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Molar enthalpy of mixing and refractive indices of choline chloride-based deep eutectic solvents with water

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ABSTRACT

The molar enthalpies of mixing were measured for binary systems of choline chloride-based deep eutectic solvents (glycerol, ethylene glycol and malonic acid) with water at 298.15 K and 308.15 K, and atmospheric pressure with an isothermal calorimeter. Refractive indices were also measured at 303.15 K and atmospheric pressure. The binary mixtures of {chcl/glycerol (1:2) + water, chcl/ethylene glycol (1:2) + water} showed exothermic behaviour over the entire range of composition, while the binary mixture of {chcl/malonic acid (1:1) + water} showed endothermic behaviour at first and then changed to be exothermic with the increasing content of chcl/malonic acid (1:1). Experimental refractive indices were fitted with the Redlich–Kister equation, and experimental molar enthalpies of mixing were correlated with the Redlich–Kister equation and the non-random two-liquid (NRTL) model. The NRTL model with the fitted parameters was used to predict the vapour pressures of these three mixtures. For mixtures of {chcl/glycerol (1:2) + water} and {chcl/ethylene glycol (1:2) + water}, the predicted vapour pressures agreed well with the experimental results from the literature. While for mixture of {chcl/malonic acid (1:1) + water}, the predicted vapour pressures showed deviation at the high concentration of chcl/malonic acid (1:1), and this was probably because of the complex molecular interaction between chcl/malonic acid (1:1) and water.

1. Introduction

Deep eutectic solvents (DESs) are eutectic mixtures that are liquids at room temperature. DESs are promising alternatives to ionic liquids (ILs) to replace organic solvents because of their low vapour pressure, high thermal stability and diversity of ionic structures [1]. However, the viscosity of pure DESs is generally higher compared to traditional organic solvents, which results in operational difficulty [2]. The addition of water may significantly decrease the viscosity and then improve the transport properties of the DESs with little effect on their other chemical properties. Aqueous solutions of DESs have been used in organic synthesis [3], catalysis [4], electrochemistry [5] and carbon capture [6].

In order to develop and design a new process based on DESs, it is essential to obtain physical and chemical properties of pure DESs and their aqueous solutions. Properties of pure DESs have been reported such as density, viscosity, conductivity and surface tension [1], while properties of DESs in aqueous solutions are still relatively limited. Recently, the excess molar volume and excess molar activation energy of chcl/urea (1:2) with water at temperature of (298.15–333.15) K have been studied, and it shows that the CO_2 dissolution enthalpy decreases with the addition of water [7]. In Li's research group, physical and chemical properties of pure DESs and their aqueous solutions have been studied systematically including densities, viscosities, refractive indices, vapour pressure, molar heat capacities, and electrical conductivities [8–15].

Molar enthalpy of mixing (H_m) is an important thermodynamic property of solutions. The H_m characterizes the non-ideal behaviour of real mixtures, and it can be used to investigate the molecular interactions and macroscopic behaviour of fluid mixtures. H_m is useful in designing chemical processes, developing and validating thermodynamic models [16–20]. Literature surveys show that there is no available molar enthalpy of mixing data for the aqueous solutions of DESs so far.

In this work, the molar enthalpy of mixing (H_m) and refractive indices for binary systems of choline chloride-based DESs (glycerol, ethylene glycol and malonic acid) with water were measured at 298.15 K and 308.15 K and atmospheric pressure. DESs of (choline chloride + glycerol), (choline chloride + ethylene glycol) at 1:2 mol ratios and (choline chloride + ethylene glycol) at 1:1 mol ratios

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were studied. The specific mole ratios of choline chloride in DESs were chosen because their other physical and chemical properties have also been reported by others [6,8,10,13–15]. Redlich–Kister equation and non-random two-liquid (NRTL) model were used to correlate the experimental results measured in this work. The model with the parameters were used to predict the vapour pressure of aqueous DESs solutions and compared with the available experimental values.

2. Experiments

2.1. Chemicals and synthesis of DESs

The molecular formula, CAS number, mass fraction and source of the chemicals used in this work are listed in Table 1. The chemicals were analytical reagent (A. R.) grade and their mass fractions were as those stated by the suppliers. All chemicals were used as received. Choline chloride, glycerol, ethylene glycol and malonic acid were used for the synthesis of DESs. Potassium chloride and THAM were used to verify the accuracy of the calorimeter. High-quality deionized water was used to prepare the solution in this work.

The DESs' ingredients were dried in a vacuum oven for 24 h to avoid the traces of moisture. The DESs were prepared by weighing using an electronic balance (Sartorius BSA124S) with a precision of $\pm 10^{-4}$ g. The corresponding uncertainty for the DES composition, *i.e.* the mole ratio of the DESs' ingredient, is within $\pm 4 \times 10^{-3}$. The DESs were prepared by stirring the two components at 373.15 K until a homogenous colourless liquid was formed [21]. Each pure liquid sample (*i.e.* DES) was dried under vacuum at 333 K for 72 h to remove any volatile impurities and stored in a dry box for further use. The moisture contents of the three DESs were detected with Karl Fischer Titrator and were found to be less than 0.0025 (mass fraction).

