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Activity coefficients at infinite dilution measurements for organic solutes in the ionic liquid *N*-butyl-4-methylpyridinium tosylate using GLC at $T = (328.15, 333.15, 338.15, \text{and } 343.15)\,\text{K}$

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ABSTRACT

Activity coefficients at infinite dilution for 19 solutes: alkanes, cycloalkanes, alk-1-enes, alk-1-ynes, benzene and alcohols in the ionic liquid *N*-butyl-4-methylpyridinium tosylate ([BMPy][TOS]) were determined by gas–liquid chromatography at four temperatures $T = (328.15, 333.15, 338.15, \text{and } 343.15)\,\text{K}$. The partial molar excess enthalpy values at infinite dilution $\Delta H_1^{\text{E},\infty}$ were calculated from the experimental gamma infinity values obtained over the temperature range. The selectivity for the hexane/benzene and cyclohexane/benzene separations was calculated from the gamma infinity values and compared to the literature values for other ionic liquids, NMP and sulfolane.

1. Introduction

Recent work has shown that some room-temperature ionic liquids (ILs) have the potential to be good solvents for separating organic liquids using solvent extraction or extractive distillation processes [1–7]. Some ILs have also been shown to have great potential as media for chemical reactions. One of the many appealing properties of ILs, that makes them so attractive in replacing many organic solvents currently used in industry, is their very low vapour pressure which eliminates volatilization and air pollution problems. It is however the thermodynamic information, which reflects how the different solutes interact with these solvents, that is crucial in assessing their usefulness and allows one to predict better and more efficient ILs.

This work is a continuation of our investigation into the solvent properties of ILs through the determination of activity coefficients at infinite dilution, γ_{13}^{∞}, using gas–liquid chromatography [6–14]. Our previous work includes measurements of γ_{13}^{∞} for organic solutes in the ILs: 1-ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]) [6], 1-ethyl-3-methyl trifluoroacetate (EMIM][TFA]) [7], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (HMIM][Tf_2N]) [8], 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)-ethyl sulfate ([BMIM][MDEGSO_4]) [9], and 1-hexyl-3-methylimidazolium tetrafluoroborate ([HMIM][BF_4]) [15]. In our work we have calculated the selectivities and capacities at infinite dilution for many different separation problems, directly from experimental γ_{13}^{∞} values. Our results are important in expanding the knowledge about the nature of ILs, in assisting in the systematic study of their physicochemical properties and in extending the applications of thermodynamic models such as UNIFAC [16].

Ionic liquids which have been shown to have potentially excellent entrainer properties for the separation of aliphatic from aromatic hydrocarbons by extractive distillation or extraction are 1-ethyl-3-methylimidazolium ethyl sulfate ([EMIM][EtSO_4]), ethyl (2-hydroxyethyl)dimethylammonium bis{(trifluomethyl)sulfonyl}imide ($\text{C}_2\text{Tf}_2\text{N}$), or [EMIM][SCN], or [BMIM][MDEGSO_4], or 4-methyl-*N*-butylpyridinium tetrafluoroborate ([BMPy][BF_4]), or *N*-methylpyridinium bis{(trifluomethyl)sulfonyl}imide [EPy][Nf_2T] [1–4,6,9,17–19]. Generally, the selectivity for the separation of aromatic hydrocarbons/aliphatic hydrocarbons decreases with increasing length of the alkyl chain on the imidazolium, or ammonium cation, or anion of the IL.

A short analysis of the presented results, showed that the IL composed of the [BMPy]$^+$ cation [2] and an aromatic based anion, such as the tosylate anion [TOS]$^-$ (increasing the solubility of benzene

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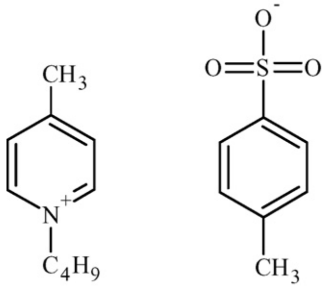
in the IL) can be an effective solvent for the separation of aromatic/aliphatic hydrocarbons [20]. This paper presents γ_{13}^{∞} values for 19 solutes (alkanes, cycloalkanes, alk-1-enes, alk-1-ynes, benzene and alcohols) in the ionic liquid *N*-butyl-4-methylpyridinium tosylate, [BMPy][TOS] at four temperatures T = (328.15, 333.15, 338.15, and 343.15) K.

2. Experimental

2.1. Materials or chemicals

The IL investigated here, *N*-butyl-4-methylpyridinium tosylate, [BMPy][TOS] was synthesized for us on request by io-li-tec, Germany, and was reported to have a purity of >98 mass percent. Unfortunately, this IL is solid up to the temperature 315.52 K. The structure of investigated ionic liquid is presented below.



