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Study on solid–liquid phase equilibria in ionic liquid 2. The solubility of alkali bromide in ionic liquid 1-ethyl-3-methylimidazolium ethyl sulfate

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Abstract

This paper reports the solubility of alkali bromide MBr (M is Na or K) in ionic liquid (IL) EMISE (1-ethyl-3-methylimidazolium ethyl sulfate), measured in the temperature range of 293.15–343.15 K. The relationship between solubility, *m*, and temperature, *T*, may be expressed in an empiric formula: $\ln(m/m^0) = A_1 + A_2T^0/T$, where T^0 is 1 K, m^0 is 1 mol kg^{-1}. The observed sequence of solubility is NaBr > KBr. The fact implies that the less the radius of alkali ion, the greater is its solubility because small ion is easy to get into the interstices of IL EMISE. In addition, the standard transfer thermodynamic functions of MBr from water to IL EMISE were calculated in terms of solubility data of MBr in water. Using Born model, the dielectric constant, $D = 8.7$, was estimated and was close to the value of typical IL measured by Wakai.

Keywords: Ionic liquid; Solubility; Solid–liquid phase equilibrium; EMISE; NaBr; KBr

1. Introduction

Ionic liquids (ILs) are viewed as a novel class of green benign solvents [1–5], which promise widespread application in industry, possibly replacing currently used organic solvents due to unique properties such as negligible vapor pressures, broad liquid temperature ranges, in particular, high specific solvent abilities for organic and inorganic compounds. But, there are very few reports of solubility of inorganic salts in ILs [6]. Since dissolving of metal ions in ILs are extremely important to the applications of ILs in synthesis and extraction, as a continuation of our previous investigation [7–11], this paper reports the solubility of alkali bromide MBr (M is Na or K) in IL 1-ethyl-3-methylimidazolium ethyl sulfate (EMISE), measured in the temperature range of 293.15–343.15 K. The relationship between solubility, *m*, and temperature *T* may be expressed in an empiric formula: $\ln(m/m^0) = A_1 + A_2T^0/T$, where T^0 is 1 K and m^0 is 1 mol kg^{-1}. In addition, the standard transfer thermodynamic functions of MX (X is Cl and Br) from water to IL EMISE were calculated in terms of solubility data of MX in water [12]. Using Born model, the dielectric constant of the IL was estimated.

2. Experimental

2.1. Chemicals

Diethyl sulfate was used as supplied. Toluene was AR reagent and was purified by standard method. 1-Methylimidazole (AR reagent) was distilled under reduced pressure. KBr and NaBr with purity more than 99.99% were dried at 373 K for 6 h.

According to Holbrey's method [5], the EMISE was synthesized and details of the synthesis procedure were described elsewhere [6]. The resulting EMISE was a colorless ionic liquid. ^{1}H NMR spectra of the product showed the same with literature [5]. The electrochemical window of EMISE was measured by cyclic voltammetry at 303.15 K. The result shows reductive and oxidative limits of −1.40 and 2.40 V, respectively, relative to an Al/Al^{3+} reference, which gives an electrochemical potential window of 3.8 V, which is in good agreement with the value in literature [6].

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2.2. Determination of solubility of MBr in EMISE

The salts solubility measurements reported here were made using a cell with a water jacket and thermostated at each temperature with an accuracy ±0.05 K in the temperature range of 293.15–343.15 K in a glove box under a dry atmosphere. Approximately 80 g of ionic liquid EMISE was placed in the cell, and then approximately 5–6 g of MBr was slowly added with stirring into the cell containing ionic liquid EMISE. The criterion for the attainment of phase equilibrium was that the solid phase of MBr does not disappear for a period of about 8 h at given temperature and at constant pressure (previous experiments show that solid-liquid phase equilibrium between EMISE and MBr at 293.15 K was only reached about 4 h). The amount of Br^- in the equilibrium composition of the liquid phase was determined by Mohr method [13] and the solubility of MBr in EMISE was calculated. The water content of the IL was measured by a Karl Fischer moisture titrator (ZSD-2 type), showing zero before and after the experiment.

3. Results and discussion

3.1. The solubility of MBr in the IL

The values of the solubility of KBr and NaBr in EMISE at 293.15–343.15 K are listed in Table 1. Each value in Table 1 is the average of three determinations.

The polarity of liquid is an important quantity while a solvent was selected for application. As is known to all, ionic liquid only composes of cation and anion so that IL was regarded as solvent with strong polarity. According to general rule, the salt would easy dissolve in the ionic liquid with strong polarity. However, in our experiments, only small amount of two typical salts (NaBr and KBr) was dissolved in the EMISE. The fact shows that ionic liquid EMISE must be classified as solvent of moderate polarity as Wakai et al. pointed out [14].

