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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

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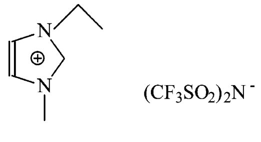
The activity coefficients at infinite dilution, γ_{13}^{∞}, for both polar and nonpolar solutes in the ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imidate have been determined by gas−liquid chromatography at the temperatures $T = 303.15$ K and $T = 318.15$ K. The results have been used to predict the solvent potential for the hexane−benzene separation using the calculated selectivity values. The results are compared to the γ_{13}^{∞} for similar systems found in the literature in an attempt to understand the effect that the nature of the cation has on the solute−solvent interactions. The partial molar excess enthalpies at infinite dilution values, $\Delta H_1^{E\infty}$, were calculated from the experimental γ_{13}^{∞} values obtained at the two temperatures.

Introduction

This work is a continuation of our investigation on ionic liquids to determine the activity coefficients at infinite dilution. Our group has previously measured γ_{13}^{∞} (where 1 refers to the solute and 3 refers to the solvent) in the ionic solvents 1-methyl-3-octyl-imidazolium chloride,[1] 1-hexyl-3-methyl-imidazolium tetrafluoroborate,[2] and 1-hexyl-3-methyl-imidazolium hexafluorophosphate.[3]

Ionic liquids are suitable for investigation because of their extremely low vapor pressures, high boiling points, relatively cheap cost, easy preparation, and wide liquid range.[4]

The activity coefficients at infinite dilution, γ_{13}^{∞} have been determined for alkanes, alkenes, alkynes, cycloalkanes, benzene, and methanol in the ionic liquid 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imidate ($C_8H_{11}S_2O_4F_6N_3$) using gas−liquid chromatography at the temperature 303.15 K or 318.15 K. The structure of 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imidate is given below



The selectivity S_{ij}^{∞}, which is the ratio of activity coefficients at infinite dilution, is given by the equation $S_{ij}^{\infty} = \gamma_{i3}^{\infty}/\gamma_{j3}^{\infty}$ where i and j refer to hexane and benzene, respectively. The selectivity value is used to determine the potential of the ionic solvent for extractive distillation in the separation of aromatic compounds from aliphatic compounds.[5]

Gas−liquid chromatography is a well-established and accurate method that is used to obtain γ_{13}^{∞}.[6,7] The partial molar excess enthalpies at infinite dilution values, $\Delta H_1^{E\infty}$, were also calculated from the γ_{13}^{∞} values obtained over the temperature range.

Experimental Section

Materials or Chemicals. The ionic liquid had a purity of 98 mass % and was supplied by Fluka. The ionic liquid was further purified by subjecting the liquid to a very low vapor pressure of about 5×10^{-4} Pa for approximately 30 min. This procedure removed any volatile chemicals and water from the ionic liquid. A Karl Fischer titration showed that the water concentration in the ionic liquid was less than 0.001 mass %. The solutes (purchased from Aldrich) were used without further purification because the GLC technique separated any impurities on the column.

Experimental Procedure. The GLC apparatus, the column preparation, and the packing method used in this work have been described previously. Stainless steel columns of 1-m length and 4.7-mm internal diameter were used. Before packing the column, we washed it with hot, soapy water, rinsed it with cold water, and flushed it with acetone to reduce the drying time. Chromosorb WHP 80/100 mesh was used as the solid support and was supplied by Supelco. The solvent dichloromethane was used to coat the ionic liquid onto the solid support by use of a rotary evaporator. The solid support and the ionic liquid was weighed before and after evaporation of the dichloromethane, and the mass agreed to within 0.5 mg of the original mass of the solid support and the ionic liquid. The coated solid support was introduced into a vertically held GLC column (sealed with glass wool at the “bottom” end) and gently tapped. The process was continued until no more solid support could be added. The GLC column was then plugged with glass wool at the “top” end, coiled and fitted to the GLC apparatus. The unused coated solid

