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Activity coefficients at infinite dilution of organic solutes in the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate using gas–liquid chromatography at $T = (313.15, 323.15, \text{and } 333.15)$ K

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ABSTRACT

Activity coefficients at infinite dilution were determined for 24 solutes: *n*-alkanes, alk-1-enes, alk-1-ynes, cycloalkanes, alkylbenzenes and alcohols in the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate, [OMIM][PF_6], by gas–liquid chromatography at three different temperatures $T = (313.15, 323.15, \text{and } 333.15)$ K. The partial molar excess enthalpy values at infinite dilution were calculated from the experimental data over the same temperature range. Capacities and selectivities at infinite dilution for the systems hexane/benzene and methanol/benzene were determined from the experimental data and compared to the literature values for other ionic liquids, as well as for industrial molecular solvents. The influence of the cation and anion of the ionic liquid on the activity coefficient is discussed, as well as the usefulness of [OMIM][PF_6] in separating organic liquids.

1. Introduction

The importance of infinite dilution activity coefficients in the field of chemistry and chemical engineering have been highlighted by Sandler [1]. Their applications include the pre-screening of solvents to be used in separation processes such as extractive distillation and liquid–liquid extraction [2–4]. There are two well known techniques used to measure activity coefficients at infinite dilution for systems of the type discussed in this work: gas–liquid chromatography and the dilutor method. The GLC technique is the most common and is used in this work. As a continuation of our studies on the solvent properties of ionic liquids (see Refs. 7–19 in [5]), experimental measurements are reported here, of infinite dilution activity coefficients of selected organic solutes in 1-octyl-3-methylimidazolium hexafluorophosphate, [OMIM][PF_6], whose structure is given in figure 1. The temperature range was between 313.15 K and 333.15 K. In this work, we investigated the potential of [OMIM][PF_6] for separating organic liquids. This work was also aimed at providing data with the view of extending the application of thermodynamic models such as Group Contribution Methods [6,7] as well as contributing to the understanding of how structure influences ionic liquids selectivity and capacity in different separation problems.

2. Experimental

2.1. Materials

The ionic liquid, 1-octyl-3-methylimidazolium hexafluorophosphate (purchased from Capital Lab Supplies), with a stated mass fraction purity greater than 0.98 was subjected to a very low pressure of about $4 \cdot 10^{-3}$ Pa at $T = 343.15 \cdot$ K for 6 h to remove any traces of volatile impurities and moisture. The density of the ionic liquid was determined at $T = 298.15$ K and 101.3 kPa using an Anton Paar DMA 5000 densitometer. The uncertainty in the density measurement is ±0.4%. The experimental value of $1.23851\ \text{g} \cdot \text{cm}^{-3}$ is in excellent agreement with the literature value of $1.2357\ \text{g} \cdot \text{cm}^{-3}$ [8–10]. Solute samples (from DLD Scientific), with a stated mass fraction purity greater than 0.98 were used without further purification since the GLC technique separates the solutes from impurities. Celite (Chromosorb W HP 80/100 mesh) was used as the solid support and dry Helium was used as the carrier gas.

2.2. Procedure

The detailed experimental procedure can be found in previous works [11–13]. The column used in the experiments was constructed of stainless steel with a length of 1 m and an inside diameter of 4.1 mm. Two different loadings were used for each temperature. Before being packed the columns were washed with hot soapy water, rinsed with cold water and flushed with acetone

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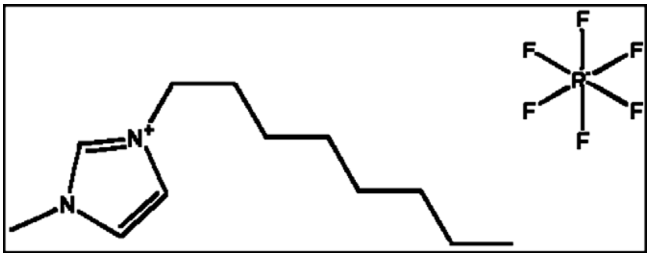

FIGURE 1. Structure of the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate.

to reduce the drying time. Dichloromethane was used as a solvent to aid the uniform coating of the ionic liquid onto the inert solid support and was removed afterwards by evaporation. The original and final masses of the ionic liquid and Chromosorb mixture before the addition and after the evaporation of dichloromethane were in agreement to within 0.005 g. The column packing contained 28.55 (6.69 mmol) and 33.26 (5.14 mmol) mass percent of ionic liquid, large enough to avoid residual adsorption effects. Experiments were performed on a Shimadzu GC-2014 gas chromatograph, equipped with a thermal conductivity detector, an auto-sampler and an auto-injector. The carrier gas flow rate was determined with the aid of a calibrated soap bubble flow meter placed at the outlet of the detector. The measured flow rates were corrected for water vapour pressure and varied from (0.6 to 0.75) $\mu m^3\ s^{-1}$. The carrier gas flow rate was allowed to stabilize for at least 15 min prior to any series of runs. The pressure drop across the column varied from (25 to 50) kPa, providing conducive retention times and sharp peaks. Solute injection volumes ranged between $(1.0 \text{ and } 3.0) \cdot 10^{-3}\ cm^3$ and were considered small enough to comply with the condition of infinite dilution of the solutes in the solvent packing. The injector and the detector temperatures were both set at 523.15 K. The equipment was able to achieve a temperature control of better than 0.01 K. The GLC technique and equipment were tested for systems of selected hydrocarbons in hexadecane as the stationary phase at various temperatures. The results were within 2.5% of literature values [14,15]. The overall errors in γ_{13}^{∞} and $\Delta H_1^{E,\infty}$ were estimated as 4% and 20% respectively. The error in γ_{13}^{∞} is made up of: the error in determining the number of moles of solvent on the GLC column (<2%); the possible error in measuring the retention time (<1%); the possible error in the vapour pressure (<0.5%) and the possible error in determining the mixed virial coefficient (<0.2%) (see equation (1) below).

