Fluid Phase Equilibria 448 (2017) 9–14

Contents lists available at ScienceDirect

Fluid Phase Equilibria

journal homepage: www.elsevier.com/locate/fluid

Indirect assessment of the fusion properties of choline chloride from solid-liquid equilibria data

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ARTICLE INFO

Article history:
Received 8 February 2017
Received in revised form
16 March 2017
Accepted 17 March 2017
Available online 21 March 2017

Keywords:
Choline chloride
Deep eutectic solvents
Melting properties
Experimental
Ideal solutions

ABSTRACT

The temperature and enthalpy of fusion of choline chloride -[Ch]Cl- are not directly measurable since this compound decomposes upon melting. Yet, given the wide use of this compound in the preparation of deep eutectic solvents (DES), its thermophysical fusion properties are very important for a better understanding of these mixtures and the thermodynamic description of their solid-liquid phase diagrams. In this work, the fusion properties of choline chloride were estimated using the solubility curves of choline chloride in ten different ionic compounds, forming simple binary eutectic mixtures with quasi-ideal liquid phases. Experimental solid-liquid equilibria data for these systems -[Ch]Cl + ionic compounds- were measured, and the ideality of the systems assessed through the quantification of the activity coefficients and their comparison in each pair of binary solutions. The values estimated for the fusion properties of choline chloride are $T_{fus,[Ch]Cl} = 597 \pm 7$ K and $\Delta_{fus}H_{[Ch]Cl} = 4300 \pm 600$ J mol^{-1}. These were additionally checked by thermodynamic consistency tests and by the prediction of the solid-liquid curves with COSMO-RS model. The results obtained with both procedures allow us to guarantee the usefulness and robustness of the estimated data.

1. Introduction

Deep eutectic solvents (DES) are a neoteric, ecofriendly, class of solvents intensively investigated in the past few years [1]. Prepared by mixing Lewis and Brønsted acids and bases, their combination gives rise to low melting points mixtures by hydrogen bond complexation [2]. The formulation does not involve any chemical reaction or additional purification steps. Additionally, the fact that their structures can be adjusted by selecting the hydrogen-bond donor–acceptor combinations, and that their phase behavior and physical-chemical properties can be tailored, classifies them as designer solvents [3]. Their exceptional properties [2,4] make them interesting in many fields [2,5–7]. Owing to their promising applications, efforts have been devoted to their characterization [2].

Due to its good solvent capacity, non-toxicity, biodegradability and economical synthesis, choline chloride ([Ch]Cl) is by far the most common compound used in DES formulation [2,7,8]. Usually, [Ch]Cl is combined with safe hydrogen bond donors such as polyols, urea, carboxylic acids or sugars [1,9,10], and their main applications include organic synthesis, biocatalysis and electrochemistry [2,7,11]. The knowledge of the fusion properties of [Ch]Cl is thus of utmost importance for a thermodynamic characterization of the choline-based DES, including the eutectic points and the complete description of the solid-liquid phase diagrams. This is relevant for the design and optimization of processes involving DES, including the search and selection of the best mixture for a particular application. As choline chloride decomposes before/upon melting [12] the use of direct technics for the measurement of its fusion properties cannot be applied. So far, a value of 575.15 K [1] is usually used as the melting temperature, however that is probably a decomposition temperature. No melting enthalpy was assigned to this compound until now.

In this work an indirect method to estimate the fusion temperature and enthalpy of [Ch]Cl is applied. This is based on the

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http://dx.doi.org/10.1016/j.fluid.2017.03.015
0378-3812/

evaluation of the solid-liquid phase equilibria of a set of quasi-ideal binary solutions formed by [Ch]Cl and other ionic compounds. Previous works [13–15] have shown that mixtures of ionic liquids, even with melting points above 373.15 K, often form quasi-ideal mixtures. Thus, the solubility curves of ten eutectic systems formed by [Ch]Cl and the ionic compounds (IC): choline acetate ([Ch][Ac]), choline propanoate ([Ch][Prop]), choline butanoate ([Ch][Buta]), tetrabutylammonium chloride ([N_{4444}]Cl), tetrabutylphosphonium chloride ([P_{4444}]Cl), benzyldimethyl(2-hydroxyethyl)-ammonium chloride ([BzCh]Cl), 1-butyl-1-methylpyrrolidinium chloride ([C_4mpyr]Cl), choline bis(trifluoromethylsulfonyl) imide ([Ch][NTf_2]), 1-ethyl-3-methylimidazolium chloride ([C_2mim]Cl) and 1-(2-hydroxyethyl)-3-methylimidazolium chloride, ([C_2OHmim]Cl), are measured. The quasi-ideality of each mixture is firstly assessed calculating the activity coefficients by COSMO-RS [16], and using the experimental data to compare the similarity of [Ch]Cl activity coefficients in each pair of binary systems. The solubility data is then used to estimate the fusion properties of [Ch]Cl by linear regression of the solid-liquid equilibrium equation. The final results are checked using two independent procedures: 1) evaluation of the thermodynamic consistency of the experimental data, and 2) estimation of the solid-liquid phase diagrams by COSMO-RS and comparison with the experimental phase equilibria diagrams.

