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Determination of Activity Coefficients at Infinite Dilution of Solutes in the Ionic Liquid, Trihexyltetradecylphosphonium Bis(trifluoromethylsulfonyl) Imide, Using Gas−Liquid Chromatography at T = (303.15, 308.15, 313.15, and 318.15) K

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The activity coefficients at infinite dilution, γ_{13}^{∞}, for hydrocarbon solutes and some alcohols in the ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide $[3C_6C_{14}P][Tf_2N]$ have been determined by gas−liquid chromatography at temperatures T = (303.15, 308.15, 313.15, and 318.15) K. The selectivity values have been calculated at T = 308.15 K, and the results indicate that the ionic liquid $[3C_6C_{14}P][Tf_2N]$ should not be considered as a solvent for separation of alkanes and aromatics. The partial molar excess enthalpy values at infinite dilution $\Delta H_1^{E\infty}$, determined in this work, together with the values γ_{13}^{∞} have been discussed in terms of intermolecular interactions and compared to results of related systems obtained from the literature.

Introduction

This work is a continuation of our investigations into the activity coefficients at infinite dilution γ_{13}^{∞} values of phosphonium ionic liquids (ILs).[1,2] Some room-temperature ionic liquids have shown great potential as media for reactions and for separations and hence may be considered as possible replacement solvents in the extractive distillation of hydrocarbon mixtures.

In the work presented here, activity coefficients at infinite dilution, γ_{13}^{∞}, values have been determined by gas−liquid chromatography (GLC) at temperatures T = (303.15, 308.15, 313.15, and 318.15) K for alkanes, alk-1-enes, alk-1-ynes, cycloalkanes, benzene, methanol, ethanol, and 1-propanol in the ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide $[3C_6C_{14}P][Tf_2N]$. The selectivity value,[3] S_{ij}^{∞}, of hexane with respect to benzene was calculated and used to predict 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 values $\Delta H_1^{E\infty}$ were also calculated from the γ_{13}^{∞} values obtained at four temperatures. These values of γ_{13}^{∞}, $\Delta H_1^{E\infty}$, and S_{ij}^{∞} determined in this work have been discussed in terms of recent results of other ionic liquids taken from the literature. These results give some indication of the nature of the interaction between the solutes (hydrocarbons or alcohols) and ionic liquids.

Other phosphonium ionic liquids[1,2] have been shown to have little potential as solvents for separating organic liquids. However, one imidazolium ionic liquid with a phosphate anion, 1,3-dimethylimidazolium dimethylphosphate, $[MMIM][(CH_3)_2PO_4]$, has shown some promise as a solvent for separating aliphatic and aromatic hydrocarbons.[4] On the other hand, some ionic liquids with (Tf_2N) anions have been shown to be potentially good solvents for separating aliphatic/aromatic mixtures. These include 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[EMIM]Tf_2N]$,[5,6] 1-hexyl-3-methylimidazole bis{(trifluoromethyl)sulfonyl}imide, $[HMIM][Tf_2N]$,[7] and many others[4,5] which are potentially better solvents for this separation than are sulfolane,[8] *N*-methyl-2-pyrrolidinone (NMP), or NMP mixed with water.[9] The latter three solvents are presently used commercially for separating aliphatic/aromatic hydrocarbons.

It is of interest to note that the magnitude of the activity coefficient usually decreases with an increase in the interaction between the solvent and the IL. This can be observed from a comparison of the activity coefficients, γ_{13}^{∞}, for different C_6 hydrocarbons in $[HMIM][Tf_2N]$.[7]

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}
pentane	304.00	469.70	998.60
hexane	370.00	507.50	977.40
heptane	432.00	540.30	957.10
octane	492.00	568.80	947.50
cyclopentane	260.00	511.60	1014.10
cyclohexane	308.00	553.50	951.30
cycloheptane	353.00	604.20	962.00
pent-1-ene	296.00	464.78	915.65
hex-1-ene	350.00	504.00	910.80
hept-1-ene	440.00	537.30	910.80
oct-1-ene	464.00	566.70	909.90
hex-1-yne	332.00	516.20	960.00
hept-1-yne	387.00	547.20	960.00
oct-1-yne	442.00	574.20	951.30
benzene	259.00	562.20	896.10
methanol	118.00	512.60	1046.90
ethanol	167.10	513.90	1010.30
1-propanol	219.00	536.80	986.10

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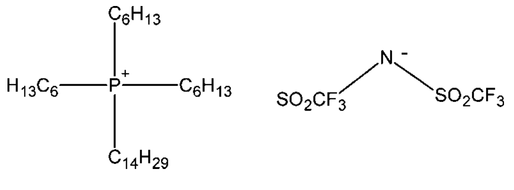
Table 2. Vapor Pressure, P_1^*, Molar Volumes, V_1^*, and Virial Coefficients B_{11} and B_{12} used in the Calculation of γ_{13}^{∞} at the Temperatures T = (303.15, 308.15, 313.15, and 318.15) K

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}
		Pentane					Hept-1-ene		
303.15	81.74	117.09	−1120.19	46.53	303.15	9.64	142.59	−2756.90	60.61
308.15	97.63	118.08	−1073.90	46.83	308.15	12.07	143.49	−2622.78	60.96
313.15	115.86	119.09	−1030.58	47.12	313.15	15.00	144.40	−2498.34	61.30
318.15	136.66	120.14	−989.99	47.39	318.15	18.49	145.34	−2382.70	61.63
		Hexane					Oct-1-ene		
303.15	24.41	132.23	−1814.37	53.26	303.15	3.13	161.65	−3727.94	62.59
308.15	30.04	133.17	−1732.27	53.59	308.15	4.03	162.62	−3534.92	62.96
313.15	36.67	134.13	−1655.82	53.91	313.15	5.15	163.60	−3356.34	63.31
318.15	44.45	135.12	−1584.52	54.21	318.15	6.51	164.61	−3190.86	63.66
		Heptane					Hex-1-yne		
303.15	7.63	147.92	−2758.14	59.44	303.15	21.54	121.93	−1709.09	48.94
308.15	9.65	148.86	−2623.49	59.80	308.15	26.64	122.75	−1630.99	49.26
313.15	12.10	149.83	−2498.59	60.15	313.15	32.69	123.58	−1558.31	49.57
318.15	15.05	150.81	−2382.53	60.48	318.15	39.83	124.44	−1490.57	49.87
		Octane					Hept-1-yne		
303.15	2.58	164.43	−4000.98	65.31	303.15	8.58	139.54	−2569.50	54.51
308.15	3.34	165.36	−3793.41	65.69	308.15	10.66	140.39	−2443.15	54.76
313.15	4.28	166.32	−3601.38	66.06	313.15	13.14	141.25	−2325.99	55.10
318.15	5.44	167.30	−3423.45	66.41	318.15	16.08	142.13	−2217.16	55.42
		Cyclopentane					Oct-1-yne		
303.15	51.13	96.85	−1201.81	40.64	303.15	2.27	154.70	−3707.51	59.86
308.15	61.63	97.54	−1149.80	40.94	308.15	2.97	155.60	−3514.19	60.23
313.15	73.80	98.23	−1101.26	41.23	313.15	3.83	156.51	−3335.38	60.59
318.15	87.82	98.94	−1055.89	41.51	318.15	4.91	157.44	−3169.74	60.94
		Cyclohexane					Benzene		
303.15	16.24	112.11	−1945.59	45.59	303.15	15.91	89.99	−1714.65	40.16
308.15	20.06	112.78	−1853.02	45.92	308.15	19.77	90.52	−1632.33	40.47
313.15	24.59	113.46	−1767.06	46.23	313.15	24.37	91.05	−1555.91	40.76
318.15	29.92	114.16	−1687.09	46.54	318.15	29.80	91.59	−1484.87	41.05
		Cycloheptane					Methanol		
303.15	3.67	124.96	−3214.05	49.60	303.15	21.86	40.93	−407.22	23.51
308.15	4.70	125.60	−3047.04	49.96	308.15	27.95	41.17	−393.48	23.74
313.15	5.96	126.25	−2892.56	50.31	313.15	35.43	41.42	−380.47	23.95
318.15	7.49	126.91	−2749.45	50.64	318.15	44.54	41.68	−368.14	24.16
		Pent-1-ene					Ethanol		
303.15	101.47	114.63	−1061.44	45.71	303.15	10.44	58.97	−579.75	30.01
308.15	120.46	115.65	−1017.81	46.00	308.15	13.72	59.33	−560.17	30.26
313.15	142.15	116.70	−976.97	46.29	313.15	17.86	59.70	−541.64	30.50
318.15	166.78	117.78	−938.69	46.56	318.15	23.03	60.08	−524.08	30.74
		Hex-1-ene					1-Propanol		
303.15	30.57	130.08	−1682.91	51.41	303.15	4.50	75.37	−940.85	35.55
308.15	37.25	131.04	−1607.05	51.73	308.15	6.01	75.80	−904.69	35.84
313.15	45.06	132.02	−1536.41	52.04	313.15	7.94	76.24	−870.73	36.12
318.15	54.15	133.02	−1470.51	52.33	318.15	10.38	76.69	−838.80	36.39

