(Liquid + liquid) equilibrium of aqueous biphasic systems composed of 1-benzyl or 1-hexyl-3-methylimidazolium chloride ionic liquids and inorganic salts

Francisco J. Deive, Ana Rodríguez *

Department of Chemical Engineering, University of Vigo, P.O. Box 36 310, Vigo, Spain

ABSTRACT

(Liquid + liquid) equilibria for {1-benzyl-3-methylimidazolium chloride ([BzMIM]Cl) or 1-hexyl-3-methylimidazolium chloride ([HMIM]Cl) + inorganic salts (potassium phosphate K_3PO_4, potassium carbonate K_2CO_3, or dipotassium hydrogen phosphate K_2HPO_4) + H_2O} aqueous biphasic systems (ABSs) are presented at $T = 298.15$ K. An empirical equation was used to correlate the binodal data. The experimental tie lines were appropriately correlated by the Othmer–Tobias and Brancroft empirical equations. The influence of the selected inorganic salts in the phase segregation was investigated by means the calculated effective excluded volume (EEV) and Setschenow-type equation. The salting-out ability of salts was also evaluated in terms of the Gibbs energy of hydration of salt (ΔG_{hyd}) and assessed with EEV values.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Ionic liquids (ILs) have lately emerged as neoteric solvents, owing to their multifaceted properties, namely, very low volatility at room temperature, and recyclability, which gives them the label of greener solvents. These appealing properties make them a good choice to minimise the risk of atmospheric pollution and to reduce health concerns associated with the use of volatile conventional organic solvents [1–3]. Another crucial aspect defining ILs is their tunability, since the selection of a particular cation or anion, will strongly influence the physical and chemical properties and reactivity. Together with this, the existence of a plethora of possible combination of cations and anions allows the design of task specific ILs, suitable for the final objectives of a selected process. This advantage is one of the most important breakthroughs that ILs have posed in the field of chemistry and chemical engineering, and made them to be christened "designer" solvents. Hence, these molten salts have triggered a considerable interest in a wide range of industrial sectors, from electrochemistry to biocatalysis [4].

Traditionally, aqueous biphasic systems (ABS) have consisted of combining two mutually incompatible salts or polymers, one of them kosmotropic or water-structuring, and the other chaotropic or water-destructuring, in the presence of water. Each phase contains mainly one of the compounds and a small amount of the other [5]. These systems have been considered as an efficient and more environmentally friendly extraction processes which

offers a remarkable advantage in which the conventional volatile organic solvents are replacement in the whole process. In addition, other inherent benefits should be remarked such as economical and lower energy requirements, mild operating conditions, rapid phase disengagement, and easy scale-up, which make this technique more competitive [6–8]. Due to these advantages, ABSs have been recognized as a useful procedure for the separation of organic chemicals and biocompounds with industrial interest, ranging from alkaloids to cyclic olefins [9–13].

Bringing together the potential of ABS and the benefits associated with these neoteric solvents, ILs-based ABS have emerged as a greener alternative for separation processes since it was first reported by Gutowski *et al.* in 2003 [14]. One of the attractions of making ILs-based ABS lies in the fact that the Hofmeister series can be usually employed to predict the salting out effect of common used inorganic salts. This series establishes the strength of salts, ordering them from kosmotropic to chaotropic, depending on their different ability to break or form water structure giving rise to salting-in or salting-out ability [15]. Due to this, several papers have focused on the study of the behaviour of different families of ILs and phase promoters such as aminoacids [16,17], sugars [18,19] or salts [20,21] and their application to separate biological products with industrial interest [22,23].

In this work, two imidazolium-based ILs ([BzMIM]Cl and [HMIM]Cl) were investigated for their ability to induce phase segregation in the presence of three potassium-based inorganic salts, K_3PO_4, K_2HPO_4 and K_2CO_3, possessing different degrees of lyotropy at $T = 298.15$ K. The binodal curves were correlated by a three-parameter empirical equation [24] and the reliability of the tie line

* Corresponding author. Tel.: +34 986 81 23 12; fax: +34 986 81 23 80.
 E-mail address: aroguez@uvigo.es (A. Rodríguez).

composition was proved by the empirical equations given by Othmer–Tobias [25] and Brancroft [20]. Moreover, the salting-out effect of the selected inorganic salts was assessed from the effect excluded volume (EEV) values and k_s Setschenow parameter [26].

2. Experimental

2.1. Materials

The ILs 1-benzy-3-methyl imidazolium chloride ([BzMIM]Cl) and 1-hexyl-3-methy- imidazolium chloride ([HMIM]Cl) were synthesized in our laboratory according to the procedure detailed by García-Lorenzo et al. (2008) and Gómez et al. (2007) respectively [27,28]. The water content of the ILs was reduced to values less than 0.2 % when vacuum at $P = 0.2$ Pa was applied during several days, always immediately prior to their use. This water content was determined using a 756 Karl Fisher coulometer.

The selected high density charge inorganic salts, potassium phosphate K_3PO_4, dipotassium hydrogen phosphate K_2HPO_4, and potassium carbonate K_2CO_3 were used as received, without further purification.

The information about ILs and potassium-based inorganic salts is summarized in table 1.

