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Measurement and correlation of phase equilibria in aqueous two-phase systems containing functionalized magnetic ionic liquids and potassium phosphate at different temperatures

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ABSTRACT

Functionalized magnetic ionic liquids ([C_2TMG][TEMPO-OSO_3], [C_3TMG] [TEMPO-OSO_3], [C_4TMG][TEMPO-OSO_3]) and K_3PO_4 were used as phase forming compounds of aqueous two-phase system at three temperatures (278.15 K, 298.15 K and 318.15 K). The effects of temperature and magnetic ionic liquid (MIL) species on the binodal curves were investigated. Three classical empirical equations were used for the correlations of the binodal curves. They have shown satisfactory performances in data fitting. An increase of the two-phase separation ability was observed when the temperature decreased. Additionally, all these three MILs have preferable phase forming ability as well as wide range of two-phase area in the binodal curve for our systems. This is strongly expected in practical applications. Furthermore, tie line data were experimentally acquired for the three MILs at 298.15 K. Three empirical formulas including Othmer–Tobias, Bancroft equations as well as an equation derived from binodal theory were used to fit the tie-line data with successful correlation. These aqueous two-phase equilibrium data should be useful in the areas of separation, purification and analysis.

1. Introduction

Ionic liquids (ILs) have negligible flammability and volatility, high ionic conductivity, high thermal and chemical stabilities, and also a strong solubilization capability for a large variety of organic and inorganic compounds [1–3]. They are typically comprised of unsymmetrical organic cations and symmetrical/unsymmetrical inorganic/organic anions. The possibility of adjusting many of their physicochemical properties makes ILs broad range of potential applications and in particular makes them promising extractive fluids [4,5]. Due to their special properties, ILs have been widely applied in the fields of catalysis, separation and electrochemistry [6–10].

The studies and applications of the aqueous two-phase systems (ATPs), involving liquid−liquid equilibrium between two phases, began in the 1950s when Albertsson [11] employed ATPs for purification process of biological materials. For a long time, the development of low-cost, recyclable, and biocompatible aqueous two-phase systems capable of offering few stages in the separation and purification of value-added products is in high demand in the biotechnological industry [12]. It is a well-known fact that the large proportion of water which is present in the phases of the ATPs provides a biocompatible environment for materials of biological origin, as well as the lower environmental impact compared to other separation/extraction processes that employ organic solvents. Therefore, in the last few decades, the application of ATPs has been extended to the separation and purification of cells, membranes, viruses, proteins, nucleic acids, enzymes, other added-value biomolecules [13] as well as metal ions [14] and dyes [15]. ATPs applications, involving both the clarification processes and partial purification in a single step, have been reported, enabling scientists to achieve high yields of recovery and purity. Easy scaling up of ATPs is of industrial interest [16] as well.

Ionic liquid aqueous two-phase systems (ILATPs) is a type of aqueous two-phase system consisting of IL and has received increasing attention from many researchers since 2003 due to its stability, activity, and selectivity [17–20]. ILATPs can be formed by some ILs and inorganic salts such as KOH, K_3PO_4, and K_2HPO_4. Studies on ILATPs have focused on imidazolium-based IL [17], pyridinium-based IL [21] and so on. It combines both features of IL and ATPs. These ILATPs have been used in extraction applications because of their stability, activity, and selectivity. ILATPs have been successfully used in the separation of pharmaceuticals, antibiotics, proteins, and amino acids [22–24]. However, ILATPs still revealed shortcomings such as low isolation efficiency of two aqueous phases for the reason of small density difference [25].

Magnetic ionic liquid (MIL) is functionalized ionic liquid which can be attracted to an external magnetic field [26]. MIL is promising

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materials with additional advantageous properties than typical ILs, such as magnetic, optical [27] or electrochromic behavior [28]. 1-butyl-3-methylimidazolium tetrachloroferrate ([bmim][$FeCl_4$]) with magnetism was synthesized and first reported by Hayashi et al. [26] in 2004. Since then, MILs have attracted increasing interest in the field of separation Processes. Jiang et al. [29] discovered that the solubility of benzene in the magnetic ionic liquid-[bmim][$FeCl_4$] was increased when applying a rotational magnetic field. Lee et al. [30] investigated the recovery of [bmim][$FeCl_4$] from its aqueous solution. Okuno et al. [31] revealed the possibility of magnetic transport of a gas in MILs. It was interpreted by the change of N_2 bubbles trajectory in the presence of a strong magnetic field. Wang et al. [32] investigated the use of [bPy][$FeCl_4$] as an effective extractant for extracting asphaltene fractions from coal direct liquefaction residues. Deng et al. [33] studied the application of the MIL [$3C_6PC_{14}$][$FeCl_4$] as an extraction solvent for the separation of phenolic compounds from aqueous solution in the presence of a neodymium magnet. The applications of metal-containing MILs were already reported in many fields. Another kind of MIL is non-metal organic MIL based on a radical ion, which was firstly discovered and proposed by Yoshida [34] in 2007. Until now, very few literatures have referred to the organic MILs.

