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Activity Coefficients at Infinite Dilution of Organic Solutes in 1-Hexyl-3-methylimidazolium Hexafluorophosphate from Gas−Liquid Chromatography

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Ionic liquids, with their very low vapor pressures and unique solvent properties, are potentially useful solvents for separating organic liquid mixtures by solvent extraction or by extractive distillation. In this work, the activity coefficients at infinite dilution, γ_{13}^{∞}, for both polar and nonpolar solutes in the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate have been determined by gas−liquid chromatography at the temperatures (298.15, 313.15, 323.15) K. The partial molar excess enthalpies at infinite dilution and the selectivity values were calculated from the γ_{13}^{∞} values obtained over the temperature range. The selectivity values have been determined and are used to predict the solvent potential of the ionic liquid for the separation of liquid mixtures by extractive distillation.

Introduction

The Montreal Protocol has made it imperative for scientists and engineers to find solvents that are environmentally friendly.[1] Process engineers are investigating alternate separation processes that have fewer byproducts and fewer volatile organic compounds.[2] Ionic liquids and supercritical fluids are "neoteric" solvents that can be used for clean technology.[1] Ionic liquids are particularly suitable for investigation because of their low vapor pressures, high boiling points, and easy preparation and because they exist as liquids over a wide temperature range.[1]

Relatively few papers have been published on the solution properties of ionic liquids.[3−6] To exploit the unique properties of ionic liquids for new and useful applications (examples of which include the removal of metal pollutants from aqueous streams and the immobilization of spent nuclear fuels), it is necessary to have good thermodynamic and solution data. This work contributes to that goal.

Gas−liquid chromatography is a well-established and accurate method for the determination of the activity coefficients at infinite dilution, γ_{13}^{∞}.[7,8] In this work, values have been determined for alkanes, alkenes, alkynes, cycloalkanes, benzene, and methanol in the ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate, $[\mathrm{HMIM}^+][\mathrm{PF}_6^-]$, using gas−liquid chromatography at the temperatures (298.15, 313.15, 323.15) K.

The partial molar excess enthalpies at infinite dilution, $\Delta H_1^{\mathrm{E}\infty}$, were calculated from the γ_{13}^{∞} values obtained over the temperature range, and some selectivities, S_{12}^{∞}, were also determined. The latter is defined as[9]

$$S_{12}^{\infty} = \gamma_{13}^{\infty}/\gamma_{23}^{\infty} \qquad (1)$$

where γ_{i3}^{∞} is the activity coefficient at infinite dilution for solute *i* in solvent 3. The selectivity indicates the suitability of a solvent for separating mixtures of components 1 and 2 by extractive distillation.[9]

Traditionally, *N*-methyl-2-pyrrolidinone (NMP) has been used commercially as an entrainer in the Lurgi Distapex extractive distillation process[10] and in the Arosolvan solvent extraction process,[11] in both cases for separating aromatic compounds from aliphatic compounds. The use of ionic liquids for these separation processes has many advantages, especially the ease with which it could be recovered as a result of its low vapor pressure.

Experimental Section

Materials and Chemicals. The solvent $[\mathrm{HMIM}^+][\mathrm{PF}_6^-]$ had a purity of 98 mass % and was supplied by Fluka. The ionic liquid was further purified by subjecting a weighed amount of the liquid to a very low pressure of about 5×10^{-4} Pa for approximately 30 min. The mass loss as a result of this treatment was measured and found to be 2.0 mass %. A Karl Fischer titration showed the water content to be less than 0.01 mass %. No halide test was done on the ionic liquid sample. The solutes (see Table 1, purchased from Aldrich), with a minimum purity of 98 mass %, were used without further purification because the gas−liquid chromatographic technique separated any impurities.

Experimental Procedures. Gas−liquid chromatography is a well-established method for determining γ_{13}^{∞}. The

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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

solute	V_c/cm^3·mol^{-1}	T_c/K	I/kJ·mol^{-1}
methanol	118	512.6	1046.9
pentane	304	496.6	998.6
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

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 = 298.15 K, T = 313.15 K, and T = 323.15 K

T/K	P_1^*/kPa	V_1^*/cm^3·mol^{-1}	B_{11}/cm^3·mol^{-1}	B_{12}/cm^3·mol^{-1}
		Methanol		
313.15	35.43	41.48	−339.8	23.9
323.15	55.53	41.99	−321.2	24.4
		Pentane		
298.15	68.34	116.11	−1356.6	45.7
313.15	115.66	118.94	−1109.5	46.6
323.15	159.22	120.88	−1096.9	47.1
		Hexane		
298.15	20.18	131.60	−1905.0	52.9
313.15	37.28	134.37	−1657.5	53.8
323.15	54.07	136.26	−1519.4	54.5
		Heptane		
298.15	6.09	147.40	−2864.0	58.3
313.15	12.33	150.29	−2456.7	59.4
323.15	18.88	152.21	−2236.4	60.0
		Octane		
313.15	4.14	166.41	−3600.6	66.6
323.15	6.71	168.38	−3257.6	67.3
		Hex-1-ene		
313.15	45.06	128.65	−1554.2	52.9
323.15	64.72	130.53	−1425.2	53.5
		Hept-1-ene		
313.15	14.92	144.54	−2348.8	58.8
323.15	22.60	146.45	−2138.8	59.5
		Oct-1-ene		
313.15	5.05	160.52	−3412.3	64.7
323.15	8.07	62.66	−3087.9	65.4
		Hex-1-yne		
313.15	33.30	121.98	−1558.3	50.0
323.15	48.82	119.74	−1427.3	53.5
		Hept-1-yne		
313.15	11.38	138.43	−2406.5	55.5
323.15	17.53	136.16	−2192.8	56.2
		Oct-1-yne		
313.15	3.86	155.05	−3335.3	61.8
323.15	6.28	159.15	−3016.05	62.8
		Cyclopentane		
298.15	42.29	94.71	−1257.7	40.3
313.15	73.90	96.66	−1101.3	41.2
323.15	103.76	98.00	−1013.4	41.7
		Cyclohexane		
298.15	13.01	108.80	−2058.0	45.4
313.15	24.63	110.71	−1778.1	46.4
323.15	36.25	112.05	−1622.6	47.0
		Cycloheptane		
313.15	6.08	126.64	−2892.5	50.7
323.15	10.38	129.63	−2295.6	51.4
		Cyclooctane		
313.15	1.72	139.70	−4612.7	56.0
323.15	3.98	142.36	−3129.5	57.1
		Benzene		
298.15	13.06	89.41	−1786.4	39.6
313.15	25.00	91.07	−1541.2	40.4
323.15	37.04	92.20	−1405.2	41.0

gas−liquid chromatographic apparatus, the column preparation, and the packing method used in this work have been described previously.[12−15] Stainless steel columns of length 1 m and diameter 0.4 mm were used. Chromosorb WHP 80/100 mesh was used as the solid support and was supplied by Supelco. A thermal conductivity detector together with helium carrier gas was used. The helium carrier gas flow rate was determined using a calibrated soap bubble flowmeter 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 vapor pressure and ranged from (0.1 to 0.5) μm^3 s^{-1}. The column temperature was controlled in a water bath using a Tronac temperature controller connected to a low heat capacity heater. At the higher temperature, the temperature control was supplemented with a heater. The water bath was adequately stirred to ensure a constant temperature throughout and to prevent the buildup of any temperature gradients. This setup was capable of controlling the temperature to within 0.01 K. The temperature was measured using a calibrated Hewlett-Packard resistance thermometer. A glass-walled manometer (i.d. 8 mm, 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 [HMIM$^+$][PF$_6^-$], large enough to prevent any residual absorption onto the column packing. Sample injections ranged from (0.1 to 1.0) μL and were considered to be at infinite dilution on the column.

