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Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-butyl-3-methylimidazolium methyl sulfate

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ABSTRACT

Activity coefficients at infinite dilution (γ_i^∞) and (gas + liquid) partition coefficients (K_L) for organic solutes: alkanes, alkenes, alkyl benzenes, acetonitrile, acetone, tetrahydrofuran, ethyl acetate, and chloromethanes in the ionic liquid (IL) 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][CH_3SO_4]) have been measured by the (gas + liquid) chromatographic 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 free energies ($\overline{G}_i^{E,\infty}$) of organic solutes in [BMIM][CH_3SO_4] at a reference temperature $T_{ref} = 298.15$ K were also calculated from the γ_i^∞ values. The solubility parameters of the IL [BMIM][CH_3SO_4] were also determined by the regular solution theory (RST). The linear free energy relationship (LFER) analysis of the results was performed to disclose molecular interactions operating between the IL and the individual solutes.

1. Introduction

Ionic liquids (ILs) are useful in many chemical applications. They have been used as novel solvent systems for organic synthesis, separation processes, and electrochemistry [1–5]. For ILs to be used effectively as solvents, it is essential to know their interaction with different solutes. Activity coefficients at infinite dilution (γ_i^∞) and (gas + liquid) partition coefficients (K_L) give a quantitative measure of interactions between unlike molecules in the absence of (solute + solute) interactions, 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 [6–9]. 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.

This work continues our studies on the determination of γ_i^∞ of various solutes (i) in ILs by the (gas + liquid) chromatographic method (GLC) [10–13]. In this paper, γ_i^∞ have been measured for organic solutes: alkanes (hexane, heptane, octane, nonane, decane, cyclohexane, methylcyclohexane, and 2,2,4-trimethylpentane), alkenes (cyclohexene and styrene), alkyl benzenes (benzene, toluene, *o*-xylene, *m*-xylene, and *p*-xylene), acetonitrile, acetone, tetrahydrofuran, ethyl acetate, and chloromethanes in 1-butyl-3-methylimidazolium methyl sulfate ([BMIM][CH_3SO_4]) 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 free energies ($\overline{G}_i^{E,\infty}$) of organic solutes in [BMIM][CH_3SO_4] at a reference temperature $T_{ref} = 298.15$ K were also calculated from the γ_i^∞ values. The Hildebrand's solubility parameters of [BMIM][CH_3SO_4] were calculated as a function of temperature with the regular solution theory (RST).

Linear free energy relationship (LFER) salvation model of Abraham [14,15] was used to analyze the obtained experimental data, and the correlative and predictive model was demonstrated. The correlation parameters were analyzed to understand the interactions that affect K_L, and it is possible to provide valuable information for specific chemical applications.

The chemical structure of [BMIM][CH_3SO_4] is given in figure 1.

2. Experimental

2.1. Chemicals and materials

The IL [BMIM][CH_3SO_4] was supplied by Shanghai Chengjie Chemical Co., Ltd. and had a purity of >0.99 mass fraction

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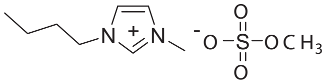

FIGURE 1. The chemical structure of [BMIM][CH_3SO_4].

according to manufacturer's specifications, with the following certified mass fraction of impurities: $w\,(Cl^-) < 5 \cdot 10^{-4}$, water $<10^{-3}$. Before use, the IL was subjected to vacuum evaporation at (323 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 shift for ^1H NMR spectrum (parts per million, D_2O) appear as follows: δ 8.596 [*s*, 1H, H(2)], 7.374 [*s*, 1H, H(4)], 7.325 [*s*, 1H, H(5)], 4.111 [*m*, 2H, NCH_2], 3.789 [*s*, 3H, NCH_3], 3.635 [*s*, 3H, OCH_3], 1.766 [*m*, 2H, NCH_2–CH_2], 1.227 [*m*, 2H, NCH_2CH_2–CH_2], 0.839 [*t*, 3H, CH_3]. 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 column preparation and the packing method used in this work have been described previously [12,13]. The GC column (stainless steel) with length of 1 m and an internal diameter of 2 mm was used. Chromosorb P-AW DMCS 80/100 mesh was used as the solid support and was supplied by SUPELCO. Coating the solid support with [BMIM][CH_3SO_4] was performed by dispersing a known mass amount of the Chromosorb in a solution of [BMIM][CH_3SO_4] 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 were 48 % mass percent of [BMIM][CH_3SO_4]. The mass of the stationary phase [BMIM][CH_3SO_4] was 0.3794 g with a precision of ±0.0001 g. The measurements for organic solutes were carried out in the temperature range of (313.15 to 363.15) K. The column was 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_G was determined with methane as the nonretainable pure component under the assumption that the effect of the solubility of methane in the IL 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

3.1. Activity coefficients at infinite dilution

In (gas + liquid) chromatography, the activity coefficient at infinite dilution γ_i^∞ were obtained by the equation proposed by Cruickshank et al. [16]. and Everett [17].

$$\ln \gamma_i^\infty = \ln\left(\frac{n_3RT}{V_N p_i^0}\right) - \frac{B_{ii}-v_i}{RT}p_i^0 + \frac{2B_{i2}-v_i^\infty}{RT}J_2^3 p_o, \qquad (1)$$

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),

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

where t_r denotes the retention time, t_G 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. [18]. Molar volumes of solutes v_i were estimated using their experimental densities [19]; 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 [20] with an uncertainty of $<\pm 10\ cm^3 \cdot mol^{-1}$. The critical parameters needed for the calculations were available from the literature [20]. The cross critical properties p_{cij}, T_{cij}, v_{cij}, Z_{cij}, and acentric factor ω_{ij} were calculated by using equations given in the literatures [20,21]. The vapor pressure of the solutes (*i*) at temperatures of (313.15 to 363.15) K, the critical constants *Tc*, *Pc*, *Zc*, *Vc*, and acentric factors ω of the solutes and the carrier gas used in calculation of the virial coefficients are presented in tables 2S to 3S in the Supplementary Materials.

The pressure correction term J_2^3 is given by [22]

$$J_2^3 = \frac{2}{3}\frac{(p_i/p_o)^3-1}{(p_i/p_o)^2-1}, \qquad (3)$$

where p_i and p_o are the inlet and outlet pressures of the GC column, respectively. The inlet column pressure p_i was determined by inner manometer. Outlet pressure p_o was kept equal to atmospheric pressure.

3.2. The regular solution theory and solubility parameters

The activity coefficients at infinite dilution of different solutes in a given solvent can be used to estimate solubility parameters of the solvents when the solubility parameters of these solutes are known. These provide a basis for the correlation of the activity coefficients at infinite dilution of solutes in ILs. The activity coefficient model can be represented by a two-term equation in which the combinatorial term can be represented by Kikic et al. [23] modification to Flory's equation, and the residual term is given by the regular solution theory: