J. Chem. Thermodynamics 108 (2017) 105–117

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Phase behaviour at different temperatures of ionic liquid based aqueous two-phase systems containing {[Bmim]BF_4 + salt sulfate (Zn^{2+} or Ni^{2+}) + water}

Cínthia das Dores Aguiar, Poliana Aparecida Lopes Machado, Bruno Giordano Alvarenga, Nelson Henrique Teixeira Lemes, Luciano Sindra Virtuoso *

Colloid Chemistry Group, Chemistry Institute, Federal University of Alfenas (UNIFAL-MG), Rua Gabriel Monteiro da Silva, 700, Zip Code 37130-000 Alfenas, MG, Brazil

ARTICLE INFO

Article history:
Received 7 December 2015
Received in revised form 10 January 2017
Accepted 12 January 2017
Available online 14 January 2017

Keywords:
Aqueous two-phase system based in ionic liquid
Liquid-liquid equilibrium
Ion exchange
Thermodynamic parameters of mixture

ABSTRACT

Phase diagrams and liquid + liquid equilibrium (LLE) data of aqueous two-phase systems (ATPSs) composed of the {1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]BF_4) + zinc sulfate ($ZnSO_4$) or nickel sulfate ($NiSO_4$) + water} systems have been determined experimentally at T = (283.15, 298.15, and 313.15) K. The effect of the temperature, composition, cation and ion exchange in the formation this ATPS were available. The temperature had a remarkable effect on the position of phase diagrams. The decrease in temperature promoted phase segregation indicating the exothermic character of formation of these ATPSs and there was phase inversion at a temperature of 283.15 K for both. A scale was established to evaluate the ability of different cations of sulfate salts to induce the formation of ATPSs in mixtures involving [Bmim]BF_4. Thermodynamic parameters of hydration were used together with experimental results of saturation solubility to make various adjustments that seem to show that the molar entropy of hydration is the driving force for the separation process. Thermodynamic parameters of transfer of components (cations, anions and water) between the phases were also calculated from the experimental values and indicated that the material transfer of the bottom phase to the top is not spontaneous and tends to be less spontaneous as the TLL value increases. It was experimentally observed that no significant exchange of ion pairs occurs in the phase separation process. Additionally, the binodal curves were fitted to an empirical non-linear expression and the salting out effect was explored using the type-Setschenow equation. Data consistencies were tested using the Othmer-Tobias and Bancroft equations.

1. Introduction

Phenomena involving segregation of phases are often observed in mixtures of two or more components and play a central role in technological processes involving extraction, purification and/or pre-concentration of specific solutes [1]. Particularly, the so-called aqueous two-phase systems (ATPSs), which contain high water content in the equilibrium phases, have been considered a promising and environmentally safe alternative to replace the traditional separation processes that impact the environment due to the use of polluting substances [2].

In general, ATPSs are formed spontaneously when mixtures of aqueous solutions of chemically different polymers [3], or a polymer + inorganic salt [4], or even an ionic Liquid + inorganic salt [5], among other possibilities [6–9]. ATPSs feature a number of advantages compared to traditional methods of extraction/purification like easy scale-up, reusability of forming components and providing a biocompatible environment in two phases, which allow the use in separation processes of solutes of biotechnological interest that are susceptible to non-aqueous environments [10]. Moreover, the assembly and use of ATPSs involve low power consumption and are based on simple unit operations [11].

In recent years, ATPSs containing ionic Liquids (ILs) have been widely used due to their high extracting capacity of certain analytes in relation to traditional ATPSs (formed by mixing polymer/polymer or polymer/salt) [12]. The ILs are preferably used because of their low vapour pressure compared to traditional organic solvents and their excellent ability to solubilize both organic and inorganic compounds [13–15]. They also present low flammability and high stability due to their physical and chemical characteristics [16,17].

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* Corresponding author.
E-mail address: lsindrav@gmail.com (L.S. Virtuoso).

http://dx.doi.org/10.1016/j.jct.2017.01.008
0021-9614/

Liquid-Liquid equilibrium studies involving ATPSs formed by ionic Liquids have been frequently reported in the literature, particularly, the ILs containing imidazole cations have been widely used in the formation of new ATPSs due to their ability to induce phase separation in aqueous mixtures [18–23]. Various applications involving the use of these ILs in processes of extraction and purification of drugs, proteins and antibiotics have been reported in literature [24–27]. Liquid-liquid equilibrium studies of imidazolium ionic liquids-based ATPSs have involved the use of inorganic salts [28], organic salts [29,30], carbohydrates [20–31] and amino acids [32]. Particularly, the ionic liquid tetrafluoroborate 1-butyl-3-methylimidazolium ($[Bmim]BF_4$) has been used in the preparation of new ATPSs [10,18,20–23]. However, most of the studies are limited at a temperature of 298 K. Furthermore, the success in the application of ATPSs in extraction processes, purification and/or pre-concentration of solutes, is directly related to the complete and accurate determination of the phase behaviour of such systems. Accordingly, the adjustment of empirical equations and thermodynamic models to experimental data allow broadening the understanding of phase behaviour to the regions that have not been evaluated experimentally. However, studies involving ATPSs formed by ILs are still relatively recent and were reported for the first time about a little more than a decade ago [33]. Accordingly, there is considerable interest in understanding the phase equilibrium behaviour involving new ATPSs formed by ILs [34,35]. Particularly, the effect of ion exchange in the phase separation process has been neglected in most work on aqueous two-phase system based in ionic liquids presented in the literature.

