



# Interactions between molecular solutes and task-specific ionic liquid: Measurements of infinite dilution activity coefficients and modeling



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## ARTICLE INFO

### Article history:

Received 8 April 2016

Received in revised form 13 May 2016

Accepted 20 May 2016

Available online 26 May 2016

### Keywords:

Ionic liquid

Activity coefficient

LSER

Solubility parameter

COSMO-RS

## ABSTRACT

Infinite dilution activity coefficients of 35 molecular compounds in novel ionic liquid (IL) 1-(2-hydroxyethyl)-1-methylpyrrolidinium dimethylphosphate are presented in a wide range of temperature. Basic thermal characteristics and liquid density of the IL at ambient pressure are also reported. The measured activity coefficients are discussed in terms of molecular interactions between the solutes and the IL's cation and anion. An impact of strongly basic anion and the cation functionalization is elucidated. Application of the studied IL in aromatic-aliphatic separations and extractive desulfurization is evaluated on the basis infinite dilution selectivity and capacity. The experimental data are treated in terms of three distinct approaches: linear solvation-energy relationship (LSER), regular solution theory and conductor-like screening model for real solvents (COSMO-RS). In particular: temperature-dependent LSER correlation able to accurately reproduce gas-liquid partition coefficients derived from activity coefficients is presented, the solubility parameters of pure IL are derived on the basis of treatment of measured data with the Scatchard-Hildebrand equation and the predictive capacity of the COSMO-RS approach in calculating limiting activity coefficients for the considered systems is tested.

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## 1. Introduction

Due to a great both scientific and utilitarian significance of ionic liquids (ILs), different aspects of this peculiar class of chemicals have been intensively investigated since over 25 years [1–3]. Application of ILs in separations of azeotropic systems with liquid-liquid extraction or extractive distillation has attracted a vast amount of attention of numerous research groups and communities [4]. In particular, numerous papers published in the open literature so far deal (from both practical and theoretical points of view) with the problems of aromatic-aliphatic separations [5–8], or fuel desulfurization [9–11].

In order to effectively design and optimize any process of this kind, a fundamental knowledge of thermodynamic properties of ILs and their mixtures with the molecular compounds to be separated is required. The properties of interest usually comprise liquid-liquid and vapor-liquid equilibrium phase diagrams and excess functions of mixing. In general, a knowledge of the deviations of the considered system from ideal behavior expressed by the excess Gibbs energy and composition- and temperature-dependent activity coefficients is sufficient to explore the phase diagrams and carry out most of the relevant thermodynamic calculations. In particular, infinite dilution activity coefficient ( $\gamma^\infty$ ) is a

powerful property that can be used to perform a rough evaluation of an IL (or any other solvent tested as an entrainer) in the separation problem under study [6,7], but also can be used in many other areas of chemical, environmental and biochemical engineering [12]. Moreover, a study of  $\gamma^\infty$  enables to get some physical insight into molecular interactions between IL and solute. In principle, difference in  $\gamma^\infty$  observed for given two solutes is closely associated with the difference in their affinities to the solvent, i.e. an essential criterion affecting a separation performance.

A key problem is thus to understand an impact of various structural characteristics of IL (cation, anion, functional groups attached to the alkyl chains of cation/anion, ...) on  $\gamma^\infty$ . Despite the fact that the community has made a huge experimental and theoretical/computational effort to achieve this goal, the structure-property relationship for the  $\gamma^\infty$  still remains an unexplored field. Therefore, further investigations are necessary to be conducted. In our opinion, nowadays the  $\gamma^\infty$ -related research projects should focus on novel cation-anion combinations. In particular, pyrrolidinium-based salts seem to be interesting alternatives to widely studied 1,3-substituted imidazolium-based ILs. Thus far, however, mostly the ILs composed of alkyl-functionalized cations  $[C_nC_1Pyr]^+$ , where  $C_n \equiv C_nH_{2n+1}$ , and different anions were studied: bis(trifluoromethylsulfonyl)imide  $[NTf_2]^-$  (with  $n$  varying from 3 to 10) [13–15], trifluoromethylsulfonate  $[OTf]^-$  (with  $n=4$ ) [16], tris(pentafluoroethyl)trifluorophosphate  $[FAP]^-$  (with  $n=4$ ) [17], thiocyanate  $[SCN]^-$  (with  $n=4$ ) [18], tricyanomethanide  $[TCM]^-$  (with  $n=4$ ) [19], tetracyanoborate  $[TCB]^-$  (with  $n=4$ ) [20], or lactate

