Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid 1-Butyl-3-methylimidazolium Octyl Sulfate Using Gas−Liquid Chromatography at a Temperature of 298.15 K, 313.15 K, or 328.15 K

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The activity coefficients at infinite dilution, γ_{13}^{∞}, for hydrocarbons and methanol solutes in the ionic liquid 1-butyl-3-methylimidazolium octyl sulfate, [BMIM][$OcOSO_3$], have been determined by gas−liquid chromatography at temperatures of 298.15 K, 313.15 K, and 328.15 K. This work is part of our research focus on activity coefficients at infinite dilution, γ_{13}^{∞}, in ionic liquids. The selectivity values have been calculated at $T = 298.15$ K, and the results indicate that the ionic liquid [BMIM][$OcOSO_3$] should not be considered to be a solvent for the separation of alkanes and aromatics. The partial molar excess enthalpy values at infinite dilution $\Delta H_1^{E\infty}$ have also been determined at temperature 298.15 K and have been discussed in terms of intermolecular interactions and packing effects. The results have been discussed in terms of measurements of γ_{13}^{∞} for other ionic liquids taken from the recent literature.

Introduction

This work is a continuation of our investigations on activity coefficients at infinite dilution, γ_{13}^{∞}, of ionic liquids.[1−5] Room-temperature ionic liquids have shown great potential as media for reactions and separations. They may be considered to be possible replacement solvents in the extractive distillation of hydrocarbon mixtures. Ionic liquids have the added advantage of extremely low vapor pressures and high boiling points, which allow for recycling.[6] Activity coefficients at infinite dilution of alkanes, alk-1-enes, and alkylbenzenes in 4-methyl-*N*-butylpyridinium tetrafluoroborate,[7] of polar solutes (alcohols, acetone, acetonitrile, ethyl acetate, alkyl ethers, and chloromethanes) in 4-methyl-*N*-butylpyridinium tetrafluoroborate,[8] and of hydrocarbons and polar solutes in 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide or 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethylsulfonyl) imide[9] were measured using gas−liquid chromatography. Activity coefficients at infinite dilution for 20 solutes (alkanes, alk-1-enes, cyclic hydrocarbons, aromatic hydrocarbons, ketones, alcohols, and water) in the ionic liquids 1-methyl-3-methyl-imidazolium bis(trifluoromethyl-sulfonyl) imide, 1-butyl-3-methyl-imidazolium bis(trifluoromethyl-sulfonyl) imide, and 1-ethyl-3-methyl-imidazolium ethyl sulfate were measured using the dilutor technique.[10] Also, the prediction of the activity coefficients at infinite dilution for 38 organic solutes using the quantitative structure−property relationship (QSPR) method in three ionic liquids was recently presented.[11] The interaction of the solutes and ionic liquids was discussed.

In our work, presented in this paper, activity coefficients at infinite dilution, γ_{13}^{∞}, have been determined for *n*-alkanes, alk-1-enes, alk-1-ynes, cycloalkanes, benzene, toluene, carbon tetrachloride, and methanol in the ionic liquid 1-butyl-3-methyl-imidazolium octyl sulfate, [BMIM]-[$OcOSO_3$], using gas−liquid chromatography at three temperatures 298.15 K, 313.15 K, and 328.15 K.

The selectivity value,[12] S^{∞}, of *n*-hexane with respect to benzene was calculated and used to determine the potential of the ionic solvent for extractive distillation in the separation of aliphatic compounds from aromatic hydrocarbon compounds. The partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E\infty}$, were also calculated from the γ_{13}^{∞} values obtained at the two temperatures. These values give some indication of the nature of the interaction between the hydrocarbons and the ionic liquid. The activity coefficients and selectivity values determined in this work have been discussed in terms of recent results, using other ionic liquids, taken from the literature.