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

	V_c	T_c	I
solute	cm^3 mol^{-1}	K	kJ mol^{-1}
methanol	118	512.6	1046.9
hexane	370	507.6	977.4
heptane	425	540.6	957.1
octane	492	568.7	947.4
hex-1-ene	354	504.0	910.8
hept-1-ene	413	537.2	910.8
oct-1-ene	464	566.7	909.9
hex-1-yne	332	516.2	960.0
hept-1-yne	387	547.2	960.0
oct-1-yne	442	574.2	951.3
cyclopentane	260	511.6	1014.1
cyclohexane	309	553.6	951.3
cycloheptane	353	604.2	962.0
cyclooctane	410	647.2	941.7
benzene	256	562.1	892.1
helium	57	5.25	2374.0

support was then weighed, and the number of moles of solvent was calculated by difference. The GLC apparatus was fitted with a thermal conductivity detector and attached to a Kipp and Zonen recorder. The carrier gas phase was helium. The carrier gas flow rate was determined using a calibrated soap bubble flowmeter that 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_{13}^{∞} determinations were made. The flow rates were corrected for water vapor pressure and ranged from 0.1 to 0.5 μ m^3 s^{-1}. The column temperature was controlled in a water bath using a Tronac temperature controller and a low heat capacity heater. To prevent any variation in temperature within the water bath, two stirrers were used. This setup was capable of controlling temperature to better than 0.01 K. A glass-walled manometer (internal diameter 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 using a Fortin barometer. The solvent column packing varied from 25 to 30 mass % of the ionic liquid, large enough to prevent any residual absorption of solute onto the column packing. For each temperature, the measurements were repeated by using two different columns with different mass % packing. Solute injections ranged from 0.1 to 1 μL and were considered to be at infinite dilution on the column.

The GLC technique was tested for the system hexane in hexadecane at 298.15 K, and the results are within 2% of the literature values.[8]

Theory

The equation developed by Everett[9] and Cruickshank[10]

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3RT}{V_N P^*{}_1}\right) - \left(\frac{(B_{11} - V^*{}_1)P^*{}_1}{RT}\right) + \left(\frac{((2B_{12} - V_1^{\infty}))P_o J_2^3}{RT}\right) \qquad (1)$$

was used in this work to calculate the γ_{13}^{∞} of solutes in an involatile solvent from gas−liquid chromatography. V_N denotes the net retention volume of the solute; P_o, the outlet pressure; $P_oJ_2^3$, the mean column pressure; n_3, the number of moles of solvent on the column packing; T, the column temperature; P_1^*, the saturated vapor pressure of the solute at temperature T; B_{11}, the second virial coefficient of 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; and B_{12}, the mixed second virial coefficient of the solute (1) and the carrier gas (2). The values of B_{11} and B_{12} were calculated using the McGlashan and Potter[11] equation

$$\frac{B}{V_C} = 0.430 - 0.886\left(\frac{T_C}{T}\right)0.694\left(\frac{T_C}{T}\right)^2 - 0.0375(n-1)\left(\frac{T_C}{T}\right)^{4.5} \qquad (2)$$

where n refers to the number of carbon atoms. Using the Lorentz[7] and Hudson and McCoubrey[12,13] combining rules, we calculated V_{12}^c and T_{12}^c from the critical properties of the pure component. The vapor pressure values were calculated using the Antoine equation from constants obtained from the literature.[14,15] Critical data[14,15] used to calculate B_{11} and B_{12} and ionization energies I[14] used in the calculation of T_{12}^c are given in Table 1. The values of P_1^*, V_1^*, B_{11}, and B_{12} used in the calculation of γ_{13}^{∞} are given in Table 2.

Table 2. Vapor Pressure P_1^*, Molar Volumes V_1^*, and Virial Coefficients B_{11} and B_{12} Used in the Calculation of γ_{13}^{∞} at T = 303.15 K and T = 318.15 K

T	$P^*{}_1$	$V^*{}_1$	B_{11}	B_{12}
K	kPa	cm^3 mol^{-1}	cm^3 mol^{-1}	cm^3 mol^{-1}
		Methanol		
303.15	21.86	40.99	−360.18	23.48
318.15	44.53	41.74	−330.29	24.14
		Hexane		
303.15	24.96	132.52	−1815.38	53.24
318.15	45.05	135.32	−1585.38	54.20
		Heptane		
303.15	7.78	148.36	−2718.08	58.67
318.15	15.32	151.25	−2347.81	59.70
		Octane		
303.15	2.45	164.48	−3998.67	65.30
318.15	5.29	118.94	−3421.53	66.40
		Hex-1-ene		
303.15	30.50	126.65	−1702.14	51.84
318.15	54.18	129.59	−1487.31	52.77
		Hept-1-ene		
303.15	9.53	142.50	−2590.67	57.67
318.15	18.43	145.50	−2238.97	58.68
		Oct-1-ene		
303.15	3.04	158.62	−3727.94	62.57
318.15	6.41	161.59	−3190.85	63.64
		Hex-1-yne		
303.15	22.04	118.29	−1709.08	48.92
318.15	40.47	120.86	−1490.56	49.85
		Hept-1-yne		
303.15	7.13	134.74	−2569.50	54.39
318.15	14.18	137.30	−2217.16	55.40
		Oct-1-yne		
303.15	2.2?	151.29	−3707.51	59.84
318.15	4.94	157.10	−3169.74	62.92
		Cyclopentane		
303.15	51.65	95.36	−1201.81	40.62
318.15	88.37	97.33	−1055.89	41.49
		Cyclohexane		
303.15	16.23	109.44	−1952.96	45.68
318.15	29.99	111.38	−1693.46	46.63
		Cycloheptane		
303.15	3.74	123.88	−3214.05	49.58
318.15	7.64	128.14	−2749.44	50.62
		Cyclooctane		
313.15	0.99	137.00	−5162.96	55.06
318.15	2.23	141.03	−4368.86	56.19
		Benzene		
313.15	16.35	89.96	−1693.87	39.79
318.15	30.54	9.16	−1466.90	40.68