It is also of interest to note that the prediction of the activity coefficients at infinite dilution for organic solutes in the IL can be made using the quantitative structure−property relationship (QSPR) method.[10]

Experimental Section

Materials. The solvent, ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide, [3C_6C_{14}P][Tf_2N], was supplied by Fluka and was reported to have a purity of > 98 mass percent. This IL is liquid at room temperature. The structure of the ionic liquid used in this work is presented below.



The ionic liquid was purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at a temperature of about 343 K for approximately 5 h. This procedure removed any volatile chemicals and water from the ionic liquid. No other attempt was made to analyze impurities in the ionic liquid. 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, and 1-propanol (Rochelle Chemicals), were used without further purification because the GLC technique separates any impurities.

Experimental Procedure. The gas−liquid chromatography method, used in this work, is a well-established and accurate method used to obtain the γ_{13}^{∞} values.[11,12] The GLC apparatus, the column preparation, and the packing method have been described previously.[1,7] Stainless steel columns of length 1 mm and 4.7 mm 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

Table 3. Individual Values for Activity Coefficients at Infinite Dilution γ_i^∞ of Organic Solutes in [3C$_6$C$_{14}$P][Tf$_2$N] for Different Column Loadings, n_3 = 3.465 and 4.417 mmol, at T = (303.15, 308.15, 313.15, and 318.15) K

