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PHASE DIAGRAM OFTHE SELECTED AQUEOUS TWO-PHASE SYSTEMS BASED ON IONIC LIQUIDS

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ABSTRACT

Liquid-liquid equilibrium data have been reported for aqueous two-phase systems formed by imidazolium-based ionic liquids, 1-hexyl-3-methyl-imidazolium chloride, and 1-*butyl*-3-methylimidazolium dicyanamide, with inorganic salts,K_2HPO_4 and K_3PO_4. The binodal curves were fitted to a three parameter equation and the tie line length was calculated.

INTRODUCTION

Aqueous two-phase systems (ATPSs) exploit the incompatibility between aqueous solutions forming two phases [1]. ATPSs have consisted of two mutually incompatible salts or polymer, 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 [2]. In the recent years, ionic liquids (ILs) have shown to be an attractive alternative to polymers in the formation of ATPSs due to their potential use as green solvents and as possible replacement for traditional volatile organic compounds [3].

Ionic liquids are salts with their ions poorly coordinated and which are liquid at temperatures below 100°C. As a new kinds of green solvents, ILs have unique properties such as negligible vapor pressure, wide liquid temperature range, non-flammability, enhanced thermal and chemical stability, tunable chemical structures, good electrical conductivity and improved solvation ability for a large matrix of compounds [3]. This makes ILs attractive as novel extractants for various metal ions and organic compounds (e.g., amino acids, dyes, proteins) [4].

Gutowski et al. demonstrated that addition of inorganic salt to aqueous solutions of ionic liquids can also cause liquid-liquid demixing and induce the formation of ATPSs.[5]

The phase diagram, comprised binodal curve and tie-lines, provides information about: the concentration of phase forming components required to form two phases, the concentration of phase components in top and bottom phases and the ratio of phase volume. Coordinates for all potential

systems will lie on a tie line, which connects two nodes on the binodal and represents the final concentration of phase components in top and bottom phases. Moving along the tie line coordinates, the systems denoted will have different total compositions and volume ratios, but with the same final concentration of phase components in the top and bottom phases. [4]
The aim of this study was forming of phase diagrams for two targeted hydrophilic ILs and determination of their tie lines. These results represent the first step of applying ATPS for extraction.

EXPERIMENTAL

The ionic liquids used in this work were 1-hexyl-3-methylimidazolium chloride, [C_6mim]Cl and 1-*butyl*-3-methylimidazolium dicyanamide, [*C_4mim*][*N*(*CN*)$_2$] with a stated purity of >99 wt % and supplied by Iolitec.Inorganic salts, 30 % solution of K_2HPO_4or K_3PO_4in deionized water.
The phase diagram was determinated by the cloud-point method at room temperature. A known amount of IL was weight into a test tube and an appropriate volume of the salt was added dropwise into the test tube while shaking. By appearance of turbidity, the total mass of the added salt was calculated. The weight percentages of both ILs and salt were calculated by measuring the weights of both ILs and the salt. The sequential addition of water and salt was repeated until sufficient data points for constructing the phase diagram were obtained [6]. The binodal curve was fitted applying following equation:

$$lnY = A + BX^3 + CX^{0.5} \qquad [1]$$

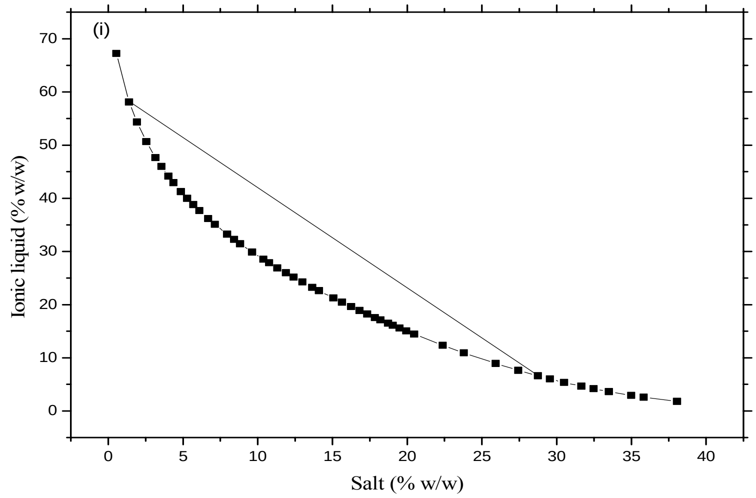
where Y and X are the concentrations (in w/w%)of IL and salt, respectively [7]. The fitting was performed using “Tablecurve 5.01” program.
The tie lines were experimentally determined through the relationship between the weight of the top phase and the overall weight by lever-arm rule. The tie line length (TLL) for different salt and IL compositions were calculated according to:

