Phase behaviour for aqueous two-phase systems containing the ionic liquid 1-butylpyridinium tetrafluoroborate /1-butyl-4-methylpyridinium tetrafluoroborate and organic salts (sodium tartrate/ammonium citrate/trisodium citrate) at different temperatures

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A B S T R A C T

The binodal curves of 1-butylpyridinium tetrafluoroborate + sodium tartrate at T = (298.15, 308.15 and 328.15) K and 1-butyl-4-methylpyridinium tetrafluoroborate + sodium tartrate/ammonium citrate/trisodium citrate at T = 298.15 K were experimentally determined. Three empirical equations were used to correlate the binodal data. The tie-line data were successfully correlated using the Othmer–Tobias and Bancroft and two-parameter equations. Factors affecting the binodal curves, such as temperature and the nature of the ionic liquids, were also studied. The two-phase area expanded with a decrease in temperature, whereas the absolute value of the slope of the ties slightly decreased with an increase in temperature. With an increase in the alkyl chain length of the ionic liquids (ILs) in the investigated systems, the binodal curves shifted closer to the origin. Finally, the effective excluded volume (EEV) values obtained from the binodal model were determined, and the salting-out ability decreased in the following order: $Na_3C_6H_5O_7 > Na_2C_4H_4O_6 > (NH_4)_3C_6H_5O_7$.

1. Introduction

Recently, aqueous two-phase systems (ATPSs) have been used to separate and purify multiple compounds in a single-step procedure. ATPSs are a novel liquid–liquid extraction technique that typically uses two or more polymers – a polymer and a salt [1], two surfactants [2] or water-soluble organic solvents and salting-out agents [3] – and constitutes a "greener" and potentially more efficient pre-treatment solution. An ATPS based on ionic liquid (IL) and salt was first reported by Rogers [4]. The benefits of the combination of IL and ATPSs into ILATPSs include negligible viscosity, minimal emulsion formation, the absence of volatile organic solvents, rapid phase separation, high extraction efficiency and a reduced impact on the environment [5–8]. ATPSs have been used in the separation and purification of various biological products [9], metal ions [10], dyes, drug molecules, small organic species [11] and nano- and micro-solid particulates [12] from the complex mixtures in which they are produced. ATPSs have also been used as green reaction media [13]. Li et al. [14] used aqueous two-phase systems of [Bmim]BF$_4$ and K$_2$HPO$_4$ to extract penicillin.

Liu *et al.* [15] used a high-performance liquid chromatography (HPLC) method to detect the quantity of chloramphenicol (CAP) in eggs using aqueous two-phase systems of the hydrophilic ionic liquid [EPy]Br and K$_2$HPO$_4$. Reliable liquid + liquid equilibrium data are beneficial to the design and process optimisation of the ILATPSs extraction technique. Several ILATPSs have been reported, such as [Bmim]BF$_4$ + sugar (sucrose, maltose, fructose, glucose and xylose) [16–18] ATPSs. In most reported studies, the salting-out of the ionic liquid has been accomplished by the use of phosphate, sulphate or carbonates. These salts, however, lead to high salt concentrations in the effluent streams and are therefore of environmental concern. To avoid this problem, biodegradable salts can be used as a substitute for the inorganic salts. Citrates and tartrate are biodegradable and nontoxic and can be discharged into biological wastewater treatment plants [19]. In the present study, we examined citrate and tartrate as alternatives to inorganic salts in IL-based ATPSs. However, only a limited amount of experimental work has been devoted to pyridinium-based ionic liquid/organic salt ATPSs [20].

Liquid + liquid equilibrium (LLE) data for 1-butylpyridinium tetrafluoroborate ([BPy]BF$_4$) + salt + water and 1-butyl-4-methylpyridinium tetrafluoroborate ([4-MBP][BF$_4$]) + salt + water systems have rarely been reported. In this work, we studied the

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Nomenclature

List of symbols

M	molecular weight ($kg \cdot mol^{-1}$)
N	number of tie-lines
T	temperature (K)
r	volume parameter
TLL	the tie-line length
S	the slope of the tie-line
V	molar volume
w	weight percent
EEV	effective excluded volume
V_{213}^*	scaled EEV of salt
f_{213}	volume fraction of unfilled effective available volume after tight packing of salt molecules into the network of ionic liquid molecules in ionic liquid aqueous solutions