Experimental Section

Chemicals. The solvent [BMIM][$OcOSO_3$], ECOENG 418, was supplied by Solvent Innovation and was reported to have a purity of >98 mass %. The ionic liquid was further purified by subjecting the liquid to a very low vapor pressure of about 5×10^{-3} Pa for approximately 30 h, resulting in a loss of material equivalent to 0.02 mass fraction. This process resulted in the sample foaming for a few seconds. This we believe was water boiling off because the water concentration in the resultant ionic liquid sample was found to be lower than 0.01 mass % from a Karl

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Table 1. Critical Constants V_c and T_c[a] and Ionization Energies I[b] of the Solutes and the Carrier Gas Used in the Calculation of the Virial Coefficients

	V_c	T_c	I		V_c	T_c	I		V_c	T_c	I
solute	$cm^3 \cdot mol^{-1}$	K	$kJ \cdot mol^{-1}$	solute	$cm^3 \cdot mol^{-1}$	K	$kJ \cdot mol^{-1}$	solute	$cm^3 \cdot mol^{-1}$	K	$kJ \cdot mol^{-1}$
n-pentane	304	496.6	998.6	hex-1-yne	332	516.2	960.0	benzene	256	562.1	892.1
n-hexane	370	507.6	977.4	hept-1-yne	387	547.2	960.0	toluene	316	591.7	851.8
n-heptane	425	540.6	957.1	oct-1-yne	442	574.2	951.3	carbon tetrachloride	276	556.4	1106.7
n-octane	492	568.7	947.4	cyclopentane	260	511.6	1014.1	methanol	118	512.6	1046.9
hex-1-ene	354	504.0	910.8	cyclohexane	309	553.6	951.3	helium	57	5.25	2374.0
oct-1-ene	464	566.7	909.9	cycloheptane	353	604.2	962.0				

[a] Obtained from refs 22 and 23. [b] Obtained from ref 22.

Fischer titration. No attempt was made to analyze any other impurities in the ionic liquid. The solutes *n*-pentane (Saarchem), *n*-hexane (Saarchem), *n*-heptane (Acros Organics), *n*-octane (Aldrich), hex-1-ene (Acros Organics), oc-1-ene (Aldrich), hex-1-yne (Acros Organics), hept-1-yne (Aldrich), oct-1-yne (Aldrich), cyclopentane (Fluka), cyclohexane (Aldrich), cycloheptane (Aldrich), benzene (Janssen Chimica), toluene (Janssen Chimica), carbon tetrachloride (Janssen Chimica), and methanol (Rochelle Chemicals) were used without further purification because the GLC technique separated any impurities.

Experimental Procedure. The gas−liquid chromatography method is a well-established and accurate method used to obtain γ_{13}^{∞} values[13,14] and was used in this work. The GLC apparatus, the column preparation, and the packing method used in this work have been described previously.[15,16] Stainless steel columns of 0.5 m length and 4.7 mm diameter were used together with Chromosorb WHP (80/100 mesh) as the solid support. The latter was supplied by SUPELCO. 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 flowmeter that 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 vapor pressure and ranged from 0.1 to 0.5 $\mu m^3 \cdot s^{-1}$. The column temperature was controlled in a water bath using a Tronac controller fitted with a low heat capacity intermittent heater. The water bath was fitted with a vigorous stirrer to ensure a uniform temperature. 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 (i.e., 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 varied from (25 to 30) mass % of [BMIM]-[OcOSO$_3$], which is large enough to prevent any residual absorption onto the column packing. Sample injections ranged from (0.1 to 0.5 μL) and were considered small enough to ensure the condition of infinite dilution of the solute on the column. The estimated overall error was less than 3%, taking into account the possible errors in determining the column loading, the retention times, and solute vapor pressure. For example, for methanol the results of γ_{13}^{∞} were 0.382 for the solvent column packing, 25 mass % of the ionic liquid or 0.378 for 25% or 0.398 for 30% (T = 298.5 K) and 0.364 for 25% or 0.365 for 25% or 0.379 for 30% (T = 313.15 K) and 0.354 for 25% or 0.357 for 25% or 0.369 for 30% (T = 328.15 K). The GLC technique was tested for the system hexane in hexadecane at 298.15 K, and the results were within 2% of literature values.[12]

Theory

The equation developed by Everett[17] and Cruickshank[18]