3. Theoretical basis

The equation developed by Everett [16] and Cruickshank *et al.* [17], was used in this work to calculate γ_{13}^{∞} of solutes in the ionic liquid:

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3 RT}{V_N P_1^*}\right) - \frac{(B_{11} - V_1^*)P_1^*}{RT} + \frac{(2B_{12} - V_1^{\infty})J_2^3 P_o}{RT}, \tag{1}$$

where n_3 is the number of moles of the stationary phase, T the column temperature, V_N the net retention volume, P_o the outlet pressure which is equal to the atmospheric pressure, 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 (taken to be equal to V_1^*), B_{12} the cross second virial coefficient of the solute (1) and the carrier gas (2) and $J_2^3 P_o$ the mean column pressure. B_{11} and B_{12} were determined using the equation of McGlashan and Potter [18]:

$$B/V^C = 0.43 - 0.886(T^C/T) - 0.694(T^C/T)^2 - 0.0375(n-1)(T^C/T)^{4.5}, \tag{2}$$

where n refers to the number of carbon atoms of the solute. The combining rules of Hudson and McCoubrey [19,20] were used to calculate the values of V_{12}^c and T_{12}^c from the critical properties of the pure components. The net retention volume of the solute V_N, is given by:

$$V_N = J_2^3 U_o (t_R - t_G), \tag{3}$$

where t_R is the retention time for the solute and t_G the unretained gas (air) retention time. The U_o denotes the inert gas flow rate at the column outlet. The pressure correction term J_2^3 is given by:

$$J_2^3 = \frac{2}{3}\frac{(P_i/P_o)^3 - 1}{(P_i/P_o) - 1}. \tag{4}$$

Saturated vapour pressures were calculated using the Antoine, modified Antoine or Wagner equations in compliance with the applicability range of each correlation. Constants for the vapour pressure correlations were found in the literature [21]. The values of P_1^*, V_1^*, B_{11}, B_{12} involved in the calculation of γ_{13}^{∞} are listed in table 1 of Ref. [5]. Critical data, obtained from the literature [22], to calculate B_{11} and B_{12} and ionization energies used in the calculation of T_{12}^c are given in table 2 of reference [5].

4. Results and discussion

Experimental γ_{13}^{∞} results for two different loadings of the solvent on the column packing, 28.55% (6.69 mmol) and 33.26% (5.14 mmol), are presented in tables 1 and 2, respectively. Table 3 lists the average γ_{13}^{∞} values over the temperature range from 313.15 K to 333.15 K. As expected from previous results [5], the values of γ_{13}^{∞} for each series of organic solutes (alkanes, alkenes, alkynes, cycloalkanes, alkanols and aromatic compounds) increase with increasing solute alkyl chain. This appears to be true for most ionic solvents, with the exception of phosphonium compounds [5]. The larger the value of the γ_{13}^{∞}, the weaker is the interaction

TABLE 1
Activity coefficients at infinite dilution γ_{13}^{∞} of organic solutes in 1-methyl-3-octylimidazolium hexafluorophosphate with n_3 = 6.69 mmol (28.55%) at T = (313.15, 333.15, 353.15, and 363.15) K.

Solute	n_3 (mmol)	Experimental γ^{∞} at T/K		
		313.15	323.15	333.15
n-Pentane	6.69	8.2	8.1	7.8
n-Hexane	6.69	10.8	10.6	10.2
n-Heptane	6.69	14.1	13.8	13.2
n-Octane	6.69	18.3	17.9	17.0
n-Decane	6.69	31.8	30.3	28.2
n-Undecane	6.69	42.1	39.6	36.5
Hex-1-ene	6.69	6.2	6.15	6.1
Hept-1-ene	6.69	8.2	8.2	8.0
Oct-1-ene	6.69	10.8	10.7	10.4
Non-1-ene	6.69	14.2	13.9	13.5
Dec-1-ene	6.69	16.3	16.5	16.3
Pent-1-yne	6.69	1.70	1.75	1.78
Hex-1-yne	6.69	2.24	2.30	2.34
Hept-1-yne	6.69	2.81	2.87	2.93
Oct-1-yne	6.69	3.77	3.87	3.94
Cyclopentane	6.69	5.02	4.92	4.77
Cyclohexane	6.69	6.7	6.56	6.29
Cycloheptane	6.69	8.2	7.97	7.63
Cyclooctane	6.69	10.2	9.9	9.4
Methanol	6.69	1.77	1.61	1.46
Ethanol	6.69	2.22	2.00	1.79
Benzene	6.69	0.96	0.99	1.00
Toluene	6.69	1.31	1.35	1.37
Ethylbenzene	6.69	1.95	1.98	1.99