Solvatochromic parameters of imidazolium-, hydroxyammonium-, pyridinium- and phosphonium-based room temperature ionic liquids

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ABSTRACT

Solvatochromic solvent parameters of different room temperature ionic liquids based on the imidazolium, hydroxyammonium, pyridinium and phosphonium cations, namely 1-butyl-3-methyl imidazolium hexafluorophosphate, 1-hexyl-3-methyl imidazolium hexafluorophosphate, 1-octyl-3-methyl imidazolium hexafluorophosphate, 1-octyl-3-methyl imidazolium tetrafluoroborate, N-octylpyridinium tetrafluoroborate, 2-hydroxyethylammonium formate, 2-hydroxypropylammonium formate, trihexyl-(tetradecyl)phosphonium chloride, trihexyl-(tetradecyl)phosphonium bromide, trihexyl-(tetradecyl)phosphonium bis(trifluoro-methylsulfonyl)imide and trihexyl-(tetradecyl)phosphonium dicyanamide were determined at 25 °C using UV–Vis spectroscopy. Specifically, we have measured the Kamlet–Taft parameters: α (hydrogen-bond donor acidity), β (hydrogen-bond acceptor basicity), π^* (dipolarity/polarizability) and the Reichardt's normalized polarity parameter, E_T^N.

In previous works, we employed the Solvation Parameter Model to predict the partition coefficients for compounds of biological and pharmacological interest and to elucidate the chemical interactions involved in the partition process of different probe molecules between water and different types of ionic liquids. In this work, we have used the obtained solvatochromic solvent parameters to explain and understand the relative magnitudes of the chemical interactions obtained with the solvation parameter model.

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1. Introduction

In the past decades, ionic liquids have been increasingly used for diverse applications such as organic synthesis [1,2], catalysis [3,4], electrochemical devices [5,6], and solvent extraction of a variety of compounds in addition to many other areas [7–10]. At present, room temperature ionic liquids (RTILs) are close to be considered as conventional solvents for extraction and sample preparation, although their use compared with typical organic solvents is still much lower [8]. The use of ionic liquids in different areas of Analytical Chemistry, particularly the RTILs, has increased considerably in recent years [8,11–13]. This is because these solvents have several characteristics that are different to those of the typical organic solvents, such as unique solubilization properties, low or none vapor pressure, no flammability and the possibility to modify their physical properties through the proper selection of the cation and anion [14,15].

Ionic liquids offer a great flexibility in their properties since the possible combinations of cations and anions are quite high. However, a wide variety of cations and anions available make a systematic study of their physicochemical properties very difficult. The selection of an appropriate ionic liquid for a particular application would require a comprehensive database of the fundamental properties like stability, density, miscibility, viscosity, and polarity for a wide range of temperature and pressure, which unfortunately at present is not available for all the classes of ionic liquids. The polarity of ionic liquids can play a crucial role in optimizing the reaction conditions for organic transformation in addition to other vital applications. For example, the high polarity of the cation pyrrolidinium, a Brønsted acid, was considered to be an important factor for the oxidative desulfurization of diesel fuel in the presence of H_2O_2 [16].

The polarity of several ionic liquids has been studied in terms of the Reichardt's normalized scale, E_T^N [17–19] and the Kamlet–Taft polarity parameter, π^*, for several ionic liquids [19–22]. Recent publications have shown that the commonly used ionic liquids are reasonably polar solvents, having polarity greater than those of solvents like acetone and dimethyl sulfoxide but less than water and short-chain alcohols [21,23,24]. A comprehensive account of the polarity of ionic liquids has been presented by C. Reichardt [17].

The ionic liquids properties have revealed many interesting characteristics not observed earlier for conventional solvents. For example, ionic liquids show a strong tendency of preferential solvation for a probe molecule in their binary mixtures with water or organic cosolvents. Although preferential solvation has been observed also in conventional binary mixtures, the effect was not as drastic as was seen in ionic liquid mixtures. The polarity studies on the binary mixture of

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tetraethylene glycol with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [BMIM][PF$_6$], showed interesting synergistic effects, which was termed as "hyperpolarity" [25]. It is believed that such phenomena arise due to the formation of highly ordered microsegregated phases in the binary mixtures.