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

was used in this work to calculate the γ_{12}^{∞} values of solutes in an involatile solvent [BMIM][OcOSO$_3$] from gas−liquid chromatography. In this work, subscript 1 refers to a solute, 2 refers to the carrier gas, and 3 refers to the solvent [BMIM][OcOSO$_3$]. V_N denotes the net retention volume of the solute, P_o is the outlet pressure, $P_o J_2^3$ is the mean column pressure, n_3 is the number of moles of solvent on the column packing, T is the column temperature, P_1^* is the saturated vapor pressure of the solute at temperature T, B_{11} is the second virial coefficient of the pure solute, V_1^* is the molar volume of the solute, V_1^{∞} is the partial molar volume of the solute at infinite dilution in the solvent, and B_{12} is the mixed 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[19] equation

$$\frac{B}{V_c} = 0.430 - 0886\left(\frac{T_c}{T}\right) 0.694\left(\frac{T_c}{T}\right)^2 - 0.0375(n-1)\left(\frac{T_c}{T}\right)^{4.5} \quad (2)$$

where n refers to the number of carbon atoms. Using the Lorentz[14] and Hudson and McCoubrey[20,21] combining rules, V_{12}^c and T_{12}^c were calculated from the critical properties of the pure component. The critical data[22,23] used to calculate B_{11} and B_{12} and ionization energies[22] 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 vapor phase is 3% to 5%, thus it is better in our opinion to consider this correction.

Results and Discussion

Table 3 lists the γ_{13}^{∞} values at T = 298.15 K, 313.15 K, and 328.15 K for the different moles of solvent on the column packing. The results were determined for different columns each operated by two different researchers. There is always some doubt concerning the determination of activity coefficients of methanol using GLC because of the possibility of adsorption onto the solid support. However, in this work the methanol peaks were found to be symmetrical, and the activity coefficients at infinite dilution were independent of the carrier gas flow rate, indicating no significant absorption. This is, no doubt, due to the high

Table 2. Vapor Pressure, P_1^*, Molar Volume, V_1^*, and Virial Coefficients B_{11} and B_{12} used in the Calculation of γ_{13}^∞ at Temperatures of T = (298.15, 313.15, and 328.15) K

T/K	P_1^*/kPa	V_1^*/cm^3·mol^{-1}	B_{11}/cm^3·mol^{-1}	B_{12}/cm^3·mol^{-1}	T/K	P_1^*/kPa	V_1^*/cm^3·mol^{-1}	B_{11}/cm^3·mol^{-1}	B_{12}/cm^3·mol^{-1}
		n-Pentane					Oct-1-yne		
298.15	68.35	116.10	−1356.14	45.69	298.15	1.72	148.53	−3916.89	59.48
313.15	115.66	118.98	−1190.15	46.61	313.15	3.86	155.06	−3335.38	60.59
328.15	185.26	121.82	−1054.28	47.45	328.15	7.92	160.97	−2873.23	61.60
		n-Hexane					Cyclopentane		
298.15	20.19	131.60	−1903.78	52.91	298.15	42.59	94.71	−1257.65	40.33
313.15	37.28	134.40	−1656.73	53.90	313.15	74.37	96.69	−1101.26	41.23
328.15	64.46	137.19	−1456.40	54.80	328.15	122.56	98.65	−973.61	42.04
		n-Heptane					Cyclohexane		
298.15	6.09	147.46	−2861.43	58.31	298.15	13.01	108.74	−2053.20	45.37
313.15	12.33	150.31	−2462.22	59.38	313.15	24.63	110.70	−1773.73	46.35
328.15	23.09	153.15	−2142.11	60.34	328.15	43.52	112.65	−1548.89	47.23
		n-Octane					Cycloheptane		
298.15	1.86	163.53	−687.24	75.94	298.15	2.89	121.25	−3394.92	49.23
313.15	4.14	166.44	−645.12	76.24	313.15	6.08	126.26	−2892.56	50.31
328.15	8.42	169.34	−606.64	76.52	328.15	11.79	131.27	−2493.23	51.28
		Hex-1-ene					Benzene		
298.15	24.80	125.89	−1784.67	51.53	298.15	13.06	89.40	−329.69	48.29
313.15	45.06	128.68	−1553.97	52.48	313.15	25.00	91.08	−310.38	48.52
328.15	76.82	131.45	−1366.77	53.35	328.15	44.61	92.76	−292.64	48.75
		Oct-1-ene					Toluene		
298.15	2.32	157.85	−642.57	72.92	298.15	3.80	106.85	−2837.20	45.97
313.15	5.05	160.71	−603.21	73.20	313.15	7.89	108.56	−2421.89	46.97
328.15	10.07	163.54	−567.24	73.48	328.15	15.15	110.28	−2091.24	47.87
		Hex-1-yne					Carbon Tetrachloride		
298.15	17.71	115.59	−1793.15	48.61	298.15	15.15	96.50	−1004.74	41.00
313.15	33.31	118.06	−1558.31	49.57	313.15	28.38	98.02	−920.50	41.98
328.15	58.50	120.52	−1368.18	50.44	328.15	49.70	99.34	−846.63	42.86
		Hept-1-yne					Methanol		
298.15	5.56	132.04	−2705.99	54.05	298.15	16.94	40.74	−371.07	23.28
313.15	11.38	135.92	−2325.99	55.10	313.15	35.43	41.49	−339.83	23.95
328.15	21.51	139.58	−2021.59	56.04	328.15	68.75	42.24	−312.40	24.56