The method used in this work was validated by comparing results obtained in our laboratory to the literature results for the system hexane in hexadecane at 298.15 K, and the results were in very good agreement. The results agreed with the literature value to within 2.0%.

Theory

The equation developed by Everett[14] and Cruickshank,[15]

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

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, $P_o J_2^3$ the mean column pressure corrected for the pressure drop across the column, 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 and the carrier gas. The values of B_{11} and B_{12}

Table 3. Number of Moles of Solvent n_3 on Each Column and the Activity Coefficients at Infinite Dilution, γ_{13}^{∞}, at T = 298.15 K, T = 313.15 K, and T = 313.15 K

solute	n_3/mmol	γ_{13}^{∞}	n_3/mmol	γ_{13}^{∞}
T = 298.15 K				
pentane	4.182	13.54	3.381	13.85
hexane	4.182	22.60	3.381	22.39
heptane	4.182	30.82	3.381	30.38
octane	3.409	44.98	3.381	44.34
cyclopentane	4.182	8.53	3.381	8.52
cyclohexane	4.182	12.49	3.381	12.80
hex-1-ene	4.182	10.18	3.381	10.65
hept-1-ene	4.182	15.44	3.381	15.20
oct-1-ene	4.182	21.93	3.381	21.85
methanol	4.182	1.94	3.381	1.94
benzene	4.182	1.02	3.381	1.05
T = 313.15 K				
pentane	4.182	12.35	3.381	11.95
hexane	4.182	19.48	3.381	18.93
heptane	4.182	25.86	3.381	25.55
octane	4.182	37.41	3.381	36.80
cyclopentane	4.182	7.26	3.381	7.16
cyclohexane	4.182	10.61	3.381	10.60
cycloheptane	4.182	14.24	3.381	14.17
cyclooctane	4.182	18.83	3.381	18.55
T = 313.15 K				
hex-1-ene	4.182	9.22	3.381	8.97
hept-1-ene	4.182	13.90	3.381	13.60
oct-1-ene	4.182	19.83	3.381	19.25
hex-1-yne	4.182	2.77	3.381	2.79
hept-1-yne	4.182	4.00	3.381	4.06
oct-1-yne	4.182	5.84	3.381	5.89
methanol	4.182	1.59	3.381	1.61
benzene	4.182	1.02	3.381	1.05
T = 323.15 K				
pentane	4.182	8.32	3.381	8.65
hexane	4.182	14.76	3.381	15.24
heptane	4.182	22.02	3.381	22.32
octane	4.182	32.26	3.381	31.74
cyclopentane	4.182	5.91	3.381	6.24
cyclohexane	4.182	9.19	3.381	9.56
cycloheptane	4.182	11.68	3.381	11.99
cyclooctane	4.182	12.22	3.381	12.21
hex-1-ene	4.182	7.74	3.381	8.02
hept-1-ene	4.182	12.23	3.381	12.48
oct-1-ene	4.182	17.90	3.381	18.06
hex-1-yne	4.182	2.68	3.381	2.95
hept-1-yne	4.182	3.98	3.381	4.15
oct-1-yne	4.182	5.69	3.381	5.92
methanol	4.182	1.44	3.381	1.44
benzene	4.182	1.07	3.381	1.06

were calculated using the method of McGlashan and Potter,[16]

$$B/V_C = 0.430 - 0.886(T_C/T) - 0.694(T_C/T)^2 - 0.0375(n-1)(T_C/T)^{4.5} \quad (3)$$

where *n* refers to the number of carbon atoms. Using the Lorentz[8] and Hudson and McCoubrey[17,18] combining rules, V_{12}^{c} and T_{12}^{c} were calculated from the critical properties of the pure component. The vapor pressure values were calculated using the Antoine equation with constants obtained from the literature.[19,20] Critical data[19,20] used to calculate B_{11} and B_{12}, and ionization energies[20] 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.

