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Properties for binary mixtures of (acetamide + KSCN) eutectic ionic liquid with ethanol at several temperatures

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ABSTRACT

Density, viscosity and conductivity were determined for the binary mixture of (acetamide + KSCN) eutectic ionic liquid with ethanol at $T = (298.15, 303.15, 308.15, 313.15, 318.15)$ K and atmospheric pressure. The density, viscosity values decrease with the increase of temperature while the conductivity values increase over the whole concentration range. The density and viscosity values decrease monotonically with the increase of the mole content of ethanol. From the experimental values, excess molar volumes V^E and viscosity deviations $\Delta\eta$ for the binary mixture were calculated and V^E and $\Delta\eta$ were both well fitted by a third order Redlich–Kister equation. With the increase mole fraction of ethanol, the conductivity values of the mixture increase gradually first and then decrease dramatically, and the highest conductivity values appear at 0.8562 mol fraction of ethanol. The relationship between the conductivity and the mole fraction of ethanol can be well described by a Castell–Amis equation. The interactions with ethanol molecular and ions of (acetamide + KSCN) ionic liquid were discussed by FTIR spectra.

1. Introduction

In the past a few years, ionic liquids (ILs) have been paid special attention as novel alternative to conventional organic solvents in chemical reaction, electrochemistry and separation process, owing to their non-volatility, thermal and chemical stability, wide liquid regions, high ionic conductivity and high solubility. Nevertheless, it should be mentioned that so far the industrial application of ILs is very few [1]; the paradoxical situation can partly be attributed to their cost and their complex preparation process. Moreover, the "green label" of ILs has long been challenged and the possible environmental toxicity and low biodegradability are currently reported in literature [2]. To overcome these drawbacks while maintaining the advantageous properties of ILs, deep eutectic solvents (DES), as a new generation of media has been developed. Due to different angles to analyze and research, these solvents were described as "eutectic mixtures" [3], "deep eutectic solvents" [4], "ionic liquids analogues" [5], "coordinated ionic liquids" [6] or "eutectic ionic liquids"(EILs) [7] in different literatures. These DESs are typically prepared by simple mixing a salt (usually quaternary ammonium salt, quaternary phosphonium salt or metal salt) with a hydrogen-bond donor (HBD) such as alcohol, carboxylic acid, amine, or amide. Usually, DES has large depression of the freezing point of mixture relative to the melting point of the individual components due to the strong interactions between the donors with the ions of salt. DES is now acknowledged as a new class of ILs because it shares many unique characteristics of ILs. Generally speaking, it has a melting point close to RT, and exhibits low volatility, wide liquid-range, high thermal stability, tunable property, and wide electrochemical potential window. However, it overcomes several limitations of its ILs cousins. DES is typically less expensive, easily prepared from industrial commodities at mild conditions, low toxic and sometimes biodegradable. Therefore, the application of DES in mental processing, synthesis and gas adsorption process has considerably increased [8]. It should be noted that compared with the arbitrary definition of ILs which consists solely of ions, DES is the mixtures of ions and organic molecular component, frequently the later as the predominant constituent. The term DES refers to liquids close to the eutectic composition of the mixtures, i.e., the molar ratio of the components which gives the lowest melting point. Considering the peculiarity of DES, whose physical properties are similar to classical ILs, while the chemical compositions are completely different, the term EIL instead of DES is selected in this paper.

Our present research interest has been focused on the preparation of newly designed ILs and exploration of their application in the desulfurization of flue gas [9,10]. EILs seem to be the ideal

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candidates from the cost point of view, but doubt exists over the absorption capacity and the recyclability [11]. Acetamide forms eutectic mixture with various compounds for its high solubility with a very large number of organic or inorganic compounds [7,12,13] and the physicochemical properties of acetamide based eutectics are similar with that of the water solution for the "water-like" acid-base properties of acetamide. At the same time, acetamide is easily obtained as a bulk commodity chemical. All these factors make acetamide a preferred donor component in the preparation of EILs. On the other hand, we have noticed that KSCN has a high solubility in liquid SO_2 [14]. Therefore, it is expected that an EIL prepared from KSCN as a salt has a high absorption of SO_2. Thus, the eutectic point of the mixtures of acetamide and KSCN was determined by cooling curve method, and then the (acetamide + KSCN) EIL with a eutectic point of $T = 278.15$ K was prepared at 3:1 mol ratio of acetamide and KSCN in our lab [15]. According to the classification of EIL by Abbott (acetamide + KSCN) belongs to type IV eutectics [8]. IR and ^{1}H-NMR analysis show that the liquids are made up of metal-containing cations in which the donor is coordinated to the cations. Data on the liquid region, decomposition temperature, density, viscosity and electrical conductivity are presented, and these are shown to be significantly similar to traditional ILs. Furthermore, (acetamide + KSCN) has unprecedented high SO_2 absorption capacity of 0.588 g/g at $T = 293.15$ K and 1 atm, showed promising industrial application prospects [15]. Considering from the industrial angle, the interactions between ILs with other molecular solvents, among which are alcohols, are indispensable for the design of practical application. Therefore, in this paper, the properties (density, viscosity and conductivity) for binary mixture of (acetamide + KSCN) EIL with ethanol were determined at $T = (298.15, 303.15, 308.15, 313.15, 318.15)$ K at the whole composition range. From the experimental data, excess molar volumes V^E and viscosity deviations $\Delta\eta$ for the binary mixture were calculated and the values were fitted to a Redlich–Kister equation.