Although phosphonium-based RTILs (PB-RTILs) have been known and synthesized for years, they have been more or less "neglected" in the literature compared to their imidazolium or pyrrolidinium based counterparts [26]. PB-RTILs are made of tetra-alkyl-phosphonium cations with different anions and can have some additional advantages compared to the nitrogen-based RTILs (NB-RTILs), such as very high thermal and chemical stability and higher solvation properties. There are about 20 different types of PB-RTILs commercially available. Cytec Industries Inc. sells phosphonium salts under the CYPHOS® trade name [27,28]. PB-RTILs have much low cost as compared to NB-RTILs and some of them have lower density than water, and advantage in extraction processes.

In previous works [26,28], we have used the Solvation Parameter Model (SPM) to elucidate the molecular interactions involved in the partition process for analytes of very different chemical nature between NB- and PB-RTILs and water. Also, we could predict liquid–liquid partition coefficients for molecules of biological and pharmacological interest. This finding will allow to theoretically predict which RTIL will be useful to obtain high recoveries and enrichment factors for any analyte (neutral at the working pH) when this type of new solvents are used as extractant.

The SPM relates the logarithm of some free-energy related physicochemical property, in this case the RTIL-water partition coefficient, $P_{IL/w}$, and several independent solute parameters or descriptors, each one reflecting a different type of solute–solvent interaction (Eq. 1). Thus, since a solvation process (relative solubility of the analyte in a biphasic system) is involved, the SPM is considered as linear solvation energy relationship (LSER).

$$\log P_{IL/w} = c + sS + aA + bB + vV + eE \qquad (1)$$

Here the solute descriptors are as follows: **S** is the solute dipolarity/polarizability; **A** and **B** are the respective solute hydrogen-bond acidity and basicity; **V**, the molar volume, accounts for both cohesive interactions (the necessary energy to form the cavity within the solvent to fit the solute) and dispersive interactions, and **E**, the excess molar refraction, accounts for interactions with electron-donor groups. The intercept, **c**, and the regression coefficients **s**, **a**, **b**, **v**, and **e** (LSER coefficients) are obtained from multivariable, simultaneous, least-squares regressions [29]. These coefficients contain chemical information since they reflect the *difference between the RTIL phase and the aqueous phase* in the complementary property to each solute parameter [29–32] as follows:

$$\log P_{IL/w} = c + s'(s_{IL}-s_w)S + a'(b_{IL}-b_w)A + b'(a_{IL}-a_w)B \\ + v'(v_{IL}-v_w)V + e'(e_{IL}-e_w)E \qquad (2)$$

where the subscripts "IL" and "w" denote the water-saturated ionic liquid phase and the ionic liquid-saturated water phase, respectively. The coefficients s', a', b', v' and e' are fitting parameters which ought to be independent of the solute and liquid phases if the formalism were rigorously correct [33,34]. The nomenclature was adapted from reference [29] to this work. It was suggested that the v'(v$_{IL}$–v$_w$)**V** term can be dissected into a "cavity term" and a "dispersive term" [26,29].

$$v'(v_{IL}-v_w)V = v'_1(\sigma_{IL}-\sigma_w)V + v'_2(D_{IL}-D_w)V \qquad (3)$$

Here **σ** denotes some measure of the cohesive energy density of forming a "hole" in a solvent and **D** is a dispersion parameter representing the strength or susceptibility of the solvent to engage in London interactions. Based on the solubility parameter theory, **σ** can

be taken as the square of Hildebrand solubility parameter, δ_H^2 [29]. Unfortunately, dispersion parameters representing the **D** term are not available in the literature for any liquid and δ_H values are known for a few RTILs [35,36].