Results and Discussion

Table 3 lists γ_{13}^{∞} at T = 298.15 K, 313.15 K, and 323.15 K for the different numbers of moles of solvent on the column. Table 4 lists the average γ_{13}^{∞} values. The values at 298.15 K are plotted in Figure 1 as a function of the number of carbon atoms of the solute. The γ_{13}^{∞} values obtained for methanol, benzene, and the alkynes are much smaller than the values for the alkanes, cycloalkanes, and alkenes. This is expected and can be explained by the intermolecular interaction between the positive [HMIM$^+$] cation and the electronegative oxygen atom of methanol or the delocalized electrons on the benzene, or alkyne, or alkene molecules. The γ_{13}^{∞} values for the alkynes are smaller than those of the alkenes because there is a greater amount of delocalized electrons in the alkynes resulting in stronger "cation–delocalized electron" interaction. The values of γ_{13}^{∞} obtained by Heintz and co-workers[3,4] for the solutes hexane (60.4), heptane (86.3), octane (129.3), cyclohexane (125), benzene (1.64), and methanol (1.08) in 4-methyl-*n*-butylpyridinium tetrafluoroborate at 313 K follow the same trend as the values reported here, in that the γ_{13}^{∞} values are large for the hydrocarbons and small for the polar compounds. This is despite the solvent being composed of a very different cation and anion. Similarly from the results of Heintz and co-workers, the calculated value of S_{12}^{∞} for the benzene/alkane mixtures is large (40). Any conclusions or general observations on the significance of a particular cation or anion must wait until a larger data set has been obtained.

Table 4. Average Activity Coefficients at Infinite Dilution, γ_{13}^{∞}, at T = 298.15 K, T = 313.15 K, and T = 323.15 K

	γ_{13}^{∞}(exp)		
solutes	T = 298.15 K	T = 313.15 K	T = 323.15 K
pentane	13.70	12.15	8.48
hexane	22.50	19.20	15.00
heptane	30.60	25.70	22.17
octane	44.66	37.10	32.00
cyclopentane	8.53	7.21	6.08
cyclohexane	12.65	10.60	9.38
cycloheptane		14.20	11.84
cyclooctane		18.69	12.22
hex-1-ene	10.42	9.09	7.88
hept-1-ene	15.32	13.75	12.36
oct-1-ene	21.89	19.54	17.98
hex-1-yne		2.78	2.82
hept-1-yne		4.03	4.07
oct-1-yne		5.86	5.81
methanol	1.94	1.60	1.44
benzene	1.03	1.04	1.07

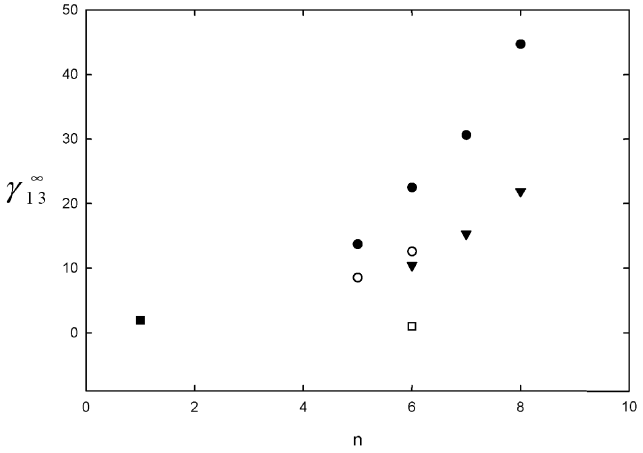

Figure 1. versus the number of carbon atoms at 298.15 K: ●, alkanes; ○, cycloalkanes; ▼, alkenes; *σ*, alkynes; ■, methanol; □, benzene.