2. Experimental

(Acetamide + KSCN) EIL were prepared according to literature method [15]. The water content determined by Karl Fischer analysis was less than 0.1%. Acetamide, KSCN and ethanol are all reagent grade in this investigation. All the materials and their sources, mass fraction purities and physical properties were listed in Tables 1 and 2. The binary mixtures of EIL with ethanol were prepared by mixing accurately weighed EIL and ethanol. The weight was measured by a analysis balance with ±0.0001 g accuracy (Shanghai Precision & Scientific Sky Beautiful Instrument Co. LTD).

The density, viscosity and conductivity of the binary mixtures were measured in a water bath with a temperature control accuracy of $T = \pm 0.01$ K. The density was determined by pycnometer method and the pycnometer was calibrated by anhydrous ethanol or ultra pure water. The viscosity was detected by Pinkevitch method according to GB/T10247-2008 with a time resolution of 0.01 s. The conductivity was measured by DDS-11A conductivity detector (Leici Xinjing instrument limited company, Shanghai, China). Each value was reported by averaging three consecutive runs. The density and viscosity of ethanol or pure water used in this study were taken from literature [16,17]. Uncertainties of density was $\pm 1 \cdot 10^{-3}$ g · cm^{-3}, and the relative standard uncertainties viscosity and conductivity were 0.03 and 0.02. Fourier transform infrared spectroscopy (FTIR) measurements were carried out using a Thermo Nicolet 6700 FTIR spectrometer with ATR attachment.

3. Results and discussion

3.1. Density of binary mixtures of (acetamide + KSCN) with ethanol

The densities of binary mixtures of (acetamide + KSCN) (3:1) with ethanol were detected at atmospheric pressure and at $T = (298.15, 303.15, 308.15, 313.15, 318.15)$ K. Prior to measurements, several mixtures were prepared in order to determine the miscibility range [18]. The results showed that (acetamide + KSCN) (3:1) is completely miscible with ethanol in the whole concentration range. The density values of binary mixtures of (acetamide + KSCN) (3:1) with ethanol are listed in table 3. It can be seen from table 3 that at the same ethanol fraction, the density values always decrease with an increase of temperature, and the property is similar to the pure EIL [15]. The densities decrease with the increase of mole fraction of ethanol (x_1) at a constant temperatures, and the fraction dependence is nonlinear. The densities decrease slightly at $x_1 < 0.8$ and then decrease sharply at $x_1 > 0.8$, similar results have been found in the study of binary mixtures of

TABLE 1
Sample purity description.

Component	Source	Initial mass fraction purity	Purification method	Final water mass fraction	Analysis method
Ethanol	Tianjin yongda chemical reagent co., Ltd, China	>0.998	Molecular Sieves	0.0002	Karl Fischer Titration
Acetamide	Tianjin bodi chemical co., Ltd, China	> 0.985	Vacuum evaporation	0.0010	Karl Fischer Titration
KSCN	Tianjin yongda chemical reagent co., Ltd, China	>0.985	Vacuum evaporation	0.0010	Karl Fischer Titration

TABLE 2
Comparison of the measured values for pure components and literature data.

Component	T/K	ρ/(g · cm^{-3})		Error/%	η/(mPa · s)		Error/%
		[a] Expt.	[b] Lit. [16]		[a] Expt.	[b] Lit. [16]	
Ethanol	298.15	0.7852	0.7855	−0.038	1.096	1.0569	3.699
	303.15	0.781	0.7803	0.09	1.003	0.9645	3.992
	308.15	0.7767	0.7760	0.09	0.914	0.8827	3.546
	313.15	0.7723	0.7720	0.039	0.834	0.8100	2.963
	318.15	0.7663	0.7674	−0.143	0.764	0.7451	2.537

[a] Standard uncertainties u are as follows: $u(P) = \pm 0.005$ MPa, $u(T) = \pm 0.01$ K, $u(\rho) = \pm 1 \cdot 10^{-3}$ g · cm^{-3}, and the relative standard uncertainties u_r in $u_r(\eta) = 0.03$.
[b] Standard uncertainties u are as follows: $u(T) = \pm 0.01$ K, $u(\rho) = \pm 5 \cdot 10^{-5}$ g · cm^{-3}, $u(\eta) = \pm 0.2$ mPa · s.