



# Infinite dilution activity coefficients of volatile organic compounds in two ionic liquids composed of the tris(pentafluoroethyl) trifluorophosphate ([FAP]) anion and a functionalized cation



Eliana Fernandes Órfão<sup>1</sup>, Vladimír Dohnal<sup>\*</sup>, Aleš Blahut

Department of Physical Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic

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## ABSTRACT

Interactions of volatile organic compounds with two ionic liquids (ILs) containing tris(pentafluoroethyl)trifluorophosphate ([FAP]) anion and a functionalized cation, 1-(2-hydroxyethyl)-3-methylimidazolium ([HO-EMIM]) and 1-(2-methoxyethyl)-1-methylpyrrolidinium ([MO-EMPYR]), were explored through systematic GLC retention measurements. Infinite dilution activity coefficients  $\gamma_1^\infty$  and gas–liquid partition coefficients  $K_L$  of 30 selected solutes in [HO-EMIM][FAP] and [MO-EMPYR][FAP] were determined at five temperatures in the range from (318.15 to 353.15) K. Partial molar excess enthalpies and entropies at infinite dilution were derived from the temperature dependence of the  $\gamma_1^\infty$  values. The Linear Free Energy Relationship (LFER) solvation model was used to correlate the  $K_L$  values. The LFER correlation parameters and excess thermodynamic functions were analyzed to identify molecular interactions operating between the ILs and the individual solutes. By comparing the behaviors of the studied ILs and of their closely similar unfunctionalized analogs, net effects imparted by cation functionalization were also disclosed. The cohesivity of the two ILs was shown to differ dramatically: while [MO-EMPYR][FAP] ranks among ILs to the least cohesive, [HO-EMIM][FAP] belongs to the most cohesive ones. Both [HO-EMIM][FAP] and [MO-EMPYR][FAP] are capable of interacting with solutes specifically through dipolarity/polarizability and hydrogen bonding, but apparently lack the ability to interact with solute lone electron pairs. The proton donating capability of [HO-EMIM][FAP], undoubtedly brought by the hydroxyl functionality, is enormous and imparts to this IL extraordinary potential for use in solvent-aided separations. As we have demonstrated on some model aliphatic/aromatic separation pairs, [HO-EMIM][FAP] as a solvent for the separation of aliphatic hydrocarbons from aromatics gives superior performance, its performance index (product of selectivity and capacity) surpassing distinctly that of conventional solvents and of most ILs studied so far. [HO-EMIM][FAP] and [MO-EMPYR][FAP] could also serve as efficient entrainers in separations of other non-petrochemical azeotropic systems of industrial importance by extractive distillation as exemplified for some mixtures of alcohols with aprotic oxygenates.

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## 1. Introduction

During more than a decade, ionic liquids (ILs) have been promoting burgeoning research due to their special chemical and physico-chemical properties offering prospects for great technological innovations. Since properties of these media can be controlled by almost countless structure variations of composing ions, still new ILs are synthesized and explored with the aim to improve their properties and tailor them for specific applications. In order to replace rather unstable hexafluorophosphate containing ILs, Merck developed and made commercially available a group of ILs based on

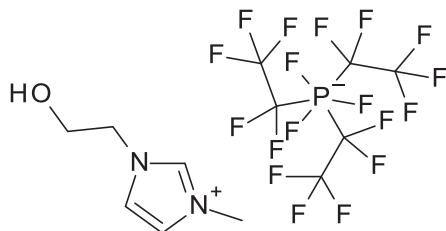
tris(pentafluoroethyl)trifluorophosphate ([FAP]) anion [1]. The [FAP] based ILs exhibit excellent hydrolytic, thermal, and electrochemical stability as well as a lower water uptake and have been shown to provide advantages in various applications in electrochemistry [2], tribology [3], analytical chemistry [4,5] and gas absorption [6,7]. Studies on solvation properties of ILs containing [FAP] anion [8,9] have indicated their great potential for use in solvent-aided separations, especially for ILs in which [FAP]<sup>−</sup> is paired with a functionalized counter-cation. Measurements of infinite dilution activity coefficients  $\gamma_1^\infty$  for a number of test solutes in [FAP] based ILs have been reported confirming this potential [10–14]. Notable in this respect are systematic  $\gamma_1^\infty$  measurements recently carried out by Marciniak and Wlazlo on 1-(3-hydroxypropyl)pyridinium [HO-PPY] [12], 4-(2-methoxyethyl)-4-methylmorpholinium [MO-EMMOR] [13], and 1-(2-methoxyethyl)-1-methylpiperidinium [MO-EMPIP] [14] [FAP]s.