Table 3. Experimental Activity Coefficients at Infinite Dilution γ_{13}^∞ for the Solutes *n*-Pentane, *n*-Hexane, *n*-Heptane, *n*-Octane, Hex-1-ene, Oct-1-ene, Hex-1-yne, Hept-1-yne, Octy-1-yne, Cyclopentane, Cyclohexane, Cycloheptane, Benzene, Toluene, Carbon Tetrachloride, or Methanol in the Ionic Liquid [BMIM][OcOSO$_3$] at Temperatures of 298.15 K, 313.15 K, and 328.15 K

solute	T = 298.15 K	T = 313.15 K	T = 328.15 K	solute	T = 298.15 K	T = 313.15 K	T = 328.15 K
n-pentane	6.63	7.14		oct-1-yne	3.25	3.42	3.65
n-hexane	7.21	7.59	7.98	cyclopentane	4.09	4.24	4.39
n-heptane	8.27	8.58	9.00	cyclohexane	4.92	5.02	5.17
n-octane	9.63	9.96	10.33	cycloheptane	5.43	5.52	5.68
hex-1-ene	5.43	5.76	6.13	benzene	1.42	1.44	1.45
oct-1-ene	7.38	7.53	7.88	toluene	1.98	2.02	2.08
hex-1-yne	2.25	2.39	2.56	carbon tetrachloride	1.65	1.74	1.85
hept-1-yne	2.66	2.85	3.08	methanol	0.386	0.369	0.360

column packing that masks the solid support from the polar solute.[18] The γ_{13}^∞ values obtained for methanol, benzene, toluene, carbon tetrachloride, and the alkynes are lower than the values for the alkanes, alkenes, and cycloalkanes. The former group is reasonably associated with the ionic liquid because they are polar solutes or have delocalized electrons. In the case of methanol, the lone pair of electrons on the oxygen atom could interact with the ionic liquid cation, and the acidic proton of methanol is no doubt strongly attracted to oxygen atoms in the anion. The benzene molecule, being an aromatic compound, has delocalized π electrons that can associate with the ionic liquid by ($n-\pi$) iteration, which is stronger than the van der Waals interactions. Anyway, these are weaker than the methanol−ionic liquid interactions. For most of the solutes in this work, γ_{13}^∞ values change little with temperature (Table 3), and the values of γ_{13}^∞ increase with an increase of temperature.

The estimated error in γ_{13}^∞ is on the order of (3 to 4)% as a result of the limitations on determining the carrier gas flow rate, the solute retention time, and the amount of solvent on the column.[20]

The chemical nature of the groups that make up an ionic liquid plays an important role in determining the magnitude of the activity coefficient of the solute dissolved in an ionic liquid. The selectivity, S_{ij}^∞, values are given in Table 4 together with the literature values for solvents that are used in industry for the separation of aromatic and aliphatic compounds. This property has been calculated from the ratio of activity coefficients at infinite dilution and is given by the equation $S_{ij}^\infty = \gamma_{i3}^\infty/\gamma_{j3}^\infty$, where i refers to hexane and j refers to benzene. The selectivity $S_{ij}^\infty = 5.1$ for [BMIM][OcOSO$_3$] at T = 298.15 K is not very large compared to the value for sulfolane (30.5) or other ionic liquids (e.g., [EMIM][EtOSO$_3$], 41.4). This result highlights the important role of choosing the proper ionic liquid when