2. Experimental

2.1. Materials

The source, purity and temperature of fusion of the compounds used in this work are described in Table 1 while the structures, CAS and full chemical names are presented in Fig. 1. [Ch][Prop] and [Ch][Buta] were synthetized in our laboratory following standard procedures presented in Supplementary Information. Before use, all individual compounds were purified under vacuum (0.1 Pa and 298 K), for at least 72 h. The water content was then measured by Karl-Fisher and was found to be always lower than 600 ppm.

2.2. Methods

The melting temperatures were determined with an automatic glass capillary device model M-565 from Buchi (100–240 V, 50–60 Hz, 150 W), which has a temperature resolution of 0.1 K. Since many ionic compounds are highly hygroscopic, in particular choline chloride, mixtures were prepared inside a dry-argon glove-box, at room temperature using an analytical balance model ALS 220-4N from Kern with an accuracy of ±0.002 g. Vials with mixtures were, whenever possible, heated under stirring until complete melting and then recrystallized. The solid mixtures were ground in the glove-box and the powder filled into a capillary. A heating rate of 0.5 K min^{-1} was used in all cases, and the melting procedure repeated at least two times. The estimated uncertainty of the melting temperatures is better than 1.2 K. The thermogravimetric analysis of pure choline chloride can be found in Fig. S1.

In a few specific cases indicated in Table 1, differential scanning calorimetry (DSC) was used. The melting properties were determined using a Hitachi DSC7000X model working at atmospheric pressure. Samples of approximately 5 mg tightly sealed in aluminium pans were submitted at least to 3 repeated cooling–heating cycles at 2 K min^{-1}. The thermal transitions temperatures were taken as the peak temperature. The temperature uncertainty calculated through the average of the standard deviation of several consecutive measurements was better than ±0.1 K. The equipment was previously calibrated with several standards with weight fraction purities higher than 99%.

3. Models and data processing

For eutectic systems with complete immiscibility in the solid phase the phase equilibrium can be described by Ref. [26]:

$$ln\left(x_i\gamma_i^L\right) = \frac{\Delta_{fus}H}{R}\left(\frac{1}{T_{fus}} - \frac{1}{T}\right) + \frac{\Delta_{fus}C_p}{R}\left(\frac{T_{fus}}{T} - ln\frac{T_{fus}}{T} - 1\right) \quad (1)$$

where x_i is the mole fraction solubility of compound i and γ_i^L its activity coefficient in the liquid phase, $\Delta_{fus}H$ and T_{fus} are the enthalpy and temperature of fusion, respectively, R is the ideal gas constant, T is the absolute temperature, and $\Delta_{fus}C_p$ is the difference between the heat capacity of the compound i in liquid and solid phases. Since values for the heat capacities of most compounds here studied have not yet been measured, and for [Ch]Cl it is not measurable since the compound decomposes before melting, the last term in Eq. (1) is neglected in this work. Moreover, even when that data are available, the contribution of this term to the phase equilibrium calculations has been shown to be very small [27,28]. If the liquid phase is an ideal mixture, Eq. (1) becomes,

Table 1
Pure component properties.

Compound	Source	Mass purity/%	T_{fus}/K		$\Delta_{fus}H$/J·mol^{-1}
			Exp.	Lit.	
[Ch]Cl	Acros Organics	98	–	575.15 [1]	–
[Ch][Ac]	Iolitec	>99	362.62[a]	324.15 [17]/345.15 [18]	8881.7[d]
[Ch][Prop][c]	–	99[e]	282.57[b]	–	2238.6[b]
[Ch][Buta][c]	–	99[e]	315.98[b]	318.15 [19]	8793.6[b]
[N_{4444}]Cl	Sigma-Aldrich	97	342.82[a]	348.15 [20]	19430[d]
[P_{4444}]Cl	Cytec	97	339.46[a]	338.15 [21]	–
[BzCh]Cl	Aldrich	97	351.42[a]	–	8730[d]
[C_4mpyr]Cl	Iolitec	99	472.98[a]	>387.15 [22]	30896[d]
[Ch][NTf_2]	Iolitec	99	305.65[b]	303.15 [23]	1226.5[b]
[C_2mim]Cl	Iolitec	98	350.42[a]	363.15 [24]	8588[d]
[C_2OHmim]Cl	Iolitec	99	358.88[a]	335.15 [25]	20974[d]

[a] Visual detection.
[b] DSC.
[c] Synthetized in this work.
[d] Estimated from experimental data using (2) and the experimental points with x_{IC}>0.6.
[e] Estimated by NMR.