J. Chem. Thermodynamics 82 (2015) 99–107

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

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

Phase equilibria and surfactant behavior of fluorinated ionic liquids with water

F.S. Teixeira [1], N.S.M. Vieira [1], O.A. Cortes [1], J.M.M. Araújo [1], I.M. Marrucho [1], L.P.N. Rebelo *,[1], A.B. Pereiro *

Instituto de Tecnologia Química e Biológica António Xavier, Universidade Nova de Lisboa, Apartado 127, 2780-157 Oeiras, Portugal

ARTICLE INFO

Article history:
Received 5 August 2014
Received in revised form 23 October 2014
Accepted 28 October 2014
Available online 7 November 2014

Keywords:
Fluorinated ionic liquids
Phase equilibria
Critical micelle concentrations
Dynamic Light Scattering
Thermodynamic functions

ABSTRACT

This work studies the phase equilibria and surfactant behavior of fluorinated ionic liquids (FILs) containing fluorinated chains equal to four carbons with water. The knowledge about the phase behavior is crucial for the applications of these novel FILs with tuneable properties. The phase equilibria of the binary mixtures FILs with water were studied at atmospheric pressure in a temperature range from (298.15 to 353.15) K. In this study, FILs containing ammonium, pyrrolidinium and imidazolium cations and the perfluorobutanesulfonate anion were included. The Non-Random Two Liquid (NRTL) thermodynamic model was successfully applied to rationalize the phase behavior of the binary (water + FILs) mixtures. Furthermore, the critical micelle concentrations (CMCs) of these FILs, which present cations and/or anions with surfactant properties were also performed at T = 298.15 K by measurements of the ionic conductivity. Finally, the Dynamic Light Scattering (DLS) was used with aim to determinate the size of the aggregates of these FILs in water.

1. Introduction

Perfluorinated surfactants, such as perfluorooctane sulfonate, are emerging pollutants of increasing public health and environmental concern due to recent reports of their world-wide distribution, environmental persistence and bioaccumulation potential [1]. It is important to realize that the production and use of these perfluorinated surfactants is clearly to increase for the foreseeable future due to their utility, economic value and industrial application [2]. All these perfluorinated surfactants have a polar head and a tail that repels water. In fluorosurfactants, the tail contains fluorine bonded to carbon which makes them repelling fats such as oil or grease, as well as, water. Moreover, they are also more effective at reducing surface tension than other surfactants [3].

Ionic liquids have attracted more attention on the recent decades due to their fascinating properties such as almost null volatility, null flammability and recyclability. The larger number of combinations between cations and anions permit the modification of properties with aim to design ionic liquids for a clearly defined purpose [4,5]. Although the research about ionic liquids field has grown exponentially, there are still numerous unexplored themes, including the fluorinated ionic liquids (FILs) family, herein defined as ionic liquids with fluorous tags equal or longer than four carbon atoms. These FILs are distinct from conventional FILs such as ionic liquids with bis(trifluoromethylsulfonyl)imide, hexafluorophosphate or tetrafluoroborate anions.

Fluorinated ionic liquids are of particular interest in areas where perfluorinated surfactants find relevant applications. The nearly null volatility of FILs at atmospheric conditions, their easy recovery, and, therefore, their recyclability, as well as their tuneable toxicity, completely justify their use as a new cleaner alternative compound to replace the harmful perfluorinated surfactants used nowadays in the industry. Solubility or phase equilibria data of (FILs + water) have not been found in the literature. However, there are already several reports of phase behaviors of fluorinated compounds with traditional ionic liquids [6–9].

The fluorinated ionic liquids studied in this work were selected according to their physical properties and cytotoxicity results in different human cells, which were previously measured in our lab [10]. Additionally, in an attempt to map several ionic liquids families, FILs based on the ammonium, pyrrolidinium and imidazolium cation, paired with perfluorobutanesulfonate anion, were included in this study. The (liquid + liquid) equilibria (LLE) were measured at atmospheric pressure in a temperature range of (298.15 to 353.15) K. The obtained equilibrium data were correlated by applying NRTL (Non-Random Two Liquids) thermodynamic model [11]. Moreover, standard molar Gibbs free energy, standard molar enthalpy and standard molar entropy were

* Corresponding authors. Tel.: +351 214469414; fax: +351 214411277.
E-mail addresses: luis.rebelo@itqb.unl.pt (L.P.N. Rebelo), anab@itqb.unl.pt (A.B. Pereiro).
[1] www.itqb.unl.pt.

http://dx.doi.org/10.1016/j.jct.2014.10.021
0021-9614/

calculated in order to explain the dissolution of water in fluorinated ionic liquids [12–17]. Furthermore, the (solid + liquid) equilibria (SLE) phase diagrams for those systems were measured at T = 298.15 K and atmospheric pressure.

On the other hand, the FILs studied in this work present cations and anions with surfactant properties in aqueous solutions. The critical micelle concentrations (CMCs) of these FILs need to be determined with aim to establish how the structure influence the use, distribution and toxicity of these novel compounds. Therefore, CMCs of these compounds at T = 298.15 K were calculated by measurements of the ionic conductivity. Finally, the size of aggregation of fluorinated ionic liquids in water has been obtained using Dynamic Light Scattering (DLS).