<sup>\*</sup> Corresponding author. Tel.: +420 220 444 297.

E-mail addresses: [Vladimir.Dohnal@vscht.cz](mailto:Vladimir.Dohnal@vscht.cz), [dohnalv@vscht.cz](mailto:dohnalv@vscht.cz) (V. Dohnal).

<sup>1</sup> Visiting Erasmus M.Sc. student from Escola Superior de Tecnologia e de Gestão, Instituto Politécnico de Bragança, Portugal.

In this work, we examine interactions of selected VOCs with two [FAP] based ionic liquids containing functionalized counteranions, namely 1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([HO-EMIM][FAP]) and 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([MO-EMPYR][FAP]).



The methodology of the present investigation is closely parallel to that we used in our previous studies devoted to selected [EMIM] or [BMPYR] based ILs [15–19]. Here we thus report infinite dilution activity coefficients  $\gamma_1^\infty$  and gas–liquid partition coefficients  $K_L$  measured by gas–liquid chromatography (GLC) for the same representative set of 30 selected hydrocarbons, alcohols, ketones, ethers, esters, haloalkanes, and nitrogen- or sulfur-containing compounds in [HO-EMIM][FAP] and [MO-EMPYR][FAP] as a function of temperature. The obtained thermodynamic properties are analyzed to disclose intermolecular interactions governing the observed behavior and identify the potential of these ILs for use as entrainers in solvent-aided separations. Through comparisons with available literature data for unfunctionalized analogs of similar structure also effects brought by the functionalization are disclosed.

Concurrently, infinite dilution activity coefficients for some of the examined solutes in [MO-EMPYR][FAP] have been measured by Marciniak and Wlazlo and presented just now [20]. A detailed comparison of our results to their values is also presented.

## 2. Theory

In gas–liquid chromatography (GLC), the infinite dilution activity coefficient  $\gamma_1^\infty$  and the gas–liquid partition coefficient  $K_L = (c_1^l/c_1^g)$  for a solute (1) partitioning between a carrier gas (2) and a non-volatile liquid solvent (3) are calculated from the solute retention according to the following equations [21]

$$\ln \gamma_1^\infty = \ln \left( \frac{RTm_3}{V_N p_1^s M_3} \right) - \left[ \frac{(B_{11} - v_1^l) p_1^s}{RT} \right] + \left[ \frac{(2B_{12} - \bar{v}_1^\infty) J_3^4 p_0}{RT} \right], \quad (1)$$

$$\ln K_L = \ln \left( \frac{RT\rho_3}{\gamma_1^\infty p_1^s M_3} \right) - \left[ \frac{(B_{11} - v_1^l) p_1^s}{RT} \right], \quad (2)$$