Table 3. Moles of Solvent n_3 on Each Column and the Activity Coefficients at Infinite Dilution γ_{13}^{∞} for Hexane, Heptane, Octane, Cyclopentane, Cyclohexane, Cycloheptane, Cyclooctane, Hex-1-ene, Hept-1-ene, Oct-1-ene, Hex-1-yne, Hept-1-yne, Oct-1-yne, Benzene, or Methanol in 1-Ethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl) Imidate at T = 303.15 K and T = 318.15 K

solute	$\gamma_{13}^{\infty}(n_3 = 2.247)$	$\gamma_{13}^{\infty}(n_3 = 2.362)$	$\gamma_{13}^{\infty}(n_3 = 2.247)$	$\gamma_{13}^{\infty}(n_3 = 2.362)$
	T = 303.15 K		T = 318.15 K	
hexane	26.1	26.3	24.0	24.2
heptane	37.0	37.2	32.3	32.6
octane	59.9	59.8	50.7	50.8
cyclopentane	6.15	6.24	5.83	5.33
cyclohexane	9.42	9.43	8.72	8.64
cycloheptane	13.0	13.1	11.5	11.4
cyclooctane	18.2	18.6	15.8	15.6
hex-1-ene	8.19	8.87	7.79	8.08
hept-1-ene	11.2	11.4	10.0	10.0
oct-1-ene	15.8	15.9	14.1	14.1
hex-1-yne	2.37	2.16	2.28	2.09
hept-1-yne	3.41	3.23	3.22	3.05
oct-1-yne	5.11	4.85	4.85	4.54
methanol	0.92	0.91	0.83	0.81
benzene	0.71	0.72	0.70	0.71

Table 4. Partial Molar Excess Thermodynamic Functions at Infinite Dilution for (1-Ethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl) Imidate + an Alkane or a Cycloalkane or an Alkene or an Alkyne or Methanol or Benzene) from This Work and That Published in the Literature

solute	$\Delta H_1^{E\infty\ a}$ kJ mol^{-1}	$\Delta H_1^{E\infty\ b}$ kJ mol^{-1}	$\Delta H_1^{E\infty\ c}$ kJ mol^{-1}
hexane	4.4	4.200	5.8[d]
heptane	7.2	6.608	6.8[d]
octane	8.8	7.725	
cyclopentane	5.6		4.2[d]
cyclohexane	4.4		6.0
cycloheptane	6.9		
cyclooctane	8.3		
hex-1-ene	3.9		2.8
hept-1-ene	6.2		4.2[d]
oct-1-ene	6.4		
hex-1-yne	1.9		
hept-1-yne	3.1		
oct-1-yne	3.2		
methanol	5.9	7.787	6.3[d]
benzene	−0.38	−0.975	−0.48

[a] This work. [b] Reference 16. [c] Reference 17. [d] Calculated from reference 17.

Table 5. Activity Coefficients at Infinite Dilution for 1-Ethyl-3-methyl-imidazolium Bis(trifluoromethylsulfonyl) Amide ($C_8H_{11}S_2F_6O_4N_3$)

solvent	$C_8H_{11}S_2F_6O_4N_3$[a]	$C_8H_{11}S_2O_4F_6N_3$[b]	$C_8H_{11}S_2O_4F_6N_3$[c]
	T = 303.15 K	T = 313.15 K	T = 303.15 K
hexane	26.2	25.34	27.9
heptane	37.1	38.37	43.8
octane	59.9	58.47	
cyclopentane	6.20		10.1
cyclohexane	9.43	7.49	15.6
hex-1-ene	8.53		12.7
hept-1-ene	11.3		19.9
methanol	0.92		1.40
benzene	0.70	1.17	1.19

[a] This work. [b] Reference 16. [c] Reference 17.