Table 4. Selectivities Values S_{ij}^{∞} at Infinite Dilution of Various Solvents for the Hexane/Benzene Separation $S_{ij}^{\infty} = \gamma_{i3}^{\infty}/\gamma_{j3}^{\infty}$ as Defined by Tiegs[13] at 298.15 K

solvent	S^{∞}	ref	solvent	S^{∞}	ref	solvent	S^{∞}	ref
sulfolane	30.5	13	dichloroacetic acid	6.1	13	[EMIM][EtOSO$_3$]	41.4[a]	10
dimethyl sulfoxide	22.7	13	aniline	11.2	13	[EMIM][(CF$_3$SO$_2$)$_2$N]	24.4[b]	10
diethylene glycol	15.4	13	[HMIM][PF$_6$]	21.6	1	[BMIM][(CF$_3$SO$_2$)$_2$N]	16.7[b]	10
N-methyl-2-pyrrolidinone	12.5	13	[HMIM][BF$_4$]	23.1	2	[BMIM][MDEGSO$_4$]	39.7	5
acetonitrile	9.4	13	[OMIM][Cl]	8.7	3	[BMIM][OcOSO$_3$]	5.1	this work

[a] Extrapolated value. [b] Interpolated value.

Table 5. Partial Molar Excess Enthalpy at Infinite Dilution, $\Delta H_1^{E\infty}$ Values Calculated from the Gibbs−Helmholtz Equation for Solutes in the Ionic Liquid [BMIM][OcOSO$_3$][a] and [BMIM][MDEGSO$_4$][b]

solute	$\Delta H_1^{E\infty}$ a / J·mol^{-1}	$\Delta H_1^{E\infty}$ b / J·mol^{-1}	solute	$\Delta H_1^{E\infty}$ a / J·mol^{-1}	$\Delta H_1^{E\infty}$ b / J·mol^{-1}	solute	$\Delta H_1^{E\infty}$ a / J·mol^{-1}	$\Delta H_1^{E\infty}$ b / J·mol^{-1}
n-pentane		8989	hex-1-yne	−3500	−1334	cycloheptane	−1240	10 598
n-hexane	−2770	9917	hept-1-yne	−3970	−516	benzene	−630	375
n-heptane	−2290	12 293	oct-1-yne	−3170	329	toluene	−1250	1244
n-octane	−1890	13 972	cyclopentane	−1880	7787	carbon tetrachloride	−3210	−2671
hex-1-ene	−3270	8400	cyclohexane	−1330	9709	methanol	1890	1906
oct-1-ene	−1790	8349						

[a] This work. [b] Reference 5.

planning the separation of organic liquids or aromatic and aliphatic compounds, in particular, by an extractive distillation process. The smaller selectivity value indicates that the ionic liquid [BMIM][OcOSO$_3$] is not the best solvent to use in solvent extraction processes when separating aromatic compounds from aliphatic compounds. This result shows the influence of the cation's alkyl chain length (butyl vs ethyl) and the anion's alkyl chain length (octyl vs ethyl). The huge decrease in magnitude of γ_{13}^{∞} in *n*-hexane is observed with the increase of the alkyl chain length on the cation and anion. The values of γ_{13}^{∞} are 92.6 and 7.59 (at 313.15 K) for [EMIM][EtOSO$_3$][10] and [BMIM][OcOSO$_3$], respectively. For benzene, this difference is not very large: the values of γ_{13}^{∞} are 2.76 and 1.44 (at 313.15 K) for [EMIM][EtOSO$_3$][10] and [BMIM][OcOSO$_3$], respectively. The selectivity, S_{ij}^{∞}, value strongly depends on the interaction or packing to packing effects of *n*-alkanes in ionic liquids. By lengthening the alkyl chain on the cation from methyl to butyl and on the anion from ethyl to octyl (unfortunately these two effects are inseparable), a noticeable increase in the interaction with *n*-alkanes is observed (better packing effects with *n*-alkanes) and a huge decrease in selectivity are noted. For polar solutes where hydrogen bonding may occur, for example, in methanol, the differences between these two ionic liquids are not significant.

For the same cation ([BMIM]) and three different anions ([(CF$_3$SO$_2$)$_2$N] vs [MDEGSO$_4$] and [OcOSO$_3$]; Table 4), the differences in selectivity are also large.

Moreover, the ionic liquid with the largest alkyl group attached to the anion has the smallest activity coefficients for *n*-hexane of all of the results presented here and in the literature.