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[La]<sup>+</sup> (with  $n = 2$ ) [21]. To account for an influence of substitution of one of carbon atoms in *n*-butyl chain in the cation by oxygen, Marciniak and Wlazło [22,23] measured and discussed infinite dilution activity coefficients of more than 50 molecular solutes in [NTf<sub>2</sub>]<sup>-</sup> [22] and [FAP]<sup>-</sup> [23] based ILs with 1-(2-methoxyethyl)-1-methylpyrrolidinium cation, [C<sub>20</sub>H<sub>17</sub>N<sub>1</sub>Pyr]<sup>+</sup>. To our best knowledge these are the only papers on concerned with an impact of pyrrolidinium cation's functionalization on  $\gamma^\infty$ .

This work is a continuation of our systematic study of infinite dilution activity coefficients of molecular solutes in ILs. The values of  $\gamma^\infty$  of 35 solutes (including *n*-alkanes, alkenes, alkynes, aromatics, ethers, ketones, alcohols and other polar solutes) are presented for the new IL (i.e. not reported so far; according to SciFinder [24] and ILThermo [25]) 1-(2-hydroxyethyl)-1-methylpyrrolidinium dimethylphosphate. Based on the experimental data measured by gas-liquid chromatography, molecular interactions between the IL and the solutes are discussed. Analysis of the collected data is presented in terms of linear solvation-energy relationship (to get a correlation for gas-liquid partition coefficient of the investigated solutes) and regular solution theory (to estimate the Hildebrand solubility parameter of pure IL as a function of temperature). Predictive capacity of conductor-like screening model for real solvents (COSMO-RS) is also demonstrated and evaluated.

## 2. Experimental methods

### 2.1. Chemicals and materials

The ionic liquid 1-(2-hydroxyethyl)-1-methylpyrrolidinium dimethylphosphate, henceforth abbreviated by [C<sub>20</sub>H<sub>17</sub>N<sub>1</sub>Pyr][DMP], was purchased from IoLiTec. The supplied sample had a certified mass fraction purity of 0.95. In order to remove any volatile chemicals and water this compound was under vacuum at temperature 353 K for approximately 24 h.

Prior to the measurements, the water content of the studied IL used was determined with Karl-Fischer method. The sample of IL was dissolved in anhydrous methanol and titrated with steps of 0.0025 cm<sup>3</sup>. This procedure was repeated until the results were precise within 10 ppm. The final mass fraction water content in the sample of IL was 850 ppm.

All the molecular compounds employed in retention measurements (henceforth referred to as solutes) were used as received without further purification. The full list of solutes including their supplier and mass fraction purity is given in Table S1 in the Supplementary Material.

### 2.2. Differential scanning calorimetry

The basic thermal characteristics of the investigated IL were measured using a differential scanning calorimetry technique (DSC). All the experiments were performed in heating mode. The applied scanning rate was +10 K·min<sup>-1</sup>. The apparatus (DSC 1 STAR<sup>e</sup> System with Liquid Nitrogen Cooling System purchased from Mettler Toledo) was calibrated with a 0.999999 mass fraction purity indium sample. The repeatability of the recorded phase transition temperature value was 0.1 K.

### 2.3. Density measurements

Ambient pressure density of pure IL was measured using an Anton Paar 4500 M vibrating-tube densimeter at different temperatures varying from  $T = (298.15 \text{ to } 368) \text{ K}$  with a step of +10 K. Resolution of the apparatus was 0.01 K for temperature and 0.01 kg·m<sup>-3</sup>. The overall uncertainties of the measurements were estimated to be 0.05 K and 0.1 kg·m<sup>-3</sup>, respectively.

