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Phase diagrams of aqueous biphasic systems composed of ionic liquids and dipotassium carbonate at different temperatures

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ABSTRACT

Phase diagrams of the {1-butyl-3-methylimidazolium nitrate ([Bmim][NO_3])/1-hexyl-3-methylimidazolium nitrate ([Hmim][NO_3]) + dipotassium carbonate (K_2CO_3)} aqueous biphasic systems (ABS) and the binodal curves of {1-octyl-3-methylimidazolium nitrate ([Omim][NO_3]) + K_2CO_3} ABS were determined experimentally at different temperatures. The binodal data were correlated with the Merchuk equation. The effect of temperature and the alkyl chain length of ionic liquid (IL) on two phase formation were investigated. The experimental data reveals the biphasic region expands with reduction in temperature; however, the absolute value of slope of the tie-lines reduces with an increase in temperature. Moreover, the ability of the studied ILs to form two phase in the presence of K_2CO_3 salt are in the order of [Hmim][NO_3] > [Omim][NO_3] > [Bmim][NO_3]. The experimental data are correlated with the NRTL model with a good accuracy.

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1. Introduction

Aqueous biphasic system (ABS) is a new method for separation and purification of biologically active substances [1]. Albertsson introduced these systems for the extraction of biological compounds in 1956 [2]. These systems can be formed by mixing the aqueous solution of two polymers, or one polymer and a salt [3]. In recent years, ABS were applied as a new method for separation of a broad range of biological compounds, including extraction, purification and recovery of proteins [4], amino acids [5,6], pharmaceutical compounds [7], small organic compounds [8,9], metallic ions [10] and nano particles [11]. ABS is a safe process from environmental point of view, because the separation process eliminate dependency on volatile organic compounds (VOCs) [5].

Rogers and coworkers [12] introduced ABS based on ionic liquids (ILs) for the first time in 2003. These systems composed of hydrophilic ILs and kosmotropic salts, abbreviated as IL-based ABS. The IL-based ABS has many advantage, such as little emulsion formation, low viscosity, rapid two phase formation, high extraction efficiency, no need of using VOC, and gentle biocompatible environment [13]. IL-based ABS has been applied to separate alkaloids [14–17], antibiotics [18–20] and proteins [21–23].

Until now, IL-based ABS has been investigated by many researchers. Zafarani-moattar and Hamzehzadeh [24] have studied the behavior of ABS composed an imidazolium-based IL ([C_4mim][Cl] or [C_4mim][Br]) and a citrate salt (tri-potassium citrate or tri-sodium citrate), at different temperature. Yu et al. [25] reported the liquid–liquid equilibrium (LLE) data for ABS composed of hydrophilic IL ([Emim][BF_4] or [Pmim][BF_4]) and Na_2CO_3 at different temperatures. They investigated the impact of temperature and the alkyl chain length of cation of IL on the binodal curves. Deive and his coworker [26] investigated IL-based ABS containing an imidazolium IL ([Bmim]Cl or [Hmim]Cl) and a salt (K_3PO_4, K_2HPO_4, K_2CO_3). Wang and his colleagues [27] studied the IL-based ABS formed by an imidazolium-IL ([C_2mim][BF_4] or [C_4mim][BF_4]) and a salt ($ZnSO_4$, $MgSO_4$, Li_2SO_4) at $T = 298.15$ K. They determined the phase diagrams of studied systems. Moreover, the salting-out abilities of the salts have been studied. Sheng et al. [28] investigated the phase behavior of hydrophilic IL ([EOMiM]Br) and kosmotropic salt (K_2CO_3, K_2HPO_4, K_3PO_4) ABS at different temperatures.

In this work, the phase diagrams of ABS composed of the hydrophilic ILs {1-butyl-3-methylimidazolium nitrate ([Bmim][NO_3]) or 1-hexyl-3-methylimidazolium nitrate ([Hmim][NO_3])} and inorganic salt dipotassium carbonate (K_2CO_3) are studied at different temperatures. The nitrate-based ILs used in this work are

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free from halogen compounds and generate no problem for environment [29]. The experimental data have not been given in literature and reported for the first time. The binodal diagrams and the experimental tie-lines data for the studied systems were determined at temperatures (288.15, 298.15 and 308.15) K. The impact of temperature on the binodal diagrams was studied and the influence of hydrocarbon chain length of IL (from butyl to octyl) on the formation of ABS was investigated. For this purpose, the binodal curves for the {1-octyl-3-methylimidazolium nitrate ([Omim][NO_3]) + K_2CO_3} ABS were determined.

Thermodynamic modeling is essential for ABS that permits one to have a strong tool to design separation processes. Regardless of wide researches in calculation of LLE data of ABS, modeling of IL-based ABS is still infancy [30,31]. In recent years, the thermodynamic modeling of IL-based ABS is applied with different models, such as NRTL and NRTL-NRF models [3], Wilson-NRF model [32], modified NRTL and Wilson models [33] and extended NRTL model [34]. As NRTL model is a powerful model for these systems, in the present study, this model [35] and asymmetric Pitzer–Debye–Huckel (PDH) equation [36] are applied to correlate the experimental tie-lines.