In this sense, the present work aimed to study the behaviour of phases separation of different ATPSs formed by mixing the ionic liquid tetrafluoroborate 1-butyl-3-methylimidazolium ($[Bmim]BF_4$) + sulfate salts (zinc or nickel) + water. The effects of temperature, mixture composition, ion exchange and the ability of the cation salt to induce phase separation were investigated.

2. Experimental

2.1. Materials

The materials used in this work, as well as their origin and purity specifications are presented in Table 1. Water content in the IL in mass fraction was determined using thermogravimetric analysis (TGA). To TGA was used a thermogravimetric balance SDTQ600 (TA Instruments, USA) with a precision of 10^{-7} g operating with a constant nitrogen gas flow rate of 100 mL/min and using an open alumina pan with 10 mm diameter and 2 mm height. The method was in good agreement with the value quoted by the suppliers of no more than 0.012 mass fraction. Waters of hydration present in the inorganic salts used in this study were also confirmed by TGA. In all studies deionized water Mili-Q (Milipore, USA) was used to prepare the solutions.

2.2. Construction of binodal curves

The binodal curves were determined using the turbidimetric titration method [23]. About 2 g of a stock solution of $[Bmim]BF_4$ of known concentration was titrated with aliquots of 10 μL of a concentrated stock solution of the salt ($ZnSO_4$ or $NiSO_4$), or vice versa, until the occurrence of turbidity in the mixture. The composition of the mixture was registered and then aliquots of water of 100 μL were added to the mixture until the complete disappearance of turbidity, an indicative of the formation of a second liquid phase. The procedure was repeated several times to obtain a set of points. The titrations occurred in controlled temperatures at (283.15, 298.15 and 313.15) K using a thermostatic bath (SOLAB, SL 152/10). All solutions and the solvent were kept in a thermostatic bath long enough to ensure strict control of temperature. Finally, the positioning of each of the turbidimetric curves (quasi-equilibrium curves) obtained was compared with the binodal points obtained by analysing the equilibrium phases at a given temperature (see Sections 2.3 and 2.4). This comparison led to the estimation of new points for the binodal that were verified experimentally (total mass of 2 g of mixture). Therefore each point of the binodal curve was determined experimentally as being located at the threshold of the composition which leads to turbidity of the mixture. The mixtures' compositions expressed as percentage of mass fraction were determined for each point of the binodal curve using an analytical balance (AG 220, Shimadzu, USA). The water content of 0.012 mass fraction determined by TGA was considered in preparing the solutions of IL.

2.3. Determination of tie lines

To study the liquid-liquid equilibrium, 5 different ATPSs of approximately 10 g each, representing five different tie lines, were assembled from the overall composition points, chosen symmetrically above the binodal curve (biphasic region). The ATPSs were mounted in falcon tubes of 15 mL and kept at controlled temperature for at least 24 h or until the phases became perfectly transparent. The upper and lower phases of the systems were then collected and their mixtures compositions were analysed.

2.4. Construction of phase diagrams

After the collection of the phases, the top and bottom phases were diluted for a number of times with fresh water, then the mass fraction of the Zn^{2+} and Ni^{2+} species, in each of the phases of the ATPSs of this study, were determined using atomic absorption spectroscopy (Thermo Scientific, ICE 3000, USA) at 213.8 nm and 261.2 nm, respectively. The concentration of the ionic liquid was determined by UV–VIS spectroscopy (Shimadzu UV-2401 PC, USA) at 211 nm, which corresponds to the typical absorption of the imidazole ring. The water content was determined by a thermogravimetric balance SDTQ600 as mentioned above. The sulfate content also was determined for the all ATPS by turbidimetric

Table 1
List of chemicals.[a]

Chemical name/Molecular formula	Purity (mass fraction)	Water contents[b] (mass fraction)	Water content analysis method	Purification method	Source
Tetrafluoroborate 1-butyl-3-methylimidazolium/ $[Bmim]BF_4$ or $C_8H_{15}BF_4N_2$	0.987	0.012	TGA	No[a]	Aldrich (USA)
Zinc sulfate heptahydrate/$ZnSO_4{\cdot}7H_2O$	> 0.99	0.417	TGA	No[a]	Merck (Brazil)
Nickel sulfate hexahydrate/$NiSO_4{\cdot}6H_2O$	0.99	0.421	TGA	No[a]	Aldrich (USA)
Water/H_2O	> 0.99	–	–	Mili-Q (Milipore, USA)	–

[a] Reagent was used without further purification as stated by the supplier.
[b] The water contents in the IL and salts were determinate by TGA.