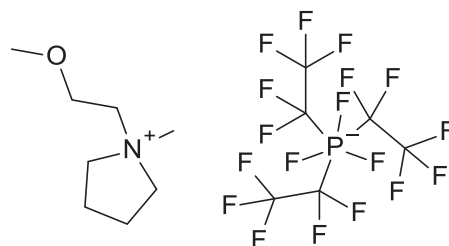
where  $T$  is temperature of the column,  $m_3$ ,  $M_3$  and  $\rho_3$  mass, molar mass and density of the solvent, respectively, and  $p_1^s$  saturated vapor pressure of the solute. The first term on the right hand side of equations (1) and (2) is of the principal importance for calculation of  $\gamma_1^\infty$  and  $K_L$ , respectively, while the remaining terms represent relatively small corrections for gas-phase nonideality. In these corrective terms  $B_{11}$  stands for the second virial coefficient of the pure solute,  $B_{12}$  for the second cross virial coefficient for the solute-carrier gas interaction,  $v_1^l$  for molar volume of the pure liquid solute,  $\bar{v}_1^\infty$  for partial molar volume of the solute at infinite dilution in component 3 and  $p_0$  for the column outlet pressure. The net retention volume  $V_N$  is calculated from the following equation

$$V_N = J_3^2 F (t_R - t_D), \quad (3)$$

where  $t_R$  is the retention time of a given solute,  $t_D$  the retention time of the non-retainable component,  $F$  the carrier gas flow at the

column temperature and column outlet pressure. The corrections  $J_n^m$  in equations (1) and (3) account for compressibility of the mobile phase and are defined as [21]

$$J_n^m = \frac{n}{m} \left[ \frac{(p_i/p_0)^m - 1}{(p_i/p_0)^n - 1} \right], \quad (4)$$



where  $p_i$  stands for the column inlet pressure.

If the infinite dilution activity coefficient is determined as a function of temperature,  $\ln \gamma_1^\infty$  can be split to its respective enthalpy and entropy components

$$\ln \gamma_1^\infty = \frac{\bar{H}_1^{E,\infty}}{RT} - \frac{\bar{S}_1^{E,\infty}}{R}. \quad (5)$$

Assuming that the temperature dependence follows a linear van't Hoff plot

$$\ln \gamma_1^\infty = a/T + b, \quad (6)$$

the partial molar excess enthalpy  $\bar{H}_1^{E,\infty} = Ra$  and entropy  $\bar{S}_1^{E,\infty} = -Rb$  at infinite dilution can be obtained from its slope and intercept, respectively.

## 3. Experimental

### 3.1. Materials

The ionic liquids 1-(2-hydroxyethyl)-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([OH-EMIM][FAP],  $M = 572.17 \text{ g} \cdot \text{mol}^{-1}$ ) and 1-(2-methoxyethyl)-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate ([MO-EMPYR][FAP],  $M = 589.24 \text{ g} \cdot \text{mol}^{-1}$ ) were obtained in the high purity grade from Merck. Their purity of these ILs according to the producer's specification was  $>0.99$ , the certified water content being  $\leq 100 \cdot 10^{-6}$  (mass basis). The samples were handled with special precautions to avoid any contact with moisture. They were pretreated by alternating exposure to vacuum and stripping with dry nitrogen to elute volatile impurities. The efficiency of this treatment was checked by headspace gas chromatographic analysis using a wide-bore (0.53 mm), 15 m long DB-WAX capillary column and flame ionization detector which detected no impurities. The IL samples contained in the GLC columns used for retention measurements underwent additional drying in situ during a longer column conditioning.

Inerton Super (Lachema, Czech Republic) of (0.125 to 0.160) mm granularity was used as a solid support for IL in the GLC column. This high-quality, AW-DMCS diatomaceous solid support is characterized by an extreme catalytic and adsorption inertness and a very low specific surface area ( $0.3$  to  $0.55 \text{ m}^2 \cdot \text{g}^{-1}$ ) [22]. Dichloromethane (Penta, Czech Rep.) used as a solvent in the coating process was of p.a. purity grade, the certified water content being  $\leq 0.0002$  (mass basis). It was further dried with molecular sieves prior to use. The volatile organic compounds (VOC) used as solutes were all of analar purity grade and were mostly used as purchased. The sources and mass fraction purities of all materials used are summarized in table A.1 of the Supplementary data.

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