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Activity coefficients at infinite dilution of organic solutes in methylphosphonate based ionic liquids using gas-liquid chromatography

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ABSTRACT

Activity coefficients at infinite dilution γ_{12}^{∞} were determined for organic solutes in two ionic liquids 1-ethyl-3-methylimidazolium methylphosphonate [EMIM][(MeO)(H)PO_2] and 1.3-dimethylimidazolium methylphosphonate [DMIM][(MeO)(H)PO_2] by gas-liquid chromatography at temperatures within the range (313.15 to 373.15) K. The values of the selectivity and capacity for few separation problems cyclohexane/benzene, cyclohexane/thiophene and cyclohexane/pyridine were calculated from activity coefficients at infinite dilution data and compared to literature values for other ionic liquids and some industrial solvents such as sulfolane, N-methyl-2-pyrrolidone (NMP) and N-formylmorpholine (NFM). The selectivity values of both ILs investigated in this study are greater than that for NMP, NFM, and sulfolane. These results indicate the potential use of the two ILs in extractive separation processes.

1. Introduction

In recent years, research on ionic liquids (ILs) is one of the most rapidly growing fields as novel prospective materials for a variety of innovative applications [1–7]. Due to their unique properties, such as negligible vapor pressure at room temperature, stable liquid phase over a wide temperature range and thermal stability at high temperatures, ionic liquids are creating an continuously growing interest to use them in synthesis and catalysis as well as extraction processes for the reduction of the amount of volatile organic solvents used in industry. Ionic liquid are alternative green solvents to common organic solvents in diverse applications such as organic synthesis, separation processes, catalysis and electrochemistry [8–11].

It is now well established that ILs may be used in various a large number of applications such as liquid-liquid extraction, catalysis, synthesis and gas separations [12–14]. Among others, extractive desulfurization using ionic liquids (ILs) is regarded as a promising process: it has a high sulfur removal ratio and a great selectivity under mild operating conditions, moreover, it is safe, simple but also reproducible. The use of such solvents in the field of extractive desulfurization presents a great potential due to their thermodynamic properties: negligible vapor pressure, great thermal chemical stabilities [15,16]. In recent work, Hassan *et al.* [17,18] have shown that alkylphosphonate based ILs could be used for the extraction of carbohydrates and cellulose. Recent studies on the dissolution of cellulose in 1-butyl-3-methylimidazolium chloride [BMIM][Cl] and dimethylimidazolium methylphosphonate [DMIM][MPh] indicate that the anion of the IL acts as a hydrogen bond acceptor which interacts with the hydroxyl groups of the cellulose [19]. The Kamlet–Taft parameters α: hydrogen bond acidity, β: hydrogen bond basicity and π^*: polarity show that [DMIM][MPh] and [BMIM][Cl] ILs displayed high basicity and polarity values compared to classical solvents. Methylphosphonate based ILs could be a good candidate for different problems of separation but there is still a lack of information concerning the behavior of this family of ILs with organic compounds.

Gas chromatography is a good tool to understand the behavior of the solutes and the stationary phase through the measurements of partition coefficients or activity coefficients at infinite dilution. [1,20–24]. Similar approaches based on gas chromatography technique were proposed to quantify various intermolecular solute-IL interactions. Among others, Abraham *et al.* have developed the Linear Solvation Energy Relationship model (LSER) allowing to correlate thermodynamic properties of phase transfer processes [25–28]. Abraham solvation parameter model for both the gas-to-solvent partition coefficient, K_L, and the water-to-solvent partition coefficient, P have the following expression:

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$$\mathrm{Log}K_{\mathrm{L}} = \mathrm{c} + \mathrm{e}\mathbf{E} + \mathrm{s}\mathbf{S} + \mathrm{a}\mathbf{A} + \mathrm{b}\mathbf{B} + \mathrm{l}\mathbf{L}, \tag{1}$$

$$\mathrm{Log}P = \mathrm{c} + \mathrm{e}\mathbf{E} + \mathrm{s}\mathbf{S} + \mathrm{a}\mathbf{A} + \mathrm{b}\mathbf{B} + \mathrm{v}\mathbf{V}. \tag{2}$$

The dependent variables in equations (1) and (2) are solute descriptors as follows: **E** and **S** refer to the excess molar refraction in units of $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})/10$ and a dipolarity/polarizability description of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and basicity, **V** is the McGowan volume in units of $(\mathrm{cm}^3 \cdot \mathrm{mol}^{-1})/100$, and **L** is the logarithm of the gas-to-hexadecane partition coefficient at $T = 298$ K. The coefficients *c, e, s, a, b* and *l* (or v) are not simply fitting coefficients, but they reflect complementary properties of the solvent phase.