Magnetic ionic liquid aqueous two-phase systems (MILATPs) is a novel system put forward by our team lately [25]. This system is composed of a novel organic MIL, inorganic salt and water. Compared with normal ILATPs, MILATPs can enhance phase separation efficiency by responding to an external magnetic field. This unique system have shown great potential in pretreatment and separation field. In the proposed MILATPs, magnetic separation, organic solvent free and rapid extraction were successfully combined together for the first time. This technique was successfully applied by us in the microextraction analysis of trace amount of chloramphenicol in water environment [35]. Some liquid-liquid phase equilibrium data of MILATPs with different inorganic salts were measured and correlated previously [36]. However, it is still not enough for the proper and extensive employment of MILATPs.

Generally, liquid-liquid phase equilibrium data are the foundation for the design and application of ATPs. The formation of ATPs is affected by many factors such as the species of IL, the type of salts and the temperature. Knowledge of accurate two-phase forming data at different composition is extremely helpful for the application of ATPs in field of separation, purification and chemical analysis. In this work, the liquid-liquid equilibrium compositions of the MILATPs containing tetramethyl guanidinium-based organic MIL and potassium phosphate at different temperatures were studied in detail. The experimental data were fitted by appropriate equations. The influences of mass fraction of the mixture, temperature and the MIL species on the phase diagram were also evaluated. In addition, tie lines were determined for a series of MILATPs and correlated with equations. The obtained experimental data could serve as a guide for the future application of these MILATPs, and the results of this study should be crucial for extraction, separation and purification process.

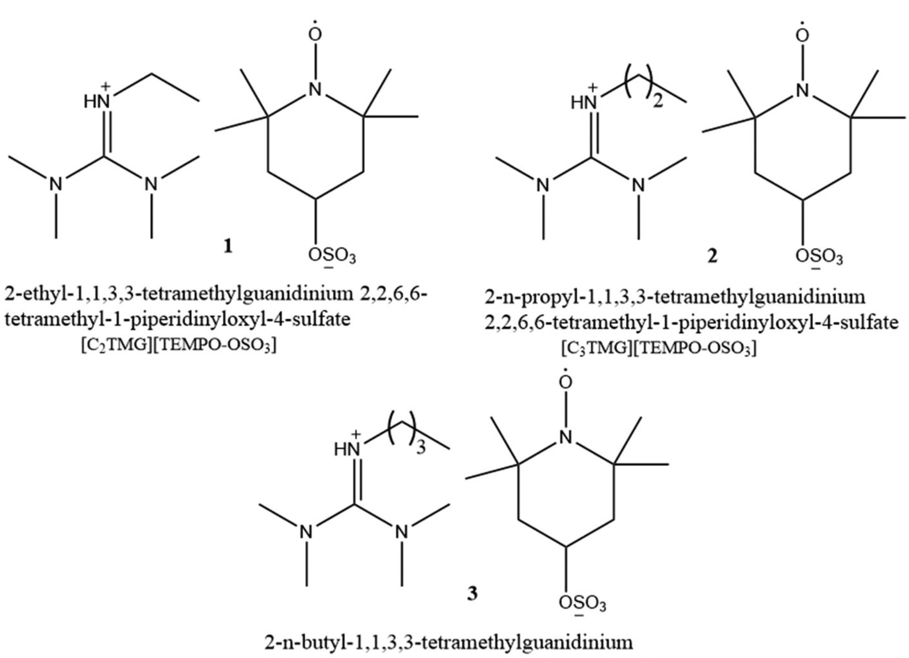
2. Experimental

2.1. Materials

All reagents used were of analytical grade or above. 4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl free radical (4-OH-tempo) and 1,1,3,3-tetramethylguanidine were purchased from Best Reagent Co., Ltd. (Chengdu, China). Anhydrous potassium phosphate with purity higher than 99% was supplied by Guangfu Superfine Chemical Industry Institute (Tianjin, China). It was stored in a vacuum drying oven. Chlorosulfonic acid was obtained from Aike Chemical Reagent Co., Ltd. (Chengdu, China). The other used chemicals and reagents were supplied by Kelong Chemical Co., Ltd. (Chengdu, China). All these purchased chemicals were used directly without any purification. Ultrapure water was obtained from ultra-pure water purification system (0.4 mm filter) manufactured by Millipore (Bedford, MA). The measured MILs in this MILATPs were [C_nTMG][TEMPO-OSO_3] (n = 2 to 4) with their chemical structures shown in Fig. 1. These MILs with mass fraction greater than 99% were synthesized, purified and characterized according to our previous work [25].

2.2. Apparatus and procedures

Phase diagrams were constructed using binodal curves. The binodal curves were determined by the cloud point method [37] at



1 2-ethyl-1,1,3,3-tetramethylguanidinium 2,2,6,6-tetramethyl-1-piperidinyloxyl-4-sulfate [C_2TMG][TEMPO-OSO_3]

2 2-n-propyl-1,1,3,3-tetramethylguanidinium 2,2,6,6-tetramethyl-1-piperidinyloxyl-4-sulfate [C_3TMG][TEMPO-OSO_3]

3 2-n-butyl-1,1,3,3-tetramethylguanidinium 2,2,6,6-tetramethyl-1-piperidinyloxyl-4-sulfate [C_4TMG][TEMPO-OSO_3]

Fig. 1. The name and chemical structures of the MILs.