The ionic liquid was purified by subjecting the liquid to a very low pressure of about 5×10^{-3} Pa at about 343 K for approximately 5 h. Next IL is during 5–8 h together with the Chromosorb at the chromatography column. We assume that this procedure removed any volatile chemicals and water from the ionic liquid and Chromosorb. We always check the weight of IL, Chromosorb and solvent before conditioning and after loading (without solvent). The same masses before and after loading confirm that that IL and Chromosorb are clean, without water and volatile chemicals. No other attempt was made to analyze impurities in the ionic liquid or Chromosorb. The solutes: pentane (Saarchem), hexane (Saarchem), heptane (Acros Organics), octane (Aldrich), cyclopentane (Fluka), cyclohexane (Aldrich), cycloheptane (Aldrich), hex-1-ene (Acros Organics), hept-1-ene (Acros Organics), oct-1-ene (Aldrich), hex-1-yne (Acros organics), hept-1-yne (Aldrich), oct-1-yne (Aldrich), benzene (Janssen Chimica), and methanol, ethanol, 1-propanol (Rochelle Chemicals) were used without further purification because the GLC technique separated any impurities.

2.2. Experimental procedure

The gas–liquid chromatography method is a well established and accurate method used to obtain the γ_{13}^{∞} values [21,22] and was used in this work. The GLC apparatus, the column preparation and the packing method used in this work have been described previously [10–15]. Stainless steel columns of length 1 m and 4.7 mm inner diameter were used together with Chromosorb WHP (80/100 mesh) as the solid support. The latter was supplied by SUPELCO, USA. A thermal conductivity detector was used and the carrier gas was dry helium. The carrier gas flow rate was determined using a calibrated soap bubble flow meter which was placed at the outlet of 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_{13}^{∞} determinations were made. The flow rates were corrected for water vapour pressure and ranged from 0.1 to 0.5 $\mu\text{m}^3\,\text{s}^{-1}$. The column temperature was controlled in a water bath using a Tronac Controller fitted with a low heat capacity intermittent heater. The solute was injected as a liquid in temperature of injector of 423 K. The detector temperature was also 423 K. The water bath was fitted with a vigorous stirrer to ensure a uniform temperature. A temperature control of better than 0.01 K was achieved. The surface of the water in the water bath was covered by polystyrene balls to reduce evaporation in the water bath. A glass-walled manometer (8 mm so as to reduce the capillary effect) was placed before the inlet of the column to determine the inlet column pressure. The outlet pressure was measured with a normal Fortin barometer. The solvent column packing for two columns was: 26.52 and 31.07 mass percent of IL, large enough to prevent any residual absorption onto the column packing. From previous experience the sample injections, ranged from 0.1 to 0.5 μl, were considered small enough to ensure the condition of infinite dilution of the solute on the column. The estimated overall error in γ_{13}^{∞} was less than 3%, taking into account the possible errors in determining the column loading, the retention times, and solute vapour pressure. The GLC technique was tested for the system hexane in hexadecane at 298.15 K and the results were within 2% of literature values [23,24].

3. Theoretical basis

The equation developed by Everett [24] and Cruickshank et al. [25] was used in this work to calculate the γ_{13}^{∞} of solutes in the ionic liquid:

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3RT}{V_\mathrm{N}P_1^*}\right) - \frac{P_1^*(B_{11}-V_1^*)}{RT} + \frac{P_\mathrm{o}J_2^3(2B_{12}-V_1^{\infty})}{RT} \quad (1)$$

V_N denotes the net retention volume of the solute, P_o the outlet pressure, $P_\mathrm{o}J_2^3$ the mean column pressure, n_3 the number of moles of solvent on the column packing, T the column temperature, P_1^* the saturated vapour pressure of the solute at temperature T, B_{11} the second virial coefficient of the pure solute, V_1^* the molar volume of the solute, V_1^{∞} the partial molar volume of the solute at infinite dilution in the solvent (assumed as the same as V_1^*) and B_{12} (where 2 refers to the carrier gas, helium), the cross second virial coefficient of the solute and the carrier gas. The values of B_{11} and B_{12} were calculated using the McGlashan and Potter equation [26]:

$$\frac{B}{V_\mathrm{c}} = 0.430 - 0.886\left(\frac{T_\mathrm{c}}{T}\right) - 0.694\left(\frac{T_\mathrm{c}}{T}\right)^2 - 0.0375(n-1)\left(\frac{T_\mathrm{c}}{T}\right)^{4.5} \quad (2)$$

where n refers to the number of carbon atoms of the solute. Using the Hudson and McCoubrey combining rules [27,28], V_{12}^c and T_{12}^c were calculated from the critical properties of the pure component.

The pressure correction term J_2^3 is given by:

$$J_2^3 = \frac{2}{3}\frac{(P_\mathrm{i}/P_\mathrm{o})^3-1}{(P_\mathrm{i}/P_\mathrm{o})^2-1} \quad (3)$$

The net retention volume of the solute V_N, is given by:

$$V_\mathrm{N} = J_2^3U_\mathrm{o}(t_\mathrm{R}-t_\mathrm{G}) \quad (4)$$

where t_R and t_G are the retention times for the solute and an unretained gas (air), respectively, U_o is the column outlet flow rate.

The vapour pressure values were calculated using the Antoine equation and constants taken from the literature [29,30]. Critical data and ionization energies used in the calculation of T_{12}^c, were obtained from literature [31,32]. The critical data used to calculate B_{11} and B_{12}, and ionization energies used in the calculation of T_{12}^c, are given in Table 1 and the values of P_1^*, V_1^*, B_{11} and B_{12} used in the calculation of γ_{13}^{∞} are given in Table 2. The effect caused by the cross virial coefficient and the fugacity coefficient in the vapour phase is 3–5%, thus it is better in our opinion to consider this correction.