Phase behavior of quaternary aqueous two-phase systems: Influence factors and extraction mechanism study

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ABSTRACT

The liquid-liquid equilibrium for five systems containing sodium carbonate + ethanol + 2-propanol + water (with different ethanol to 2-propanol mass ratios), sodium sulphate + ethanol + 2-propanol + water, sodium carbonate/sodium dihydrogen phosphate + ethanol + 1-butyl-3-methylimidazolium tetrafluoroborate + water were determined at T = 308.15 K and atmospheric pressure. The binodal curves were correlated by Merchuk equation and another empirical formula while tie-lines were satisfactorily reproduced by a two-parameter equation with two other expressions respectively developed by Othmer-Tobias and Bancroft. Numerous factors were introduced to explore their impacts on the salting-out abilities of the quaternary aqueous two-phase systems. Results have shown that the anion species, ratio of organic components and system types significantly affected the phase behavior of investigated systems. Besides, the optimal system in this work was selected to extract vitamin B6 under laboratory conditions and the influences of pH value, temperature and extraction time on extraction process were investigated as well.

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1. Introduction

Aqueous two-phase systems (ATPSs) have been studied in some detail over the past few decades and have found extensive application in comprehensive extraction, purification, and fraction of drugs [1,2], proteins [3,4], amino acids [5] and antibiotics [6,7], etc. Recently, many researchers have found that ATPSs composed of ionic liquids (ILs) or micro-molecular organics and salts are preferential to the originally polymer-based systems due to the lower viscosity, lower consumables, and smaller phase separation time [8]. These systems are generated by mixing an ionic liquid or a small-molecule organic solvent with a certain salt (like potassium phosphate, sodium citrate, etc.) above critical concentrations determined by the corresponding binodal curves. It takes some time for a system to reach the equilibrium with the mixtures separated into two liquid layers. The as-obtained two phases both have a high water content and are respectively enriched in ionic liquid (or small molecule organic reagent) and salt, which plays an important role in the extraction processes.

The liquid-liquid equilibrium (LLE) data are the basis and precondition to design and construct ATPSs, which mainly includes two pars: binodal curves and tie-lines. The binodal data points are generally collected by the cloud point method [9] while tie-lines calculated using the lever-arm rule [10]. In recent years, Han with her group have done a lot of research on the phase behavior of imidazolium IL-salt ATPSs [11,12] and successfully applied some of the systems to the purification procedure of chloramphenicol [13], sulfonamides [14], etc. Lin et al. [15] have measured LLE for the [Bmim]BF4-CH2Cl2-H2O

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ATPS at 298.15 K and atmospheric pressure. Ge et al. [16] have established a simple, rapid, efficient and highly sensitive method for the total flavonoids enrichment using [C$_4$mim]Cl-K$_2$HPO$_4$ aqueous two-phase flotation system coupled with UV spectrophotometry. Su and co-workers [17] have greatly increased the extraction efficiency utilizing [Bpy]Br-K$_2$HPO$_4$ ATPS in the process of extracting curcumin from Curcuma longa L. For ATPSs based on small-molecule organic solvents, Han et al. have investigated the temperature effect on the salting-out strength of ethanol/2-propanol/1-propanol ;+ sodium hydroxide + water system [18]. In the research of Nan et al., systems comprise ethanol/1-propanol/2-propanol/acetone-(NH$_4$)$_2$SO$_4$ and 1-propanol-(NH$_4$)$_2$SO$_4$/NaCl/KCl were constructed and the effects of temperature, solvent, and salt on the linear liquid-liquid-solid boundaries were thoroughly studied [19]. Zhang et al. have successfully put ethanol-ammonium sulphate ATPS into practical use for total flavonids purification in grape seeds [20] and propyl alcohol-ammonium sulphate ATPS has been employed by Cao and her co-workers to deal with the para-aminophenol in water [21]. Other ATPSs of this kind, such as ethanol/2-propanol/1-propanol-MgSO$_4$/ZnSO$_4$ [22] and alcohol-ester- water-CaCl$_2$ [23] have also been reported.

In our previous works, we have determined LLE data for ternary systems based on pyridinium ionic liquid [EPy]Br [24], [EPy]BF$_4$ [25,26], [4-MBP]BF$_4$ [27] or [BPy]BF$_4$ [28] with numerous organic salts and inorganic salts. The effects of anion type and branched chains of ionic liquids, salt species and temperature on the phase-separation behaviors were thoroughly investigated. Later on, we have shifted our attention to the phase behavior of quaternary ethanol + 2-propanol + salt [(NH$_4$)$_2$SO$_4$/Na$_2$SO$_4$] + water ATPSs at different temperatures [29]. Factors affecting the liquid-liquid equilibrium of the investigated systems, such as the temperature, mass fraction of ethanol in the alcohol mixture and type of salt were also studied. However, our study on systems based on ILs or small-molecular organics is not thorough and systematic enough, which is also insufficient to the extensive application of these two kinds of ATPSs.

This paper determined LLE data for ethanol + 2-propanol + Na$_2$CO$_3$ + H$_2$O (the ratios of ethanol to 2-propanol are 1:1 and 1:3), ethanol + 2-propanol + Na$_2$SO$_4$ + H$_2$O (the ratio of ethanol to 2-propanol is 1:3) and ethanol + 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF$_4$) + Na$_2$CO$_3$/NaH$_2$PO$_4$ + H$_2$O (the ratio of ethanol to [Bmim]BF$_4$ is 1:4) systems at T = 308.15 K and atmospheric pressure. The binodal curves and tie-lines were correlated by numerous appropriate equations, which shows good correlations. Then, the effect of anion species, ratio of organic components and system types on the salting-out behaviors of investigated systems were discussed. Moreover, the ethanol + [Bmim]BF$_4$ + Na$_2$CO$_3$ + H$_2$O system was successfully applied to extracting vitamin B6 and the conditions has been optimized. This work is of great significance for predicting the phase equilibrium compositions of unknown systems and provides basis for further application research of this kind of ATPS as a green, mild separating technique in the determination and purification of metal ion, enzyme, nucleic acid, growth hormone, virus, etc. or as a reaction medium in areas like environmental modification, metallurgy.

2. Experimental section

2.1. Materials

The sources and purities of the materials used in this study are presented in Table 1. All chemicals were used without further purification and double-distilled deionized water was used throughout the experiment.

2.2. Apparatus and procedure

The experiment process is divided into three parts—the determination of binodal curves, tie-line calculation and vitamin B6 extraction. Before the experiment, the organic constituents in each system, i.e., ethanol and 2-propanol (or [Bmim]BF$_4$) were blended in certain ratios. The method is described as follow: adding an appropriate amount of ethanol into 2-propanol (or [Bmim]BF$_4$) until the ethanol to 2-propanol (or [Bmim]BF$_4$) mass ratio reached 1:1, 1:3 or 1:4, respectively, followed by homogeneous mixing. The mixtures were then kept under seal in cool and dry place and were used throughout the follow-up experiment. For convenience, the ratios of ethanol to 2-propanol and ethanol to [Bmim]BF$_4$ in mass fraction are collectively called "ratio of organic components (ROC)" in the following text.

The binodal curves in this paper were determined by the cloud point method [9] at T = 308.15 K and atmospheric pressure. First, 0.5 mL of organic mixture prepared in advance at a certain ratio was added into a colorimetric tube, and a salt solution of known mass fraction was then added dropwise using an injection syringe until the mixture became cloudy, and the first binodal data point was obtained. Next, double-distilled water was added dropwise until the mixture was clear again. Thereafter, the prior steps were repeated to get more data points for a complete binodal curve until some sludge was seen floating near the bottom of the vessel. The whole experiment was conducted under constant temperature of (308.15 ± 0.05) K with a DC-2008 water thermostat (Tianjin Taisite Instrument Co., China) and the constitute of each cloud point was noted by a BS 124S analytical balance (Beijing Sartorius Instrument Co., China) with a precision of ±0.0001 g.

Tie-lines were determined by a gravimetric method also under thermostatic waterbath. First, specified amounts of three components (organic mixture, salt, water) were thoroughly transferred in a centrifuge tube with an 80-2 centrifuge (Shanghai Surgery Instrument Factory, China) for 10 min. After that, the tube was settled in the water thermostat for 12 h to separate phases. The equilibrium state was characterized by the absence of turbidity in both top and bottom phases. When a phase equilibrium was achieved, the top phase was carefully withdrawn using a 1 mL micropipet. This step may be repeated multiple times as it is difficult to completely separate the phases at one time. Then, the bottom phase was weighted so the errors caused by infiltration of impurities or volatilization of solution during the aspiration of the top phase could be eliminated. And the mass of top phase was obtained by the subtraction method. This helped more thoroughly separating the two phases compared to the old ways using separating funnels [30,31]. In our previous articles [24,27,29,32], the phase equilibrium compositions were generally determined by instrumental analysis. Given that there do exist ion distribution equilibria between the phase-forming components (i.e., the IL and salt) of an ATPS which causes about 5% error, as has been proven by Rogers et al. [33,34] in their articles using radioactive tracer method, the lever-arm rule [10] was employed in our later work [35] to further verify the data accuracy of as-obtained tie-lines. Results have shown great consistency between the data obtained by instrumental analysis and geometric calculation using lever arm rule. In this work, the equilibrium compositions of two phases were calculated by MATLAB, using the lever-arm rule [10] (1 and 2) with an empirical formula with four parameters (3 and 4). In this study, all measurements were taken in triplicate, and the average value was used so as to reduce the contingency as well as the