solute	n_3/mmol	γ_i^∞	n_3/mmol	γ_i^∞
		T = 303.15 K		
pentane	3.46	0.94	4.42	0.94
hexane	3.46	1.09	4.42	1.09
heptane	3.46	1.25	4.42	1.26
octane	3.46	1.31	4.42	1.32
cyclopentane	3.46	0.67	4.42	0.68
cyclohexane	3.46	0.77	4.42	0.79
cycloheptane	3.46	0.88	4.42	0.88
pent-1-ene	3.46	0.77	4.42	0.78
hex-1-ene	3.46	0.88	4.42	0.88
hept-1-ene	3.46	1.00	4.42	1.00
oct-1-ene	3.46	1.11	4.42	1.11
hex-1-yne	3.46	0.66	4.42	0.66
hept-1-yne	3.46	0.59	4.42	0.59
oct-1-yne	3.46	0.52	4.42	0.53
benzene	3.46	0.38	4.42	0.38
methanol	3.46	1.25	4.42	1.26
ethanol	3.46	1.34	4.42	1.37
1-propanol	3.46	1.42	4.42	1.42
		T = 308.15 K		
pentane	3.46	0.96	4.42	0.96
hexane	3.46	1.10	4.42	1.10
heptane	3.46	1.27	4.42	1.27
octane	3.46	1.36	4.42	1.36
cyclopentane	3.46	0.69	4.42	0.69
cyclohexane	3.46	0.79	4.42	0.80
cycloheptane	3.46	0.90	4.42	0.91
pent-1-ene	3.46	0.80	4.42	0.79
hex-1-ene	3.46	0.90	4.42	0.90
hept-1-ene	3.46	1.02	4.42	1.02
oct-1-ene	3.46	1.14	4.42	1.13
hex-1-yne	3.46	0.68	4.42	0.68
hept-1-yne	3.46	0.62	4.42	0.63
oct-1-yne	3.46	0.55	4.42	0.55
benzene	3.46	0.39	4.42	0.39
methanol	3.46	1.24	4.42	1.24
ethanol	3.46	1.32	4.42	1.33
1-propanol	3.46	1.40	4.42	1.40
		T = 313.15 K		
pentane	3.46	0.99	4.42	0.99
hexane	3.46	1.13	4.42	1.13
heptane	3.46	1.29	4.42	1.30
octane	3.46	1.39	4.42	1.40
cyclopentane	3.46	0.71	4.42	0.70
cyclohexane	3.46	0.82	4.42	0.81
cycloheptane	3.46	0.92	4.42	0.91
pent-1-ene	3.46	0.82	4.42	0.82
hex-1-ene	3.46	0.92	4.42	0.92
hept-1-ene	3.46	1.04	4.42	1.04
oct-1-ene	3.46	1.16	4.42	1.16
hex-1-yne	3.46	0.71	4.42	0.70
hept-1-yne	3.46	0.66	4.42	0.66
oct-1-yne	3.46	0.58	4.42	0.58
benzene	3.46	0.40	4.42	0.40
methanol	3.46	1.23	4.42	1.22
ethanol	3.46	1.31	4.42	1.30
1-propanol	3.46	1.39	4.42	1.39
		T = 318.15 K		
pentane	3.46	1.02	4.42	1.02
hexane	3.46	1.18	4.42	1.16
heptane	3.46	1.32	4.42	1.33
octane	3.46	1.44	4.42	1.47
cyclopentane	3.46	0.73	4.42	0.73
cyclohexane	3.46	0.84	4.42	0.85
cycloheptane	3.46	0.93	4.42	0.95
pent-1-ene	3.46	0.85	4.42	0.85
hex-1-ene	3.46	0.97	4.42	0.96
hept-1-ene	3.46	1.09	4.42	1.09
oct-1-ene	3.46	1.21	4.42	1.21
hex-1-yne	3.46	0.73	4.42	0.74
hept-1-yne	3.46	0.70	4.42	0.70
oct-1-yne	3.46	0.63	4.42	0.63
benzene	3.46	0.42	4.42	0.42
methanol	3.46	1.23	4.42	1.23
ethanol	3.46	1.30	4.42	1.30
1-propanol	3.46	1.38	4.42	1.38

Table 4. Experimental Activity Coefficients at Infinite Dilution γ_{13}^∞ ± 3 % for the Solutes in [3C$_6$C$_{14}$P][Tf$_2$N] at Different Temperatures

	average γ_i^∞ values			
solute	T = 303.15 K	T = 308.15 K	T = 313.15 K	T = 318.15 K
pentane	0.94	0.96	0.99	1.02
hexane	1.09	1.10	1.13	1.17
heptane	1.26	1.27	1.30	1.33
octane	1.32	1.36	1.40	1.46
cyclopentane	0.68	0.69	0.71	0.73
cyclohexane	0.78	0.80	0.82	0.85
cycloheptane	0.88	0.91	0.92	0.94
pent-1-ene	0.78	0.80	0.82	0.85
hex-1-ene	0.88	0.90	0.92	0.97
hept-1-ene	1.00	1.02	1.04	1.09
oct-1-ene	1.11	1.14	1.16	1.21
hex-1-yne	0.66	0.68	0.71	0.74
hept-1-yne	0.59	0.63	0.66	0.70
oct-1-yne	0.53	0.55	0.58	0.63
benzene	0.38	0.39	0.40	0.42
methanol	1.26	1.24	1.23	1.23
ethanol	1.36	1.33	1.31	1.30
1-propanol	1.42	1.40	1.39	1.38

Table 5. Partial Molar Excess Enthalpy at Infinite Dilution, $\Delta H_1^{E\infty}$, ± 0.1 kJ·mol^{-1} Values Calculated from the Gibbs−Helmholtz Equation for Solutes in the Ionic Liquid [3C$_6$C$_{14}$P][Tf$_2$N]

solute	$H_i^{E,\infty}$/kJ·mol^{-1}
pentane	−4.5
hexane	−3.5
heptane	−3.2
octane	−5.2
cyclopentane	−4.3
cyclohexane	−4.0
cycloheptane	−3.2
pent-1-ene	−4.8
hex-1-ene	−5.0
hept-1-ene	−4.7
oct-1-ene	−4.6
hex-1-yne	−5.7
hept-1-yne	−9.2
oct-1-yne	−9.7
benzene	−5.3
methanol	1.4
ethanol	2.0
1-propanol	1.6

