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Thermophysical properties of binary mixtures of {ionic liquid 2-hydroxy ethylammonium acetate + (water, methanol, or ethanol)}

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ABSTRACT

In this work, density and speed of sound data of binary mixtures of an ionic liquid consisting of {2-hydroxy ethylammonium acetate (2-HEAA) + (water, methanol, or ethanol)} have been measured throughout the entire concentration range, from the temperature of (288.15 to 323.15) K at atmospheric pressure. The excess molar volumes, variations of the isentropic compressibility, the apparent molar volume, isentropic apparent molar compressibility, and thermal expansion coefficient were calculated from the experimental data. The excess molar volumes were negative throughout the whole composition range. Compressibility data in combination with low angle X-ray scattering and NMR measurements proved that the presence of micelles formed due to ion pair interaction above a critical concentration of the ionic liquid in the mixtures. The Peng–Robinson equation of state coupled with the Wong–Sandler mixing rule and COSMO–SAC model was used to predict densities and the calculated deviations were lower than 3%, for binary mixtures in all composition range.

1. Introduction

Ionic liquids are organic salts which are liquid at room temperature. They have emerged as possible "green" solvents because they have very low vapor pressure and are stable within a wide temperature range and therefore have no polluting gas emissions. Through the adequate combination of cations and anions, the design of ionic liquids can enable the development of more efficient processes and products. Ionic liquids can be used as solvents in catalytic reactions [1], separation processes [2,3], electrolytic cells [4], heat transfer fluids [5], and other applications. However, there are two main problems with these new solvents: (i) their resistance to photodegradation [6] and low biodegradability [7], turning them into persistent pollutants that break through classical treatment systems into natural waters; (ii) their expensive production costs; for example, through using the task-specific ionic liquids designed by tethering amine functional groups to improve the absorption of CO_2 the process costs are increased [8]. These facts have led to the search for a new class of ionic liquids.

Bicak [9] synthesized 2-hydroxy ethylammonium formate (2-HEAF) through the reaction of monoethanolamine with formic acid. Yuan *et al.* [10] and Iglesias and co-workers [11,12] synthesized several ionic liquids from this hydroxyl ethylammonium family, by modifying the aliphatic chain of the organic acid, emphasizing the low cost, simplicity of synthesis, and different applications of this new family. Moreover, it was verified that some ionic liquids in this family present a negligible toxicity [13]. As a part of the characterization of these new compounds, physicochemical properties for pure ionic liquids and its mixtures with organic substances and water are of technological and theoretical interest.

Among several thermodynamic properties, volumetric and isentropic compressibilities are some of the most important for design and theoretical study. Previous studies [14] have shown that the addition of even small amounts of a low molecular weight solvent can dramatically increase or decrease the density and viscosity of ionic liquids. In a previous work, the densities and speed of sound for pure 2-HEAF and its binary mixtures with water, methanol, or ethanol were studied [15].

Therefore, this work is a continuation of our research on the thermophysical properties of ammonium based ionic liquids. The ionic liquid 2-hydroxy ethylammonium acetate (2-HEAA) is synthesized and purified. The density and speed of sound data for the binary systems {2-HEAA + (water, or methanol, or ethanol)} at temperatures from (298.15 up to 313.15) K over the whole composition range are reported at atmospheric pressure. The measured data is used to obtain the excess molar volumes, variations in the

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TABLE 1
Physical properties of pure compounds at 298.15 K and properties of the substances used in the modeling.

Compound	$M/(g \cdot mol^{-1})$	r/nm	$\rho/(g \cdot cm^{-3})$		$u/(m \cdot s^{-1})$		T_c/K	p_c/MPa	ω	COSMO segments[g]	V_{COSMO}/nm^3[g]
			Exp.	Lit.	Exp.	Lit.					
2-HEAA	121.14	0.22	1.149039		1790.73		699.22[e]	4.139[e]	0.93590[e]	717	0.160550
Water	18.02	0.12	0.997040	0.99705[a]	1496.89	1496.69[b]	647.13[f]	22.055[f]	0.34486[f]	136	0.025750
Methanol	32.04	0.16	0.786710	0.78637[a]	1102.98	1102.00[c]	512.50[f]	8.084[f]	0.56583[f]	258	0.048548
Ethanol	46.07	0.18	0.785261	0.78493[a]	1143.50	1143.00[d]	514.00[f]	6.137[f]	0.64356[f]	384	0.069856