From Table 1, the observed sequence of solubility is NaBr > KBr, that is, the less the radius of alkali ion, the greater is its solubility. This fact shows that since the large size and the asymmetric shape, the ions in ionic liquid may not be closely packed so that there are lots of interstices among ions of IL EMISE and small ion of alkali is easy to get into the interstices [8]. In comparison with the solubility of NaCl and KCl in IL EMISE [6], the sequence of solubility of alkali bromide is analogous to alkali chloride, that is, solubility of sodium salt is the larger than one of potassium salt.

Table 1
Values of solubility, m (mol kg^{-1}), of MBr in EMISE at 293.15–343.15 K

T (K)	NaBr	KBr
293.15	0.2654 ± 0.0001	0.2500 ± 0.0002
298.15	0.2692 ± 0.0001	0.2527 ± 0.0002
303.15	0.2733 ± 0.0001	0.2557 ± 0.0002
308.15	0.2774 ± 0.0001	0.2589 ± 0.0002
313.15	0.2817 ± 0.0001	0.2620 ± 0.0002
318.15	0.2859 ± 0.0001	0.2654 ± 0.0002
323.15	0.2901 ± 0.0001	0.2696 ± 0.0002
328.15	0.2948 ± 0.0001	0.2726 ± 0.0002
333.15	0.2990 ± 0.0001	0.2765 ± 0.0002
338.15	0.3037 ± 0.0001	0.2807 ± 0.0002
343.15	0.3083 ± 0.0001	0.2849 ± 0.0002

Table 2
The values of parameters, A_i, in Eq. (1)

	A_1	A_2	r	s
NaBr	−0.30012	−302.09	0.999	0.00252
KBr	−0.49631	−262.74	0.996	0.00392

The values of solubility of NaBr and KBr in EMISE at different temperatures were fitted by the method of least-squares with an empirical equation, namely:

$$\ln\left(m/m^0\right) = A_1 + A_2T^0/T \quad (1)$$

where m is solubility expressed in molality, $m^0 = 1$ mol kg^{-1}, $T^0 = 1$ K. The values of the parameters obtained are A_i, correlation coefficients, r, and the standard deviation of the fitting, s, are listed in Table 2. From Table 2, $r > 0.99$ and $s < 4 \times 10^{-3}$ show that the Eq. (1) is a good empirical equation. Fig. 1 is the plot of ln(m/m^0) vs. 1/T. Fig. 1 shows that solubility of MBr (KBr or NaBr) increases with temperature.

3.2. The transfer function of MBr from water to the IL

In as much as the solubility of alkali chloride and alkali bromide in pure water is available from literature over the same temperature range above [12], it is possible to derive the thermodynamic function for the transfer process:

MX (in pure water) → MX (in IL EMISE)

where X is Cl or Br. According to Bates and co-workers [15], the standard transfer Gibbs energy, $\Delta_t G^\circ_\mathrm{m}$ is expressed as following equation:

$$\Delta_t G^\circ_\mathrm{m} \approx RT \ln\left(\frac{m_\mathrm{w}}{m}\right) \quad (2)$$

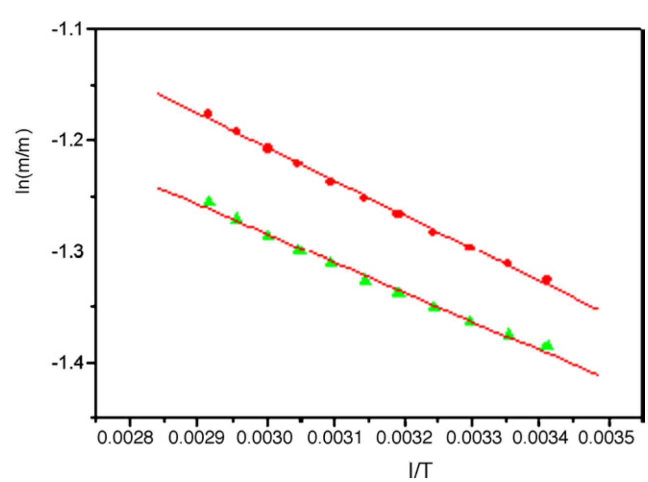

Fig. 1. Plot of ln(m/m^0) vs. 1/T. Reference to Table 4 for the equations of the fitting line (( ) NaBr; ( ) KBr exp.; (–) Cal.).