Table 5 lists the partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E\infty}$, which were determined using the

Table 5. Partial Molar Excess Enthalpies at Infinite Dilution from Equation 4 and the Correlation Coefficients, R^2

solute	R^2	$\Delta H_1^{E\infty}$ $J \cdot mol^{-1}$	solute	R^2	$\Delta H_1^{E\infty}$ $J \cdot mol^{-1}$
pentane	0.8360	14500	hex-1-ene	0.9762	8750
hexane	0.9326	12500	hept-1-ene	0.9822	6800
heptane	0.9919	10200	oct-1-ene	0.9979	6300
octane	0.9947	10600	methanol	0.9989	9600
cyclopentane	0.9801	10600	benzene	0.8655	−1020
cyclohexane	0.9988	9500			

Table 6. Selectivities S_{12}^{∞} at Infinite Dilution of Various Solvents for the *n*-Hexane−Benzene Separation[a]

solvent	S_{12}^{∞}
sulfolane[b]	30.5
dimethyl sulfoxide[b]	22.7
diethylene glycol[b]	15.4
N-methyl-2-pyrrolidinone[b] (NMP)	12.5
acetonitrile[b]	9.4
dichloroacetic acid[b]	6.1
aniline[b]	11.2
$[HMIM^+][PF_6^-]$ (this work)	21.6

[a] S_{12}^{∞} as defined by Tiegs (ref 3) at 298.15 K. [b] Reference 9.

equation

$$\ln \gamma_{13}^{\infty} = a + b/T \tag{4}$$

$\Delta H_1^{E\infty}$ was calculated from the slope, *b*, of eq 4 which is related to the Gibbs−Helmholtz equation

$$\left[\frac{\partial \ln \gamma_i^{\infty}}{\partial (1/T)}\right]_p = \frac{\Delta H_1^{E\infty}}{R} \tag{5}$$

Table 5 also lists the correlation coefficient values, R^2, obtained for the fitting of eq 4. The correlation values are very good, indicating the reliability of the $\Delta H_1^{E\infty}$ values. The correlation coefficient values for pentane and benzene are lower, probably due to the greater error in their γ_{13}^{∞} values (small retention times and very long retention times, respectively). The negative value of $\Delta H_1^{E\infty}$ for benzene in $[HMIM^+][PF_6^-]$ indicates that there is probably a weak induced-dipole−dipole interaction between the benzene molecules (due to the aromatic electrons) and the $[HMIM^+]$ cation.

In general, within each of the series alkane, cycloalkane, alkene, and alkyne, the $\Delta H_1^{E\infty}$ values decrease as the number of carbon atoms increases. We presume that this is due to the greater amount of delocalized electrons available as the carbon number increases, resulting in a greater interaction between the cation and the aliphatic compound.

The selectivity, S_{12}^{∞}, value for the separation of hexane/benzene mixtures using $[HMIM^+][PF_6^-]$ at 298.15 K is large (21.6) compared to S_{12}^{∞} values for related solvents (see Table 6), including *N*-methyl-2-pyrrolidinone (12.15), which is used in the Arosolvan process for the separation of aromatics from alkanes. The S_{12}^{∞} values calculated from the γ_{13}^{∞} values given in Table 4 for benzene/heptane and benzene/octane are 30 and 40, respectively, highlighting the important role that $[HMIM^+][PF_6^-]$ can play in separating benzene (and presumably other aromatic compounds) from alkanes. A further analysis of the data in Table 4 shows that S_{12}^{∞} decreases with temperature. By way of example, S_{12}^{∞} for benzene/hexane changes from 21.6 to 14.0 when the temperature changes from 298.15 K to 323.15 K. This implies that the solvent is more effective as an entrainer in extractive distillation at a lower temperature.

Conclusion

The γ_{13}^{∞} and S_{12}^{∞} data presented in this work indicate that $[HMIM^+][PF_6^-]$ is a potentially useful solvent for separating benzene (and probably other aromatic hydrocarbons) from alkanes.

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