



Activity coefficients at infinite dilution of alkanes, alkenes, alkyl benzenes in dimethylphosphate based ionic liquids using gas–liquid chromatography



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ABSTRACT

Activity coefficients at infinite dilution (γ_i^∞) for organic solutes: alkanes, alkenes, and alkyl benzenes in two ionic liquids (ILs) 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP]) and 1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM][DMP]) have been measured by the gas–liquid chromatographic method (GLC). The measurements were carried out in the temperature range of (313.15 to 363.15) K. The values of the partial molar excess enthalpies at infinite dilution ($\overline{H}_i^{E,\infty}$) were derived from the temperature dependence of the γ_i^∞ values. The entropies ($T_{ref}\overline{S}_i^{E,\infty}$) and Gibbs energies ($\overline{G}_i^{E,\infty}$) of organic solutes at a reference temperature $T_{ref} = 298.15$ K were also calculated from the γ_i^∞ values. Selectivity (S_{ij}^∞) and capacity (k_j^∞) at infinite dilution at $T = 323.15$ K have been determined for hexane (i)/benzene (j), cyclohexane (i)/benzene (j). The results were analyzed in comparison to literature data for other ILs with the [MMIM] and [EMIM] cations. For three isomeric xylenes separation problems, selectivity at $T = 323.15$ K were also obtained from the γ_i^∞ values.

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1. Introduction

Ionic liquids (ILs) have been considered to be environmental friendly solvents in recent years due to their unique physical and chemical properties, such as negligible vapor pressures, a high solvating capacity for both polar and non-polar compounds, high thermal stability, high ionic conductivity, nonflammability, and large liquid-state temperature range [1–4].

For ILs to be used effectively as solvents, it is essential to know their interaction with different solutes. The activity coefficient at infinite dilution (γ_i^∞) describes the degree of nonideality for species i in a mixture, gives a quantitative measure of interactions between unlike molecules in the absence of solute–solute interactions. Values of γ_i^∞ also provide information on the intermolecular energy between ILs and organic solutes and can be used to quantify the selectivity and solvent power of ILs [5–8]. Activity coefficients at infinite dilution have a wide range of applications in the field of chemical engineering and can be used for the pre-screening of solvents to be used in unit operations such as extractive distillation and liquid–liquid extraction. The use of a steady-state gas–liquid

chromatographic (GLC) technique for the determination of γ_i^∞ has been employed by many researchers and has proved quite reliable [9]. ILs are in particular reliable for the determination of γ_i^∞ by this method because their negligible vapor pressures and high thermal stability make themselves to be ideal stationary phases [2]. Until now, many research groups have measured γ_i^∞ of various solutes in a number of ILs using the gas–liquid chromatograph [10–16]. Our group has focused attention on the determination of γ_i^∞ of various solutes (i) in ILs by the GLC method [17–20]. In this paper, γ_i^∞ have been measured for 16 organic solutes: alkanes (pentane, hexane, heptane, octane, nonane, decane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane), alkenes (cyclohexene and styrene), and alkyl benzenes (benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene) in 1,3-dimethylimidazolium dimethylphosphate ([MMIM][DMP], CAS Registry No. 654058-04-5) and 1-ethyl-3-methylimidazolium dimethylphosphate ([EMIM][DMP] CAS Registry No. 945611-27-8) by the GLC method in the temperature range of (313.15 to 363.15) K. The values of the partial molar excess enthalpies at infinite dilution ($\overline{H}_i^{E,\infty}$) were derived from the temperature dependence of the γ_i^∞ values. The entropies ($T_{ref}\overline{S}_i^{E,\infty}$) and Gibbs energies ($\overline{G}_i^{E,\infty}$) of organic solutes at a reference temperature $T_{ref} = 298.15$ K were also determined from the γ_i^∞ values.

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The selectivity (S_{ij}^∞) and the capacity (k_j^∞) at infinite dilution directly calculated from γ_i^∞ offer an important means to evaluate the performance of ILs as solvents in various separation problems. S_{ij}^∞ and k_j^∞ at $T = 323.15$ K for two ILs have been also calculated for hexane (*i*)/benzene (*j*), cyclohexane (*i*)/benzene (*j*). The results were analyzed in comparison to literature data for other ILs with the [MMIM] and [EMIM] cations. For three isomeric xylenes separation problems, selectivity at $T = 323.15$ K were also obtained from the γ_i^∞ values.

2. Experimental

2.1. Chemicals and materials

The ILs [MMIM][DMP] and [EMIM][DMP] were purchased from Shanghai Chengjie Chemical Co., Ltd. and had a purity of >0.99 mass fraction according to manufacturer's specifications, with the following certified mass fraction of impurities: $w(\text{Cl}^-) < 5 \cdot 10^{-4}$, water $< 10^{-3}$. Before use, the ILs were subjected to vacuum evaporation at $T = (323 \text{ to } 333)$ K over 24 h to remove possible traces of solvents and moisture. The water mass fraction analyzed by Karl Fischer analysis was less than $4 \cdot 10^{-4}$. The chemical structures of [MMIM][DMP] and [EMIM][DMP] are given in figure 1. The organic solutes were purchased from Beijing Chemical Reagents Company. Their mass fraction purities were greater than 0.99. The solutes were used without further purification. The sources and mass fraction purities of materials used are listed in table 1S in Supplementary Material.