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 Controller fitted with a low heat capacity intermittent heater. 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 (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 percent of IL, 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 uncertainty of the calculated overall value of γ_{13}^∞ is 3 %, taking into account the possible errors in determining the column loading, the carrier gas flow rate, the retention times, and solute vapor 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.[3]

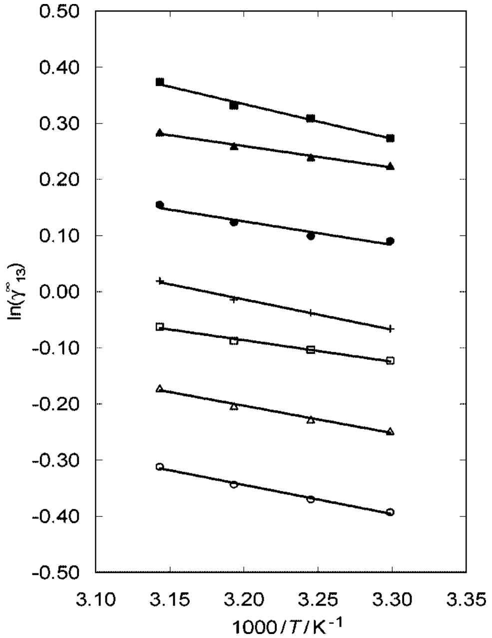


Figure 1. Plot of $\ln(\gamma^{\infty}_{13})$ versus $1/T$ for the solutes: +, pentane; ●, hexane; ▲, heptane; ■, octane; ○, cyclopentane; Δ, cyclohexane; □, cycloheptane.

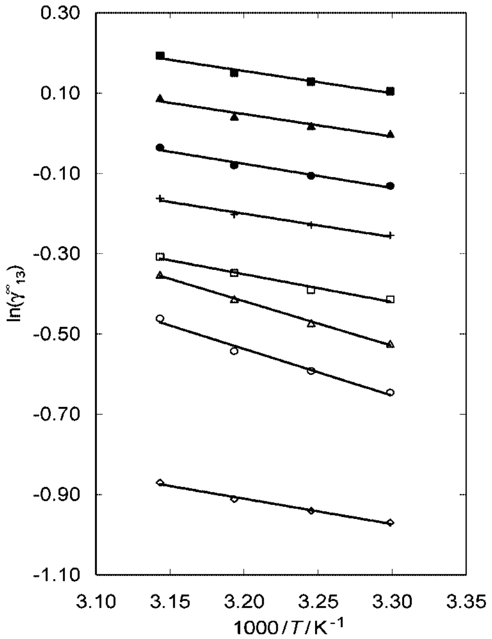


Figure 2. Plot of $\ln(\gamma^{\infty}_{13})$ versus $1/T$ for the solutes: +, pent-1-ene; ●, hex-1-ene; ▲, hept-1-ene; ■, oct-1-ene; ○, hex-1-yne; Δ, hept-1-yne; □, oct-1-yne; ◇, benzene.

Theory. The equation developed by Everett[13] and Cruickshank[14]

$$\ln \gamma^{\infty}_{13} = \ln\left(\frac{n_3 RT}{V_N P^*_1}\right) - \left(\frac{(B_{11} - V^*_1)P^*_1}{RT}\right) + \left(\frac{(2B_{12} - V^{\infty}_1)P_o J^3_2}{RT}\right) \quad (1)$$

was used in this work to calculate the γ^{∞}_{13} values of solutes in the involatile solvent $[3C_6C_{14}P][Tf_2N]$. In this work, the subscript 1 refers to a solute, 2 to the carrier gas, and 3 to the solvent $[3C_6C_{14}P][Tf_2N]$. V_N denotes the net retention volume of the solute, P_o the outlet pressure, $P_o J^3_2$ 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 and the carrier gas. The values of B_{11} and B_{12} were calculated using the McGlashan and Potter[15] equation