Table 5 lists the partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E\infty}$, that were calculated from the Gibbs−Helmholtz equation,

$$\left[\frac{\partial \ln \gamma_i^{\infty}}{\partial(1/T)}\right] = \frac{\Delta H_1^{E\infty}}{R} \tag{3}$$

The uncertainties in the average value of ln γ_i^{∞} for two different temperatures are 7% to 10%. The $\Delta H_1^{E\infty}$ values are negative for every solute except methanol. Very large negative values were observed for alkynes, hex-1-ene, and carbon tetrachloride (<-3000 J·mol^{-1}). The small negative value obtained for the benzene molecule (-630 J·mol^{-1}) indicates that there is some interaction between the benzene molecule and the ionic liquid but it is of different character than that between alkynes and an ionic liquid. This is the result of the polarizability of the benzene molecule. The $\Delta H_1^{E\infty}$ value for methanol is positive (1890 J·mol^{-1}) and can be thought as a sum of the destabilizing effect of the methanol molecule on the ionic liquid surrounding the molecule of methanol at infinite dilution and due to the dissociative or even repulsive interaction between the methanol molecule and the ionic liquid. In the *n*-alkane and cycloalkane series, the $\Delta H_1^{E\infty}$ values increase with increasing carbon number. The most important quantity is the difference in the $\Delta H_1^{E\infty}$ values in *n*-alkanes and benzene for different ionic liquids. Table 5 also lists the data obtained by us recently for [BMIM][MDEGSO$_4$], and very large differences may be noted for two salts with the same cation, [BMIM], and different anions, [MDEGSO$_4$] and [OcOSO$_3$]. The $\Delta H_1^{E\infty}$ values for *n*-hexane are -2770 J·mol^{-1} (this work) and 9917 J·mol^{-1}, and for benzene, they are -630 J·mol^{-1} (this work) and 375 J·mol^{-1} for [BMIM][OcOSO$_3$] and [BMIM][MDEGSO$_4$],[5] respectively. The other published values for *n*-hexane are 4400 J·mol^{-1}, 3900 J·mol^{-1}, and 4037 J·mol^{-1}, and for benzene, they are -380 J·mol^{-1}, 5100 J·mol^{-1}, and -228 J·mol^{-1} for 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imide,[4] 1-octyl-3-methyl-imidazolium chloride,[3] and 4-methyl-*N*-butylpiridinium tetrafluoroborate,[7] respectively. These results show that for most tested ionic liquids high positive values of $\Delta H_1^{E\infty}$ were observed for *n*-hexane and small negative values were observed for benzene.

The results of γ_{13}^{∞} and $\Delta H_1^{E\infty}$ obtained in this work suggest not only that the interaction between the solute and ionic liquid as hydrogen bonding, ion-induced dipole interaction ($n - \pi$) or ($\pi - \pi$) interactions but also that the "free volume" and the interstitial effects in the solute and ionic liquid species might be expected to play a major role in determining γ_{13}^{∞} and $\Delta H_1^{E\infty}$ values. These effects strongly depend on the alkyl chain in the anion.

Literature Cited

(1) Letcher, T. M.; Soko, B.; Ramjugernath, D.; Naicker, P. Activity Coefficients at Infinite Dilution of Organic Solutes in 1-Hexyl-3-methyl-imidazolium Hexafluorophosphate from Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2003**, *48*, 708−711.

(2) Letcher, T. M.; Soko, B.; Reedy, P.; Deenadayalu, N. Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid 1-Hexyl-3-methyl-imidazolium Tetrafluoroborate from Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2003**, *48*, 1587−1590.

(3) David, W.; Letcher, T. M.; Ramjugernath, D.; Raal, J. D. Activity Coefficients of Hydrocarbon Solutes at Infinite Dilution in the Ionic Liquid, 1-Methyl-3-octyl-imidazolium Chloride from Gas−Liquid Chromatography. *J. Chem. Thermodyn*. **2003**, *35*, 1335−1341.

(4) Deenadayalu, N. J.; Letcher, T. M.; Reddy, P. Determination of Activity Coefficients at Infinite Dilution of Polar and Nonpolar Solutes in the Ionic Liquid 1-Ethyl-3-methyl-imidazolium Bis-(trifluoromethylsulfonyl) Imidate Using Gas−Liquid Chromatography at the Temperature 303.15 K or 318.15 K. *J. Chem. Eng. Data* **2005**, *50*, 105−108.