### 2.4. Gas-liquid chromatography

The Perkin-Elmer Clarus 500 gas chromatograph equipped with a TCD was used to determine infinite dilution activity coefficients based on gas-liquid chromatographic (GLC) retention data of molecular solutes (denoted by “2” in the following symbols and formulas) through the column coated with a thin film of IL (denoted by “1” in the following symbols and formulas). The procedure for the column preparation is as follows. Chromosorb W/AW-DCMS 100/120 mesh (Sigma-Aldrich) was used as the solid support. To be coated, the support was dispersed in the methanol solution of the IL. After coating, methanol was removed using a rotary evaporator and the Chromosorb finally coated with IL was placed in glass columns of approximate length internal diameter of 1 m and 0.04 m, respectively.

In total, three columns differing in mass percent packing were prepared (mole numbers of IL given in parentheses): 45.1% ( $n_1 = 8.58 \text{ mmol}$ ), 49.9% ( $n_1 = 10.2 \text{ mmol}$ ) and 54.6% ( $n_1 = 12.2 \text{ mmol}$ ). The masses of both solid support and IL were weighed with an uncertainty of 0.0001 g. The values of column packing were chosen on the basis of our previous experience with the discussed GLC method. In particular, such large column packing prevents the residual adsorption of solute onto the solid support, what is an effect competitive with gas-liquid partitioning – the only effect which is relevant from the point of view of infinite dilution activity coefficient determination.

Helium was used as a carrier gas (denoted by “3” in the following symbols and formulas). Its inlet pressure  $P_{\text{in}}$  was measured by a pressure gauge installed on the gas chromatograph with an uncertainty of 0.1 kPa. In turn, the outlet pressure  $P_{\text{out}}$  was kept at atmospheric pressure, whereas the flow rate  $U_0$  of the carrier gas (stabilized for at least 15 min before any determinations and additionally corrected for the vapor pressure of water) was measured by a calibrated soap bubble flow meter which was placed at the outlet after the detector. The pressure drop ( $P_{\text{in}} - P_{\text{out}}$ ) in the column varied from 15 to 60 kPa, depending on the polarity of the solute and temperature. The temperature of the column varied from  $T = (298.15 \text{ to } 368.15) \text{ K}$  with interval +10 K with standard uncertainty of 0.05 K.

Solute injections ranged from  $(0.01 \text{ to } 0.3) \cdot 10^{-3} \text{ cm}^3$  and such amounts can be considered to be at infinite dilution on the column. For each injection, retention times were measured for the retained solute ( $t_R$ ) and non-retained components ( $t_C$ ). Three injections per determination were performed resulting in retention times reproducible within  $(10^{-3} \text{ to } 10^{-2}) \text{ min}$ .

Given all the important retention data, infinite dilution activity coefficient of molecular solute in ionic liquid ( $\gamma_2^\infty$ ) can be obtained from the following the well-known formula proposed by Everett and Cruickshank [26,27]

$$\ln \gamma_2^\infty = \ln \frac{n_1 RT}{P_2^0 V_N} - \frac{P_2^0 B_{22} - V_2}{RT} + \frac{P_{\text{out}} J_2^3 2B_{23} - \bar{V}_2^\infty}{RT} \quad (1)$$

where  $R$  stands for universal gas constant,  $P_2^0$  is the saturated vapor pressure of pure solute,  $V_2$  is the molar volume of the solute,  $\bar{V}_2^\infty$  is the partial molar volume of the solute at infinite dilution in IL (approximated as a molar volume of the solute,  $\bar{V}_2^\infty \approx V_2$ ),  $B_{22}$  and  $B_{23}$  are the second virial coefficient of pure solute and mixed second virial coefficient of the solute and carrier gas. Finally, the symbol  $V_N$  refers to the net retention volume of the solute defined as

$$V_N = (J_2^3)^{-1} U_0 (t_R - t_C) \quad (2)$$

where

$$J_2^3 = \frac{2 P_{\text{in}} / P_{\text{out}}^3 - 1}{3 P_{\text{in}} / P_{\text{out}}^2 - 1} \quad (3)$$

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