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

where n refers to the number of carbon atoms. Using the Lorentz and Hudson and McCoubrey[16,17] combining rules, V^c_{12} and T^c_{12} were calculated from the critical properties of the pure component. The vapor pressure values were calculated using the Antoine equation and constants taken from the literature.[18,19] Critical data and ionization energies used in the calculation of T^c_{12} were obtained from the literature.[20,21] The critical data used to calculate B_{11} and B_{12}, and ionization energies used in the calculation of T^c_{12}, 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 saturated liquid molar volumes, V^0_1, were calculated through the use of the Modified Rackett equation.[21] 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.

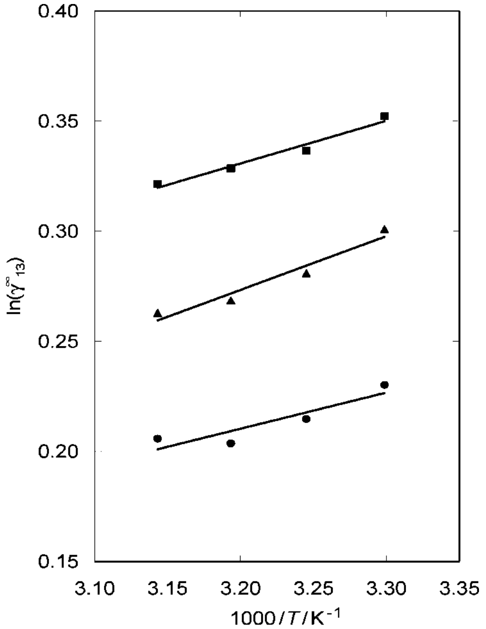


Figure 3. Plot of $\ln(\gamma^{\infty}_{13})$ versus $1/T$ for the solutes: ●, methanol; ▲, ethanol; ■, propan-1-ol.

Results and Discussion

Table 3 lists the γ^{∞}_{13} values at T = (303.15, 308.15, 313.15, and 318.15) K for different amounts 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 alcohols using GLC because of the possibility of adsorption onto the solid support. However, in this work, the alcohol peaks were found to be symmetrical, and the activity coefficients at infinite dilution were independent of the carrier gas flow rate, indicating no significant adsorption. This is, no doubt, due to the high column packing which masks the solid support from the polar solute.[14] The γ^{∞}_{13} values obtained for alk-1-ynes and

Table 6. Selectivities S_{12}^{∞} and Capacities k_2^{∞} at Infinite Dilution for $[3C_6C_{14}P][Tf_2N]$, Several Ionic Liquids, NMP, and Sulfolane for Different Separation Problems at $T = 308.15$ K

	S_{12}^{∞}		k_2^{∞}	
solvent	hexane (1) + benzene (2)	hex-1-ene (1) + benzene (2)	cyclohexane (1) + benzene (2)	benzene
$[3C_6C_{14}P][Tf_2N]$	2.8	2.3	2.0	2.6
$[3C_6C_{14}P][(C_8H_{17})_2PO_2]$[a]	1.5	1.4	1.1	2.1
$[3C_6C_{14}P][(C_2F_5)_3PF_6]$[b]	3.3	2.6	2.45	5
$[MMIM][(CH_3)_2PO_4]$[c,k]	103[c]	26.6[l]	13.4	0.28
[EMIM][TFA][d]	28.3	11.8	13.5	0.36
$[MMIM][Tf_2N]$[e]	28.5[k]	12.5	16.21[k]	0.75[k]
$[EMIM][Tf_2N]$[e]	22.5[k]	10.4	12.6[k]	0.84[k]
$[HMIM][Tf_2N]$[f]	11.8[k]	6.8[k]	7.7[k]	1.5[k]
$[BMIM][MDEGSO_4]$[g]	35.0	15.5	14.9	0.49
[EMIM][SCN][h]	84.3	28.1	29.9	0.29
NMP[i]	11.9[k]	6.1[k]	7.3[k]	0.95[k]
NMP + 3 % (w/w) water[i]	14.5[k]	7.5[k]	8.7[k]	0.72[k]
NMP + 6 % (w/w) water[i]	17.1[k]	8.4[k]	9.8[k]	0.52[k]
sulfolane[j]	18.64[k]	-	10.4[k]	0.42[k]

