observed that the difference in the affinity between the PILs and different solvents can be used to increase the relative volatility between ethanol and water, which makes the use of such ionic liquids attractive for extractive distillation.

In order to provide relevant data for the (vapor + liquid) equilibrium of aqueous solutions of PILs, this work presents experimental results of the boiling point elevation of water in the presence of PILs derived from diethanolamine cationic base with acetic, propanoic, butanoic and pentanoic acids over a wide range of mole fraction of water and sub atmospheric pressure. This approach makes it possible to evaluate the influence of the carboxylic anion chain size on the interaction between PILs and water. The non-random two liquid (NRTL) model [9] was used for the calculation of activity coefficients of water and PILs in the liquid phase. Besides the simplicity of the model, Shen et al. [6] successfully correlated experimental (vapor + liquid) equilibrium data of (ethanol + water) solutions in PILs with the non-electrolyte NRTL model.
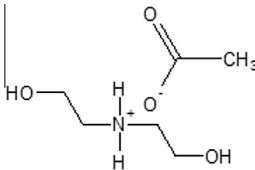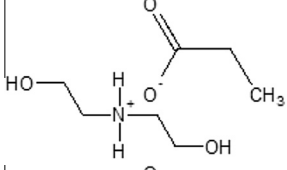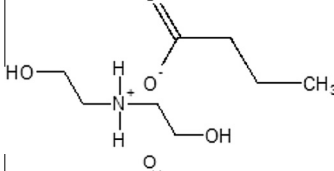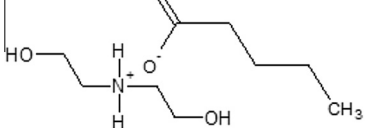
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TABLE 1
Provenance and mass fraction purity of the samples studied.

Chemical name	Source	Initial mass fraction purity	purification method	Final mass fraction purity	Analysis method
Acetic acid	Nuclear	$\geqslant 0.995$	None		
Propanoic acid	Sigma Aldrich	$\geqslant 0.99$	None		
Butanoic acid	Sigma Aldrich	$\geqslant 0.99$	None		
Pentanoic acid	Sigma Aldrich	$\geqslant 0.99$	None		
Diethanolamine base	Synth	$\geqslant 0.98$	None		
Diethanolamine acetate	Synthesis		Rotary evaporation	$\geqslant 0.93$	NMR/Karl Fisher
Diethanolamine propanoate	Synthesis		Rotary evaporation	$\geqslant 0.97$	NMR/Karl Fisher
Diethanolamine butanoate	Synthesis		Rotary evaporation	$\geqslant 0.94$	NMR/Karl Fisher
Diethanolamine petanoate	Synthesis		Rotary evaporation	$\geqslant 0.88$	NMR/Karl Fisher
Water			Distillation		

TABLE 2
Ionic liquids used in the BPE experiments.

Name and abbreviation	Molar mass/$(g \cdot mol^{-1})$	Ester excess in mass percentage	Structure
Diethanolamine acetate [DEOA][Ac]	165.19	3.3	
Diethanolamine propanoate [DEOA][Pr]	179.21	0.0	
Diethanolamine butyrate [DEOA][B]	193.24	4.7	
Diethanolamine pentanoate [DEOA][Pe]	207.27	10.3	

2. Materials and methods

2.1. Materials

The materials used for the ionic liquid synthesis are described in table 1. The synthetized ionic liquids and water used in boiling point elevation measurements are also included.

2.2. Methods

2.2.1. Ionic liquids synthesis

The ionic liquids used in this work (structures are shown in table 2) were produced and purified according to procedures described by Alvarez et al. [10], Bicak [11] and Cota et al. [12].

A volume of 193 mL of diethanolamine, which was previously melted in an oven at $T = 313$ K for 24 h, was added in a 500 mL three-necked glass flask equipped with a reflux condenser, also equipped with a digital thermometer and a mechanic stirrer. A thermostatic bath was used to maintain the system at $T = 295$ K. The organic acid (acetic, propanoic, butanoic or pentanoic) was slowly dripped into the system, which was kept under constant stirring. The dripping time was continued until an equimolar ratio of acid and base was achieved.

After the neutralization reaction, the ionic liquids were rotary evaporated (using a Edwards vacuum pump, model D-LAB 34-8) at $T = 323$ K for 48 h for the removal of water and non-reacted solvents. Molecular structure and purity were checked by Nuclear Magnetic Resonance (NMR). The analysis was performed on a Bruker Avance III 500 spectrometer, operating at 11.75 Tesla (500 MHz for 1H), using D_2O as solvent. The spectra are presented in figures A.1–A.4 in the Appendices. By evaluating the integral area of the hydrogen from acetate, propionate, butyrate and pentanoate attached to diethanolamine, we can observe that not all non-reacted esters evaporated. Correlating the integral values of the hydrogens of the diethanolamine group with hydrogens from esters, we observe an excess of 3.3%, 0.0%, 4.7% and 10.3% of acetate, propionate, butyrate and pentanoate, respectively. This suggests the need for more time to evaporate the solvent. The integral values were referenced to diethanolamine hydrogens.

The water content (mass fraction) in the PILs produced was determined by Karl Fisher titration using Volumetric KF Titrator V30 equipment, and the mass fraction was 0.0343, 0.0232, 0.0124 and 0.0187 for [DEOA][Ac], [DEOA][Pr], [DEOA][B] and [DEOA][Pe], respectively.

Thermogravimetric analyses (TGA) of PILs were carried out in a Netzsch equipment, model STA 409 PG/4/G Luxx. The decomposition