2.2. Measurement of refractive index

Refractive indices (n_D) were measured using WYA Abbe Refractometer. Deionised water was used for calibration before each experiment. The average uncertainty in measurements was estimated to be ±0.0003.

2.3. Measurement with microcalorimeter

The TAM Air isothermal microcalorimeter (TA Instruments, USA) was used to determine the mixing enthalpies of the binary systems (*i.e.* choline chloride-based DESs with water). The operating temperature range of the calorimeter was from 278.15 K to 333.15 K and the temperature was controlled by circulating air to keep the temperature very stable within ±0.02 K. The parallel twin-chamber measuring channels were used for the measurements: one was used as the measurement chamber and the other was as the reference chamber. In the measurement chamber, DESs and water were placed separately. DESs were placed in a 20 mL ampoule on the lower measurement chamber and water was in the Hamilton syringe on the top of ampoule. The DESs and water were premixed to the desired proportion and placed in the reference chamber. Water was injected into the ampoule by a Hamilton syringe after the ampoule temperature was stable. The corresponding thermal power curve was recorded automatically by a computer. The reference chamber was used to eliminate the heat supplied by the outside temperature disturbances, and the heat of stirring was negligible.

The accuracy of the calorimeter was verified by measuring the dissolution enthalpy of KCl in water and THAM in 0.1 M HCl at 298.15 K. The measured molar solution enthalpies of these two systems were (17.5314 ± 0.046) kJ·mol^{-1} and (29.7766 ± 0.02) kJ·mol^{-1}, respectively. The results from the literature are (17.536 ± 0.009) kJ·mol^{-1} for KCl [22,23] and (29.739 ± 0.01) kJ·mol^{-1} for THAM [23]. The average deviations were 0.03% for KCl and 0.13% for THAM.

3. Results and discussion

3.1. Refractive indices

The refractive indices of aqueous DESs were measured at 303.15 K and atmospheric pressure. The mole fraction of DES x_1 was calculated based on the DES and H_2O (*i.e.* x_1 = (mol DES)/(mol DES + mol H_2O). The number of moles of H_2O (mol H_2O) includes two parts, that is, the H_2O from the sample of DES and the H_2O added to prepare the aqueous solvents. The experimental results are listed in Table 2. Refractive index, n_D increased with the increasing content of DESs. Such results were expected since the mixture generally became denser as the content of DES solution increased, resulting in an increase of refractive indices. The measured refractive indices for chcl/glycerol (1:2) were compared with the available results in the literature [15,24] and the relative deviations (RDs) were −0.059% [15] and −0.069% [24], respectively. For chcl/ethylene glycol(1:2), the RD was 0.11% compared with the literature [15]. Part of the slight deviation may be from the different water content of the sample of DESs. In addition, the experimental refractive indices of {chcl/glycerol (1:2) + water} and {chcl/ethylene glycol(1:2) + water} were compared with those reported by Leron et al. [15] as illustrated in Fig. 1. As we can see from Fig. 1, the measured experimental results in this work are in agreement with the literature data. The values of n_D for the mixture of {chcl/glycerol (1:2) + water} and {chcl/ethylene glycol (1:2) + water} interpolated from those measured data points in this work were compared with those reported by Leron et al. [15], and the average relative deviations (ARDs) of n_D are 0.047% and 0.14%,

Table 1
Chemicals used in this work.

Chemical name	Molecular formula	CAS number	Mass fraction purity[c]	Source	Purification method
ChCl[a]	$C_5H_{14}ClNO$	67-48-1	⩾0.98	Sinopharm Chemical Reagent Co., Ltd	None
Glycerol	$C_3H_8O_3$	56-81-5	⩾0.99	Sinopharm Chemical Reagent Co., Ltd	None
Ethylene glycol	$C_2H_6O_2$	107-21-1	⩾0.99	Shanghai No.4 Reagent &H.V. Chemical Co., Ltd	None
Malonic acid	$C_3H_4O_4$	141-82-2	⩾0.98	Shanghai Lingfeng Chemical Reagent Co., Ltd	None
Potassium chloride	KCl	7447-40-7	0.998	Aladdin	None
Hydrochloric acid	HCl	7647-01-0	0.36–0.38	Shanghai Lingfeng Chemical Reagent Co., Ltd	None
THAM[b]	$C_4H_{11}NO_3$	77-86-1	⩾0.999	Aladdin	None

[a] ChCl = Choline chloride.
[b] THAM = Tris(hydroxymethyl) aminomethane.
[c] As stated by the suppliers.