1.1. Material

The types of chemicals, their purities, suppliers and the analysis method are represented in Table 1. The studied ILs were synthesized in our laboratory based on the procedure in the literature [37]. The procedure method is existed in our previous studies [38,39]. The structures of the ILs were tested with nuclear magnetic resonance (NMR) spectroscopy. Before use, the ILs were inserted under vacuum for 24 h at moderate temperature (343 K) in order to be dry and degas. The purified ILs were kept in under argon gas to avoid moisture and their water content were measured with a Karl Fischer titration 684 model.

The water mass fraction was less than 6×10^{-4}. This amount of water in the IL, was calculated during the preparation of the ABS. Double-distilled deionized water was applied for preparation of all the studied systems.

1.2. Apparatus and procedure

The binodal curves were obtained by performing a series of titration and turbidi-metric experiments at different temperatures. A known mass of IL was inserted into a glass vessel, and mixed with water until to obtain a clear mixture. The temperature of the glass vessel was controlled with circulation of water at constant temperature into an external jacket using a thermostat bath (Model: FP50-HL, Julabo Co., Germany). The precision of thermostat bath was ±0.1 K. The solution of salt with known concentration was added drop wise to the mixture until the turbidity was observed. Addition of water made the solution clear again, and this procedure repeated several times. The binodal data was determined by measurement the mass of each component using an analytical balance (Model: ED224S, Sartorius Co., Germany) with an uncertainty of $\pm 1 \times 10^{-4}$ g.

The preparations of ABS were performed by mixing appropriate amounts of ILs, K_2CO_3 and water in glass tube. The ABS was stirred with shaker (IKA HS-260) for at least 30 min at 300 rpm. The phase separation happened after termination the stirring process. In order to ensure the complete phase separation, the mixtures are centrifuged for 10 min at 2000 rpm. Then, the samples were inserted into a thermostat bath for 24 h. These systems normally reach to thermodynamic equilibrium after 2–4 h and it can be easily ensure about this matter by measurement the composition of both phases at different times. However, in order to ensure the complete phase separation, the samples were inserted for 24 h in the thermostat bath. Then, the two phases are separated and analyzed.

In the IL-based ABS the mixtures consist of two anions and two cations that ion exchange could take place for these ions between the coexisting phases so that the distribution ratios for the cations and anions are not exactly 1:1, as verified by Gutowski et al. [12] for the {[Bmim]Cl + K_3PO_4}. Nonetheless, Bridges et al. [40] have shown that in the same IL-based ABS the differences in the distribution ratios between $[Bmim]^+$ and Cl^- or K^+ and PO_4^{3-} are small enough that the analysis of the result based on individual ion concentrations yields an operationally sufficient representation of concentration of the salt exist at any tie-line. Following Bridges et al. [40], in this work the concentrations of salts in both phases were measured based on the potassium analysis using a flame photometer (Model: 410, Sherwood, Scientific Ltd., UK), and the concentration of ILs ([Bmim][NO_3], [Hmim][NO_3]) were determined using a UV–vis spectrometer (PerkinElmer-Lambda 25, USA), at wavelength of 302 nm. The uncertainties in the measurements of the mass fractions of the salts and ILs are ±0.001.

The tie-line length (TLL) and slope (S) were calculated at various compositions using following equations, respectively.

$$\mathrm{TLL} = \left[\left(w_1^t - w_1^b\right)^2 + \left(w_2^t - w_2^b\right)^2\right]^{0.5}, \tag{1}$$

$$S = \frac{w_1^t - w_1^b}{w_2^t - w_2^b}, \tag{2}$$

where w_1^t, w_1^b, w_2^t and w_2^b denote the mass fractions of ILs (1) and K_2CO_3 (2) in the top (t) and bottom (b) phases, respectively.

2. Results and discussion

2.1. Binodal data and correlation

The binodal data of {([Bmim][NO_3], [Hmim][NO_3] or [Omim][NO_3]) (1) + K_2CO_3 (2) + H_2O (3)} ABS at temperatures (288.15, 298.15, and 308.15) K are given in Tables 2–4. The Merchuk equation [41] were used for fitting the binodal data:

$$Y = a \exp\left(bX_2^{0.5} - cX_2^3\right), \tag{3}$$

where Y and X represent the weight percent of IL and salt, respectively. The constant a, b and c are Merchuk parameters. This equation has been correlated the binodal data of polymer-based

Table 1
The purities and suppliers of the chemicals.

Chemical name	Supplier	Mass fraction purity	Water mass fraction	Analysis method
Dipotassium carbonate	Merck	≥0.99	None	Flame photometer
[Bmim][NO_3]	Synthesized in lab	≥0.98	6×10^{-4}	UV-spectroscopy
[Hmim][NO_3]	Synthesized in lab	≥0.98	6×10^{-4}	
[Omim][NO_3]	Synthesized in lab	≥0.98	5×10^{-4}	

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