The system constants are identified as the opposing contributions of cavity formation and dispersion interactions, *l*, the contribution from interactions with lone pair electrons, e, the contribution from dipole-type interactions, *s*, the contribution from the hydrogen-bond basicity of the stationary phase (because a basic phase will interact with an acid solute), *a*, and *b* the contribution from the hydrogen-bond acidity of the stationary phase. The system constants are determined by multiple linear regression analysis of experimental logSP($\log K_L$ in this work) values for a group of solutes of sufficient number and variety to establish the statistical and chemical validity of the model.

In this work, we present experimental measurements of γ_{12}^{∞} for selected organic solutes (alkanes, alkynes, cycloalkanes, alcohols, aromatics and ketones) in 1-ethyl-3-methylimidazolium methylphosphonate [EMIM][(MeO)(H)PO_2] and 1.3-dimethylimidazolium methylphosphonate [DMIM][(MeO)(H)PO_2] from $T = (313.15$ to $373.15)$ K using gas-liquid chromatography.

2. Experimental

2.1. Materials and reagents

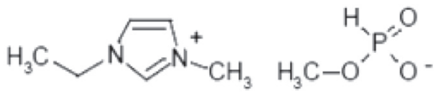
The ionic liquids 1-ethyl-3-methylimidazolium methylphosphonate [EMIM][(MeO)(H)PO_2] and 1.3-dimethylimidazolium methylphosphonate [DMIM][(MeO)(H)PO_2] were purchased from Solvionic with a purity of 98% by mass. The structures of investigated ionic liquids are presented in figure 1. The ionic liquids were dried for more than 24 h at $T = 323.15$ K under reduced pressure to remove volatile impurities and trace water. Most of the solutes were purchased from Sigma Aldrich and Fluka and the purities were more than 99.5%, and were used without further purification because the GLC technique separated any impurities on the column. Water content was determined with a TIM550 Karl Fischer volumetric titration (Titralab) using the HYDRANAL-Solvent E as analyte (from Sigma–Aldrich). The results obtained have shown the water content to be less than $725 \cdot 10^{-6}$ for [DMIM][(MeO)(H)PO_2] and $1580 \cdot 10^{-6}$ for [EMIM][(MeO)(H)PO_2]. The error on the water content was ±2%. Chemical sources and purity of all solvent and test solutes are given in supporting information table 1S.

2.2. Apparatus and experimental procedure

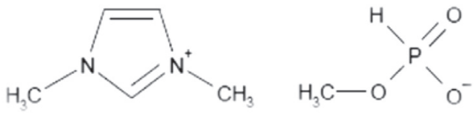
Inverse chromatography experiments were carried out using a Bruker 450-GC gas chromatograph equipped with a heated on-column injector and a thermal conductivity detector (TCD). The injector and detector temperatures were kept at 523 K during all experiments. The helium flow rate was adjusted to obtain adequate retention times. Air was used to determine the column hold-up time. Exit gas flow rates were measured with a soap bubble flow meter. The temperature of the oven was determined with a Pt100 probe and controlled to within $T = \pm 0.1$ K. A computer directly recorded the detector signals and the corresponding chromatograms were generated using the Galaxie Chromatography Software. Using a rotary evaporation preparatory technique, 1.0 m length columns were packed with a stationary phase, consisting of 0.35 mass fraction of IL on in Chromosorb WAW-DMCS (60–80 mesh) sorbent media. After the solvent (ethanol) evaporation, under vacuum, the support was let to equilibrate, at $T = 333$ K during 6 h. Prior to the measurements, each packed column was conditioned for 12 h at $T = 363$ K with a flow rate of $20\ \mathrm{cm}^3 \cdot \mathrm{min}^{-1}$. The packing level was calculated from the masses of the packed and empty columns and was checked throughout experiments. The masses of the stationary phase were determined to a precision of ±0.0003 g. A headspace sample volume of (1 to 5) μL was injected to satisfy infinite dilution conditions and each experiment was repeated at least twice to confirm reproducibility. Retention times were generally rigorously reproducible to within (0.01 to 0.03) min. To verify stability under these experimental conditions, ruling out elution of the stationary phase by the helium stream, measurements of retention time were repeated systematically each day for three selected typical solutes. No changes in the retention times were observed during this study.

2.3. Density measurements

Experimental densities of ILs were measured using an Anton Paar DMA 60 digital vibrating-tube densimeter, with a DMA 512P measuring cell in the temperature range (298.15 to 343.15) K at



1-Ethyl-3-methylimidazolium methylphosphonate [EMIM][(MeO)(H)PO_2]



1.3-dimethylimidazolium methylphosphonate [DIMIM][(MeO)(H)PO_2]

FIGURE 1. Structure of the ionic liquids 1-ethyl-3-methylimidazolium methylphosphonate and 1.3-dimethylimidazolium methylphosphonate.