$$TLL = \sqrt{(Y_T - Y_B)^2 + (X_T - X_B)^2} \qquad [2]$$

The symbols T and B refer to the top (IL-rich) and bottom (salt-rich) phases.

RESULTS AND DISCUSSION

A sufficiently high concentration of inorganic salts added in an aqueous solution of hydrophilic IL can cause phase separation a salt-reach bottom phase which is in equilibrium with Il-reach top phase. The first step in designing of ABSs is forming of phase diagram for the investigated system. The experimental phase diagrams for two investigated IL/salt systems([C_6mim]Cl/ K_2HPO_4 and [*C₄mim*][*N*(*CN*)₂]/ $K_3PO_4$are presented in Figure 1.



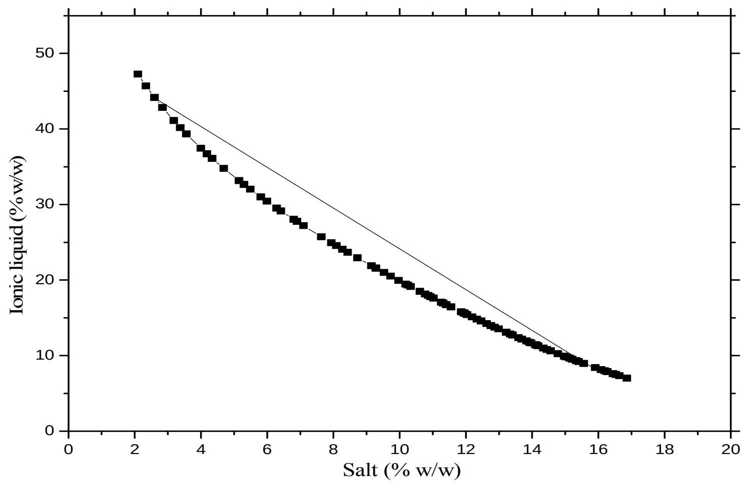


Figure 1. Phase diagramsof (i)[C_6mim]Cl/K_2HPO_4 and (ii) [C_4*mim*][*N*(*CN*)$_2$]/K_3PO_4systems

The data were fitted according to the empirical relationships of Merchuk (Eq. 1), and the parameters for this equation as determinated by least-squares regression of the cloud point data are shown in Table 1. Literature results confirmed that the method can satisfactorily correlate binodal curves and determinated tie lines in these systems. TLL wasexperimentally determined for each system and given in Table 2.

Table 1. Correlation parameters used in Eq. 1 to describe the binodals.

System	A	B	C	R
$[C_6mim]Cl/K_2HPO_4$	4.45364	$-3.33576\ 10^{-5}$	-.033085	0.99904
$[C_4mim][N(CN)_2]/K_3PO_4$	4.44272	$-1.73984\ 10^{-4}$	-0.40424	0.99905

Table 2. Tie-line lengths for IL+Salt systems

	System	IL	Salt	TLL
1	$[C_6mim]Cl+K_2HPO_4$	27.5	17.6	45.129
2	$[C_4mim]\ [N(CN)_2]$	7.9	29.1	32.481

CONCLUSION

The phase diagrams of ATPS for two imidazolium-based ILs were determinated by cloud point method at 298K. The binodal curves were fitted to the Merchuk equation, and tie-line lengths were determinated. The results showed that the empirical equation is satisfactory for correlating the investigated systems [7]. It can be seen that $[C_6mim]Cl/K_2HPO_4$ system has greater ability to promote ATPS than $[C_4mim][N(CN)_2]/K_3PO_4$ system.

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