$a, b, c, d, a_1, b_1, a_2, b_2, r, k, n, K$ fitting parameters

R^2	correlation coefficient
sd	standard deviation

Greek letters

β	interaction parameter

Subscripts

b	bottom phase
cal	calculated value
exp	experimental value
t	top phase
1	ionic liquid
2	salt
3	water

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phase behaviour of the 1-butylpyridinium tetrafluoroborate ($[BPy]BF_4$) + salt + water at different temperatures and 1-butyl-4-methylpyridinium tetrafluoroborate ($[4-MBP][BF_4]$) + salt + water systems. The obtained binodal data and tie-lines were correlated using empirical equations. The effect of temperature on the binodal curves and tie-lines was studied. In addition, the effect of ionic liquids on the binodal curves was investigated. Finally, the influence of salts on the phase-forming ability was also studied.

2. Experimental

2.1. Material

Table 1 summarizes the sources and purities of chemicals used in the study. 1-Butylpyridinium tetrafluoroborate ($[BPy]BF_4$) and 1-butyl-4-methylpyridinium tetrafluoroborate ($[4-MBP][BF_4]$) (99% mass fraction) were obtained from Cheng Jie Chemical Co., Ltd. (Shanghai, China) and used without further purification. Sodium tartrate/ammonium citrate/trisodium citrate (99% mass fraction) was supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). The ionic liquids and salts were used without further purification. Double-distilled deionised water was used for the preparation of all solutions.

2.2. Apparatuses and procedure

The phase diagram includes the binodal curves and the tie-lines. The binodal curves were determined by the titration method. A few grams of pure ILs was weighed into a vessel, and a known mass of water was added to obtain a clear mixture. The glass vessel featured an external jacket in which water was circulated at a constant temperature using a DC-2008 water thermostat (Tianjin Taisite Instrument Factory, China), and the temperature was main-

tained within ±0.05 K. A salt solution of known mass fraction was added drop-wise to the vessel until the mixture became turbid or cloudy. The composition of this mixture was noted. Adding a few drops of water made the mixture clear again. The above procedure was repeated to obtain sufficient data for the construction of a phase diagram. The composition of the mixture was determined by mass using an analytical balance (BS124S, Beijing Saiduolisi Instrument Co., Ltd., China) with an uncertainty of $\pm 10 \cdot 10^{-7}$ kg. The maximum uncertainty of the mass fraction of both ILs and salt determined by the titration method used here was ±0.001.

To determine the tie-lines, a series of ATPSs were prepared by mixing appropriate amounts of ILs, salts and water in the vessels, which were then placed in a thermostated bath for 48 h until they reached phase equilibrium. The temperature was controlled to within ±0.05 K. The volumes of the top and bottom phases were estimated. The salt concentrations in the top and bottom phases were determined by elemental analysis using atomic absorption spectroscopy (AAS). The AAS measurements were performed with a Shimadzu atomic absorption spectrophotometer, model AA-670 G. The average relative deviation of the weight percent of salt determined by this method was approximately 0.2%. The mass fractions of ILs in both the top phase and the bottom phase were determined with a UV–vis spectrometer, model UV-2450 (Shimadzu Corporation, Japan), at 211 nm. The mass fraction of water was then calculated. A mass balance was performed between the initial mass of each component and the amounts in the top and bottom phases based on the equilibrium compositions.

The tie-line length (TLL) and the slope of the tie-line (S) were calculated at different compositions using equations (1) and (2), respectively:

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

TABLE 1
The sources and purities of chemicals used in the study.

Chemical Name	Source	Initial mass fraction purity	Purification method	Final mass fraction purity	Analysis method
$[BPy]BF_4$	Chengjie Chemical Reagent Co., Ltd. (Shanghai, China)		None	Greater than 0.99	
$[4-MBP][BF_4]$	Chengjie Chemical Reagent Co., Ltd. (Shanghai, China)		None	Greater than 0.99	
$Na_2C_4H_4O_6$	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)		None	Greater than 0.99	
$Na_3C_6H_5O_7$	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)		None	Greater than 0.99	
$(NH_4)_3C_6H_5O_7$	Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China)		None	Greater than 0.99	