(5) Letcher, T. M.; Domańska, U.; Marciniak, M.; Marciniak, A. Activity Coefficients at Infinite Dilution Measurements for Organic Solutes in the Ionic Liquid 1-Butyl-3-methyl-imidazolium 2-(2-Methoxyethoxy) Ethyl Sulfate using GLC at T = (298.15, 203.15 and 308.15) K. *J. Chem. Thermodyn*., in press, 2005.

(6) Seddon, K. R. Room-Temperature Ionic Liquids: Neoteric Solvents for Clean Catalysis. *Kinet. Catal.* **1996**, *37*, 743−748.

(7) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids.1. Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkylbenzenes in 4-Methyl-*N*-butyl-pyridinium Tetrafluoroborate Using Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2001**, *46*, 1526−1529.

(8) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids. Activity Coefficients at Infinite Dilution of Polar Solutes in 4-Methyl-*N*-butyl-pyridinium Tetrafluoroborate Using Gas−Liquid Chromatography. *J. Chem. Thermodyn.* **2002**, *38*, 1341−1347.

(9) Heintz, A.; Kulikov, D. V.; Verevkin, S. P. Thermodynamic Properties of Mixtures Containing Ionic Liquids. 2. Activity Coefficients at Infinite Dilution of Hydrocarbons and Polar Solutes in 1-Methyl-3-ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) Amide and in 1,2-Dimethyl-3-ethylim-idazolium Bis(trifluoromethylsulfonyl) Amide Using Gas−Liquid Chromatography. *J. Chem. Eng. Data* **2002**, *47*, 894−899.

(10) Krummen, M.; Wasserscheid, J.; Gmehling, J. Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique. *J. Chem. Eng. Data* **2002**, *47*, 1411−1417.

(11) Eike, D. M.; Brennecke, J. F.; Maginn, E. J. Predicting Infinite-Dilution Activity Coefficients of Organic Solutes in Ionic Liquids. *Ind. Eng. Chem. Res.* **2004**, *43*, 1039−1048.

(12) Tiegs, D.; Gmehling, J.; Medina, A.; Soares, M.; Bastos, J.; Alessi, P.; Kikic, I. *Activity Coefficients at Infinte Dilution*; Chemistry Data Series; Dechema: Frankfurt/Main, 1986; Vol. 9, Part 1.

(13) Bayles, J. W.; Letcher, T. M.; Moollan, W. C. The Determination of Activity Coefficients at Infinite Dilution Using GLC with Moderately Volatile Solvents. *J. Chem. Thermodyn*. **1993**, *25*, 781−786.

(14) Young, C. L.; Conder, J. R. *Physicochemical Measurements by Gas Chromatography*; Wiley: New York, 1979.

(15) Letcher, T. M.; Moollan, W. C. The Determination of Activity Coefficients of Hydrocarbons at Infinite Dilution using a GLC Technique. *J. Chem. Thermodyn*. **1995**, *27*, 867−872.

(16) Moollan, W. C. M.Sc. Thesis, University of Natal, Durban, 1993.

(17) Everett, D. H. Effects of Gas Imperfections on GLC Measurements. *Trans. Faraday Soc*. **1965**, *61*, 1637−1645.

(18) Cruickshank, A. J. B.; Gainey, B. W.; Hicks, C. P.; Letcher, T. M.; Moody, R. W.; Young, C. L. Gas−liquid Chromatographic Determination of Cross-term Second Virial Coefficients Using Glycerol. *Trans. Faraday Soc*. **1969**, *65*, 1014−1031.

(19) McGlashan, M. L.; Potter, D. J. B. An Apparatus for the Measurements of the Second Virial Coefficient Using Glycerol. *Proc. R. Soc. London* **1951**, *267*, 448−456.

(20) Hudson, G. H.; McCoubrey, J. C. Intermolecular Forces Between Unlike Molecules. *Trans. Faraday Soc*. **1960**, *56*, 761−771.

(21) Cruickshank, A. J. B.; Windsor, M. L.; Young, C. L. Prediction of Second Virial Coefficients of Mixtures from the Principle of Corresponding States. *Trans. Faraday Soc.* **1966**, *62*, 23341−2355.

(22) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvents: Physical Properties and Methods of Purification*, 4th ed.; Wiley-Interscience: New York, 1986.

(23) *CRC Handbook of Chemistry and Physics*, 72nd ed.; Lide, D. R., Ed.; CRC Press: Boston, 1991−1992.

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