2.2. Apparatus and procedure

The experiments were performed on a SP-3420A gas chromatograph equipped with a thermal conductivity detector. The columns preparation and the packing method used in this work have been described previously [16,20]. Chromosorb WAW DMCS 80/100 mesh was used as the solid support and was supplied by SUPELCO. Coating the solid support with ILs was performed by dispersing a known mass amount of the Chromosorb in a solution of IL in ethanol followed by evaporation of the solvent in a rotating evaporator. The Chromosorb was weighed on an electronic balance of precision of ± 0.0001 g before and after the coating process. The column packing in this work were 35.98% (3.374 mmol) mass percent of [MMIM][DMP] and 44.11% (2.077 mmol) mass percent of [EMIM][DMP] with a precision of ± 0.0001 g. In our experimental

work we always use the large column packing, which prevents the residual adsorption of solute onto the column packing.

The measurements for organic solutes were carried out in the temperature range of (313.15 to 363.15) K. The columns were filled uniformly with the help of an ultrasound vibrator and finally heated under nitrogen for 8 h at the column temperature of 160 °C. Dry nitrogen was used as the carrier gas. The flow rate of carrier gas was determined using a calibrated soap bubble flowmeter which was placed at the outlet after the detector. The flow rate was set for a series of runs and was allowed to stabilize for at least 15 min before any γ_i^∞ determinations were made. The volume of the samples injected into the GC probes was about (0.05 to 0.5) μL , and the peaks were found to be symmetrical, independent of the carrier gas flow rate. The temperature of the GC column was maintained constant within ± 0.05 K. At a given temperature, each operation was repeated at least three times to check the reproducibility. The deviation of the retention time of the three measurements was within ± 0.05 min. The value of the dead time t_C was determined with methane as the nonretainable pure component under the assumption that the effect of the solubility of methane in the ILs was negligible. The measured dead time in the temperature range has a deviation of ± 0.01 min.

To check the stability of the experimental conditions, such as the possible elution of the stationary phase by the carrier gas stream, the measurements of retention time were repeated systematically every (6 to 8) h for hexane and benzene. No change of the retention time was observed during 80 h of continuous operation.

3. Theory

In (gas–liquid) chromatography, the activity coefficient at infinite dilution γ_i^∞ were obtained by the equation proposed by Cruickshank *et al.* [21] and Everett [22].

$$\ln \gamma_i^\infty = \ln \left(\frac{n_3 RT}{V_N p_i^0} \right) - \frac{B_{ii} - v_i p_i^0}{RT} + \frac{2B_{i2} - v_i^\infty}{RT} J_2^3 p_o, \quad (1)$$

where γ_i^∞ is the activity coefficient of solute *i* at infinite dilution in the stationary phase (3), p_i^0 is the vapor pressure of the pure liquid solute *i*, n_3 is the number of moles of the stationary phase component on the column, and V_N is the standardized retention volume obtained by equation (2),

$$V_N = (J_2^3)^{-1} U_0 (t_r - t_C) \frac{T_{col}}{T_f} \left[1 - \frac{p_w^0}{p_o} \right], \quad (2)$$

where t_r denotes the retention time, t_C the dead time, U_0 the flow rate of the carrier gas, T_{col} the column temperature, T_f the flowmeter temperature, p_w^0 the saturation vapor pressure of water at T_f , and p_o the pressure at the column outlet.

The second and third terms in equation (1) are correction terms arising from the nonideality of the mobile gaseous phase and the effect of pressure. B_{ii} is the second virial coefficient of the solute, B_{i2} is the cross second virial coefficient of the solute (*i*) with the carrier gas (2), v_i is the liquid molar volume of pure solute, and v_i^∞ is the partial molar volume of the solute in the stationary phase (3) at infinite dilution.

For all solutes, values of p_i^0 were calculated from the Antoine equation, with Antoine coefficients given by Boublik *et al.* [23]. Molar volumes of solutes v_i were estimated using their experimental densities [24]; partial molar volumes of solutes at infinite dilution v_i^∞ have been assumed to be equal to v_i . B_{ii} and B_{i2} have been estimated according to the equations suitable for nonpolar liquids by Tsonopolous's method [25] with an uncertainty of $< \pm 10 \text{ cm}^3 \cdot \text{mol}^{-1}$. The critical parameters and acentric factor ω needed for the calculations were available from the literature

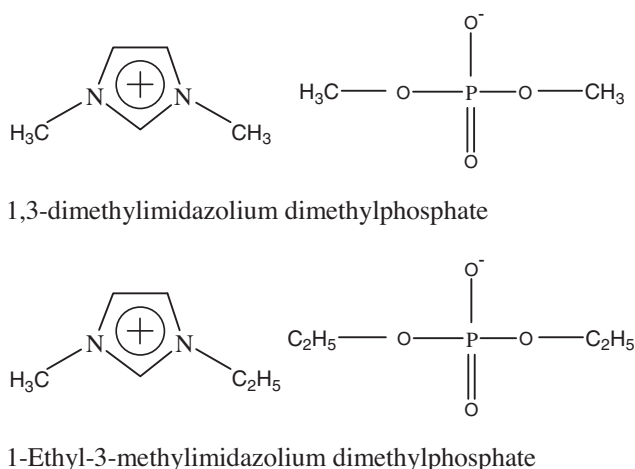


FIGURE 1. The chemical structures of 1,3-dimethylimidazolium dimethylphosphate and 1-ethyl-3-methylimidazolium dimethylphosphate.

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