M: molar mass.
r: molecular radii.
ρ: density.
u: speed of sound.
T_c: critical temperature.
p_c: critical pressure.
ω: Pitzer acentric factor.
V_{COSMO}: molecular volume calculated by the COSMO salvation model.
[a] Reference [35].
[b] Reference [36].
[c] Reference [37].
[d] Reference [38].
[e] Reference [39].
[f] Reference [40].
[g] This work.

isentropic compressibility, the apparent molar volume, the apparent molar isentropic compressibility, and the thermal expansion coefficient of the mixtures. Compressibility data, in combination with low angle X-ray scattering and NMR measurements proved the formation of a complex mediated by ion pair interaction over a critical concentration of the ionic liquid in the mixtures.

2. Experimental

2.1. Materials and methods

Ethanolamine was obtained from Aldrich at 0.99 purity by mass, while acetic acid was obtained from Sigma at 0.996 purity by mass. The alcohols used in the preparation of the samples were supplied by Merck with purity levels greater than 0.996 by mass. These compounds were used as received, without further purification. Double distilled deionized water was used for preparation of the solutions. During the experiments, the purity of solvents was monitored by density and speed of sound measurements. In table 1, experimental density and speed of sound of pure compounds are compared with literature data. The pure compounds were protected from sunlight and maintained at constant humidity and temperature.

Density and speed of sound of the pure liquids and mixtures were measured using a DSA 5000 density and speed of sound meter (Anton Paar) with accuracy of ±0.01 K for temperature, $\pm 5 \cdot 10^{-6}$ g · cm^{-3} for density, and ± 0.01 m · s^{-1} for speed of sound. Dry air and double distilled deionized water was used as a reference fluid to calibrate the densimeter. The mass of each compound was determined on a Kern 770 mass balance with an accuracy of $\pm 1 \cdot 10^{-4}$ g.

2.2. Ionic liquid synthesis

Ethanolamine was placed in a triple necked glass flask equipped with a reflux condenser, a PT-100 temperature sensor for controlling temperature and a dropping funnel. The flask was mounted in an ice bath. The acetic acid was added dropwise to the flask while stirring with a magnetic bar. Stirring was continued for 24 h at room temperature in order to obtain a final viscous liquid. The reaction is a simple acid–base neutralization forming a Brønsted ionic liquid, as shown in figure 1. Ionic liquid 2-HEAA is hygroscopic, and in order to decrease the water content as much as possible, it was dried for 48 h at room temperature under a vacuum of 20 kPa while stirring, before each use.

2.3. Experimental procedure

Each mixture was prepared with a known mass of ionic liquid and solvent, both injected into a glass vial using a syringe. The mixtures were sealed in the vials with an aluminum cap and a rubber plug. Also, the empty space in the vials was minimized, in order to avoid evaporation losses. The mixtures were injected into the DSA 5000 densimeter, and simultaneous measurements of density and speed of sound at each temperature and atmospheric pressure (≈100 kPa) were obtained. The density and speed of sound experimental uncertainties were less than $\pm 3 \cdot 10^{-5}$ g · cm^{-3} and ±0.5 m · s^{-1}, respectively.

2.4. NMR spectroscopy

All the NMR experiments were performed at 298 K in a 17.6 T Varian Inova-750 spectrometer (operating at 750 MHz proton frequency). The spectra were processed with Mestre-C software [16].

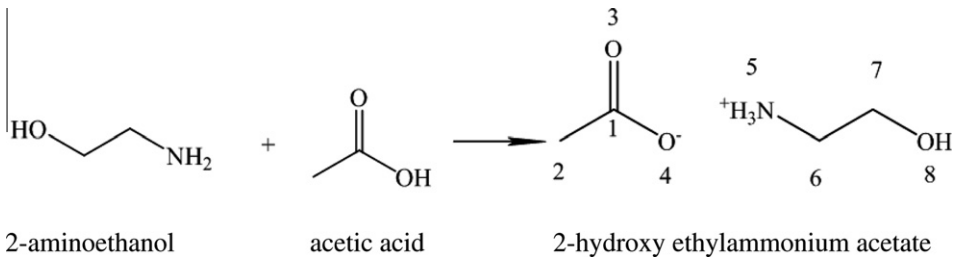

FIGURE 1. 2-HEAA Brønsted ionic liquid synthesized by acid-based neutralization. The numbering system used in the text is indicated.