2.2. Apparatus and experimental procedure

The binodal curves were carried out by means of the cloud point titration method at $T = 298.15$ K [5]. A known amount of salt was added to the different IL aqueous solutions until the detection of turbidity, and then followed by the drop-wise addition of ultra-pure water until a clear monophasic region was achieved. The system was always operating under constant stirring. The ternary system compositions were determined by the mass quantification of all components with a precision of $\pm 10^{-4}$ g. The temperature was controlled with a F200 ASL digital thermometer with an uncertainty of ±0.01 K.

The tie-lines (TLs) were experimentally determined by a gravimetric method. The determination started with the addition of a ternary mixture within the immiscibility region of known mass fraction to the ampoules, the temperature was kept constant and the mixture was stirred vigorously and left to settle for 24 h to ensure a complete separation of the layers. The estimated uncertainty in the determination of the IL and salt phases mass compositions are less than $2 \cdot 10^{-4}$. The TL data were obtained by the lever arm rule taking into account the relationship between the upper phase and the overall system mass composition [24].

3. Results and discussion

3.1. (Liquid + liquid) equilibrium of aqueous systems and correlation

Herein, the experimental binodal curve for the ternary mixtures of {[BzMIM]Cl + salt + H$_2$O} and {[HMIM]Cl + salt + H$_2$O} at $T = 298.15$ K are reported in tables 2 and 3, respectively, and are illustrated in figures 1 and 2. They provide information about the

TABLE 2
Binodal data for the {[BzMIM]Cl (1) + salt (2) + H$_2$O (3)} at $T = 298.15$ K.[a]

K$_3$PO$_4$		K$_2$HPO$_4$		K$_2$CO$_3$	
100 w_2	100 w_1	100 w_2	100 w_1	100 w_2	100 w_1
0.51	64.93	1.51	55.79	1.71	60.83
1.43	55.87	1.87	53.60	2.03	58.50
2.30	50.12	1.91	53.47	2.24	58.36
3.89	43.79	4.04	44.74	3.80	47.88
6.12	37.66	4.33	43.27	4.97	44.79
9.52	30.29	6.37	38.52	7.00	37.99
12.45	24.46	8.40	35.09	10.46	30.61
15.06	19.59	9.75	32.11	12.05	28.00
15.44	17.31	12.62	26.87	13.83	23.98
16.54	15.96	16.61	20.83	15.54	21.29
18.42	13.12	17.74	19.20	17.28	19.02
19.59	11.63	19.00	18.04	18.46	16.74
21.54	9.83	19.74	16.50	19.70	15.30
22.77	8.62	20.74	15.04	20.32	14.06
24.05	7.28	21.69	14.34	21.55	12.27
25.14	6.52	22.45	13.23	23.36	10.26
25.48	6.13	23.77	11.45	24.34	9.26
26.13	5.58	25.32	10.04	25.46	7.98
26.05	4.53	28.11	8.60	25.49	6.42
27.07	3.88	29.02	7.27	26.74	5.40
28.03	3.35	29.56	6.30	28.33	5.01
28.91	2.87	30.35	6.12	28.44	4.34
29.49	2.60	31.09	5.16	30.03	3.80
30.36	2.44	31.92	4.14	32.83	2.27
32.45	1.33	33.60	3.56	36.69	0.98
34.50	0.79	35.68	2.53		

[a] Standard uncertainties are $u(w) = 0.0002$, $u(T) = 0.01$ K.

concentration of phase-forming components required to form two phases; the concentration of phase components in the top and bottom phases; and the ratio of phase volumes. The information coming from the literature [29,30] indicates that experimental data related to [HMIM]Cl-based ABS are available, and the comparison can be graphically visualized in figure 2. This IL was reported to be the one with the best phase forming ability in the alkylimidazolium chloride series, which led us to keep it as a model IL with adequate chaotropicity for this study [29].

The binodal curves allowed us to draw a conclusion about the main driving forces that can control the phase segregation of the systems. It is also interesting to see that the use of ILs containing a benzyl radical in the imidazolium ring entails a drastic change in the ABS phase behaviour, and a depression in the equilibrium data obtained can be clearly noticed. Traditionally, an increased molecular weight of the chaotropic compound leads to greater immiscibility regions, probably as a result of the incompatibility between the phase-forming components due to the more hydrophobic character of the one with larger molar mass [31]. However, anomalous behaviour found for alkylimidazolium chloride series, point that other factors must be taken into account [29].

A three-parameter empirical equation developed by Merchuk et al. [24] and widely used to correlate of binodal curves of IL-based ABS is presented:

$$Y = A \exp \left\{ \left(BX^{0.5} \right) - \left(CX^3 \right) \right\} \tag{1}$$

TABLE 1
Sample provenance and purities.[a]

Chemical name	Mass fraction purity	Supplier	Method of analysis
1-Benzyl-3-methylimidazolium chloride	0.98		NMR and positive FABMS
1-Hexyl-3-methylimidazolium chloride	0.98		NMR and positive FABMS
Potassium phosphate	0.98	Sigma-Aldrich	None
Potassium carbonate	0.99	Sigma-Aldrich	None
Dipotassium hydrogen phosphate	0.98	Sigma-Aldrich	None

[a] Deionised water was used in all the experiments.