In this work, we have obtained the solvatochromic solvent parameters π^* of polarity–polarizability, β of hydrogen bond acceptor capacity and α of hydrogen bond donor capacity for imidazolium-, pyridinium-, hydroxyammonium- and phosphonium-based ionic liquids. For validation purpose, we obtained these parameters for some RTILs already reported in the literature. The α parameter was obtained indirectly through the Reichardt's normalized solvent parameter, E_T^N. The obtained solvent parameters were used to understand and explain the chemical interactions involved in biphasic systems formed by different ionic liquids and water studied in previous works.

2. Experimental

2.1. Chemicals and materials

Trihexyl-(tetradecyl)phosphonium chloride, [(C$_6$)$_3$C$_{14}$P][Cl] (CYPHOS® IL 101), trihexyl-(tetradecyl)phosphonium bromide, [(C$_6$)$_3$C$_{14}$P][Br] (CYPHOS® IL 102), trihexyl-(tetradecyl)phosphonium dicyanamide, [(C$_6$)$_3$C$_{14}$P][N(CN)$_2$] (CYPHOS® IL 105) and trihexyl-(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide, [(C$_6$)$_3$C$_{14}$P][NTf$_2$] (CYPHOS® IL 109) were provided by Cytec Industries Inc. (New Jersey, USA). 1-hexyl-3-methylimidazolium hexafluorphosphate [HMIM][PF$_6$], 97.0% (Fluka Buchs, Germany). *N*-octylpyridinium tetrafluoroborate, [OPy][BF$_4$] was synthesized and purified in our laboratory by adapting a procedure from Ref. [37]. 1-octyl-3-methylimidazolium hexafluorophosphate, [OMIM][PF$_6$], 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF$_6$] and 1-octyl-3-methylimidazolium tetrafluoroborate [OMIM][BF$_4$] were synthesized and purified in our laboratory by adapting a procedure from Ref. [26,28]. 2-Hydroxypropylammonium formate [OH–C$_3$NH$_3$][For] and 2-Hydroxyethylammonium formate [OH–C$_2$NH$_3$][For] were obtained and purified as previously reported in by adapting a procedure from Ref. [38]. In Fig. 1, the chemical structures for these studied RTILs are shown. In Table 1, the names and the corresponding abbreviations are depicted.

Reagents were of analytical grade or better: sodium hexafluorophosphate, 98.0% (Aldrich, Wisconsin, USA), *1*-Methylimidazole, ≥99.0% (Merck, Hohenbrunn, Germany), 2-aminoethanol (Fluka, Buchs, Switzerland), pyridine, 99.0% (Sigma-Aldrich, St. Louis, USA), tetrafluoroboric acid, 48.0% (w/v) in water (Sigma-Aldrich, St. Louis, USA), *N,N*-diethyl-4-nitroaniline (Frinton Laboratories Inc., NJ, USA), *4*-nitroaniline and Reichardt's dye 30 (Sigma-Aldrich, St. Louis, USA), sodium hydroxide and potassium hydroxide (Analar, Poole, England), *1*-Bromoctane, 99.0% (Aldrich, WI, USA), sodium sulfate anhydrous (Merck, Buenos Aires, Argentina), silver nitrate and formic acid 85.0% (Anedra, Industria Argentina), acetonitrile (Carlo Erba, Divisione Chimica Industriale—Milano, Italy), acetone (Merck, Industria Argentina), ethanol anhydrous (Carlo Erba, Divisione Chimica Industriale—Milano, Italy) and methanol and dichloromethane HPLC grade (J. T. Baker, Edo. de Mexico, Mexico). The micropipettes were purchased from Eppendorf, Hamburg, Germany.

2.2. Equipment

A single-beam Helios-Gamma UV–Vis spectrophotometer (Thermo) with 1 mm path length quartz cuvettes was used to register the UV–Vis spectra for the different probe molecules shown in Fig. 2 used to obtain the solvent parameters. A thermostat controlled bath (Lauda T) maintained at 25.00 ± 0.05 °C was employed for the experiments, a Vortex Genie 2 (Scientific Industries, USA) mixer allowed thorough mixture of the aqueous and the RTIL phases. Water was purified with a Milli-Q system (Millipore Co.).