2. Experimental section

2.1. Chemicals

1-Hexyl-3-methylimidazolium perfluorobutanesulfonate, [HexMeIm][(PFBu)SO_3] (>99% mass fraction purity, halides (IC) < 250 ppm, cation (IC) > 99%, anion (IC) > 99%),1-methyl-3-octylimidazolium perfluorobutanesulfonate, [OcMeIm][(PFBu)SO_3] (>99% mass fraction purity, halides (IC) < 250 ppm, cation (IC) > 99%, anion (IC) > 99%), 1-dodecyl-3-methylimidazolium perfluorobutanesulfonate, [DoMeIm][(PFBu)SO_3] (>98% mass fraction purity, halides (IC) < 1%, cation (IC) > 98%, anion (IC) > 98%), 1-butyl-1-methylpyrrolidinium perfluorobutanesulfonate, [BuMepyr][(PFBu)SO_3] (98% mass fraction purity, cation (IC) > 98%, anion (IC) > 98%) and tetrabutylammonium perfluorobutanesulfonate, [NBu_4][(PFBu)SO_3] (98% mass fraction purity, cation (IC) > 98%, anion (IC) > 98%) were supplied by IoLiTec GmbH, and the structures of cations and anions are presented in table 1. To reduce the volatile chemicals and water, all FILs were dried under vacuum ($3 \cdot 10^{-2}$ Torr) with vigorous stirring at T = 323.15 K for at least 2 days, immediately prior to their use. Water content in FILs was analyzed by Karl Fischer (KF) titration technique (Methonm Ion analysis, 831 KF Coulometer). The KF solvents were Hydranal-Coulomat AG No. 34836-R and Hydranal-Coulomat CG No. 34840-R that are the analyte and catholyte, respectively. The water content was less than 100 ppm for all the studied fluorinated ionic liquids. No further purification was carried out and the purity of all FILs was checked by ^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR. Milli-Q water (Milli-Q Integral Water Purification System) was used in all experiments throughout the work.

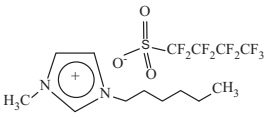
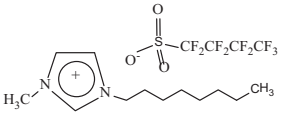
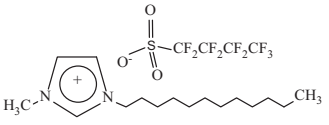
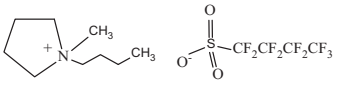
2.2. Experimental procedures

2.2.1. (Liquid + liquid) equilibria

The phase diagram measurements started with the addition of 3 ml of an immiscible (water + FIL) binary mixture of known composition inside a glass vial. Each mixture was prepared using an analytical high-precision balance (Sartorius CP|Gem^{plus} series with an uncertainty of $\pm 10^{-5}$ g) by syringing known masses of each component into stoppered glass vials in an inert-atmosphere (nitrogen flux) glove box. The mixing was assured by magnetic stirring. The experiments were performed in an automatic bath Huber Cc-212b, offering a good temperature control, capable of maintaining the temperature within ±0.01 K. The mixture was vigorously stirred for 1 h, a needle was inserted through the septum of the glass vial in the water-rich upper phase and left to settle for 24 h until the complete separation of the two phases was achieved. Then, no further variations in mole fraction solubilities were observed. In order to not disturb the equilibrium, avoid contamination from one phase with the other, special capped needles were used. Samples from the water-rich phase were taken using one heated syringe and a series of LLE measurements were made by sampling the water-rich phase at the different temperatures. The compositions of the FIL in the water-rich phase were determined by refractometry, measuring the refractive index of each sample at T = 353.15 K which is the upper limit of the studied temperature range, to avoid immiscibility issues. For that purpose, an automatic refractometer ABBEMAT 500 Anton Paar was used with a resolution of $\pm 10^{-6}$ and an uncertainty in the experimental measurements of $\pm 5 \cdot 10^{-5}$. Calibration curves were previously made by measuring the refractive index of samples with known composition at T = 353.15 K. The estimated uncertainty is of $\pm 10^{-4}$ in molar fraction and 0.001 in molar fraction in the phase diagram.

The solubility of water in the FIL-rich phase was determined using Metrohm 831 Karl Fisher coulometer. IL-rich phase samples of about (0.1 to 0.2) g were taken from the equilibrium vials using a glass syringe maintained in dry and warm conditions. The KF is a

TABLE 1
Chemical structure and respective acronyms of the fluorinated ionic liquids (FILs) used in this work.

FIL designation	Purity	Chemical structure
1-Hexyl-3-methylimidazolium perfluorobutanesulfonate, [HexMeIm][(PFBu)SO_3]	>99% Mass fraction	
1-Methyl-3-octylimidazolium perfluorobutanesulfonate, [OcMeIm][(PFBu)SO_3]	>99% Mass fraction	
1-Dodecyl-3-methylimidazolium perfluorobutanesulfonate, [DoMeIm][(PFBu)SO_3]	>98% Mass fraction	
1-Butyl-1-methylpyrrolidinium perfluorobutanesulfonate, [BuMepyr][(PFBu)SO_3]	>98% Mass fraction	
Tetrabutylammonium perfluorobutanesulfonate, [NBu_4][(PFBu)SO_3]	>98% Mass fraction