Table 6. Selectivities S_{ij}^{∞} at Infinite Dilution of Various Solvents for the *n*-Hexane−Benzene Separation $S_{ij}^{\infty} = \gamma_{i3}^{\infty}/\gamma_{j3}^{\infty}$ as Defined by Tiegs[5] at 298.15 K or 303.15 K

solvent	S_{ij}^{∞}
sulfolane[a]	30.5
dimethyl sulfoxide[a]	22.7
diethylene glycol[a]	15.4
N-methyl-2-pyrrolidinone[a] (NMP)	12.5
acetonitrile[a]	9.4
dichloroacetic acid[a]	6.1
aniline[a]	11.2
[HMIM$^+$][BF$_4^-$]	23.7
$C_8H_{11}S_2O_4F_6N_3$ (this work)	37.5
$C_8H_{11}S_2O_4F_6N_3$[b]	24.1
$C_8H_{11}S_2O_4F_6N_3$[e]	23.4
$C_9H_{13}S_2O_4F_6N_3$[b]	21.6
[HMIM][BF$_4^-$][c]	23.1
[HMIM][PF$_6^-$][d]	21.6

[a] Reference 5. [b] Reference 16. [c] Reference 3. [d] Reference 2. [e] Reference 17.

Results and Discussion

Table 3 lists the γ_{13}^{∞} values at 303.15 K and 318.15 K for the varying amounts of solvent on the solid packing. The γ_{13}^{∞} value for the *n*-alkanes increases with an increase in carbon number. The values of γ_{13}^{∞} for the corresponding cyclic alkane carbon numbers are small and become even smaller for the corresponding alkenes and alkynes. The more polar the solute, the greater the interaction with the cation moiety. This is particularly true for the γ_{13}^{∞} values for the alkynes. Benzene (with its six π-delocalized electrons) has the smallest γ_{13}^{∞} value, presumably because of the interaction with the cation species. The single lone-pair electron on the methanol molecule can form strong intermolecular interactions with the cation moiety of the ionic liquid. The average percent deviations for the two sets of data are ±5% at 303 K and ±4% at 318.15 K. The absolute error for both temperatures is estimated by taking into account the estimated errors δn_3 (<10^{-6} moles), δT (0.01 K), δP_1^* (1 Pa), δP_o (0.01 mmHg), δP_i (0.01 mmHg), and the overall error in γ_{13}^{∞} with respect to eq 1 (±0.5%).

Table 4 lists the partial molar excess enthalpies at infinite dilution values, $\Delta H_1^{E\infty}$, which were determined from the Gibbs−Helmholtz equation:

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

In general, within each of the series (alkane, cycloalkane, alkene, and alkyne) the $\Delta H_1^{E\infty}$ values increases with increasing carbon number. The value for benzene is small and negative, indicating that the intramolecular $\pi-\pi$ interactions are of similar magnitude to the intermolecular π−cation interactions. The estimated error in $\Delta H_1^{E\infty}$ is ±10%. The values for $\Delta H_1^{E\infty}$ in Table 4 are within 1 kJ to 1.5 kJ of the literature values for all solutes except for benzene, for which it is within 0.1 kJ to 0.5 kJ of the literature values.[16,17]

Table 5 lists the γ_{13}^{∞} values for 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) amide ($C_8H_{11}S_2O_4F_6N_3$)[16] at T = 313.15 K (taken from the literature) and 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imidate ($C_8H_{11}S_2O_4F_6N_3$) at T = 303.15 K from this work and from the literature.[17] A comparison of the γ_{13}^{∞} values obtained in this work with those obtained from the literature[16,17] shows a large discrepancy for some γ_{13}^{∞} values.

The S_{ij}^{∞} selectivity values for the separation of the hexane(i)/benzene(j) mixture is given in Table 6. The ionic liquid used in this work, 1-ethyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl) imidate (37.5), has the largest selectivity value, even greater than that for sulfolane (30.5). When compared with the selectivity values for other ionic liquids (again taken from the literature), the selectivity value is larger for the ionic liquid used in this work. The potential of the ionic liquid used in this work for the hexane−benzene separation is greater than that of traditional solvents used in extraction or extractive distillation processes.

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