[a] From ref 2. [b] From ref 1. [c] From ref 4. [d] From ref 25. [e] From ref 6. [f] From ref 7. [g] From ref 26. [h] From ref 27. [i] From ref 9. [j] From ref 8. [k] Interpolated values. [l] For the system hept-1-ene/benzene.

benzene are lower than the values for the alkanes, alkenes, cycloalkanes, and alcohols. The low values for the alk-1-ynes and the benzene can be explained as being due to the interaction of the delocalized π electrons with the positive charge on the cation of the IL. For the alcohols, the low values can be attributed to the interactions between the lone pair of electrons on the oxygen atom of the alcohol with the positively charged anion of the ionic liquid and between the acidic proton of the alcohol and the oxygen atoms of the anion. It is interesting that the values for alkanes are similar to the values of alcohols, which implies that the van der Waal's interactions between alkanes and the alkane chains of cations are of the same order of magnitude as the alcohol/IL interactions. This is probably due to the large alkyl chains on the cation. The values of γ_{13}^{∞} for alkanes increase as the number of carbon atoms of alkane increases, as was observed for many ILs. Our data indicate that no adsorption is observed, while it is well-known that hydrocarbons are prime candidates for interfacial adsorption, as tested in recently published works.[22,23] However, the γ_{13}^{∞} values for alkanes and 1-hexadecyl-3-methylimidazolium tetrafluoroborate, $[C_{16}MIM][BF_4]$, reveal that no adsorption was observed.[24] It seems to be a generality for the long chain substituent at the imidazolium ring of the ionic liquid. For all solutes in this work, the γ_{13}^{∞} values change little with temperature (see Table 4), and the values of γ_{13}^{∞} increase with an increase of temperature (with the exception of alcohols). The values of γ_{13}^{∞} presented in Table 4 should be read as $\gamma_{13}^{\infty} \pm 3$ %.

Table 5 lists the partial molar excess enthalpies at infinite dilution, $\Delta H_1^{E\infty}$, values which 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 calculated $\Delta H_1^{E\infty}$, independent of temperature values, were found to be negative for all solutes other than the alcohols. Even though the temperature range is small (only 15 degrees), the following discussion may be presented. The large negative values obtained for the alk-1-yne molecules (from −5.7 $\text{kJ}\cdot\text{mol}^{-1}$ to −9.7 $\text{kJ}\cdot\text{mol}^{-1}$) indicate a strong interaction between the alk-1-yne and the IL. This again is most likely due to the interactions mentioned above. These interactions are strong, in spite of the long alkyl chains on the cation, and imply that the possible steric hindrance due to these chains is unimportant. The $\Delta H_1^{E\infty}$ values for alcohols are positive (from 1.6 $\text{kJ}\cdot\text{mol}^{-1}$ to 2.0 $\text{kJ}\cdot\text{mol}^{-1}$) and can be thought of as being due to the breakdown of the alcohol self-association on mixing. The deviations of the first-order function of $\ln(\gamma_{13}^{\infty})$ versus $1/T$, presented in Figures 1 to 3, were caused by the very small dependence of γ_{13}^{∞} on temperature. The uncertainties of $\Delta H_1^{E\infty}$ can be assumed as ± 0.1 $\text{kJ}\cdot\text{mol}^{-1}$. In the cycloalkane series, the $\Delta H_1^{E\infty}$ values decrease with increasing carbon number as for many ILs.

One interesting result is seen when comparing the $\Delta H_1^{E\infty}$ values for alkanes and benzene in different, but related, ionic liquids. The $\Delta H_1^{E\infty}$ values for hexane and benzene in $[3C_6C_{14}P][Tf_2N]$ are −3.5 $\text{kJ}\cdot\text{mol}^{-1}$ (this work) and −5.3 $\text{kJ}\cdot\text{mol}^{-1}$ (this work), respectively, and for hexane and benzene in $[3C_6C_{14}P][(C_8H_{17})_2PO_2]$, the results are 3.2 $\text{kJ}\cdot\text{mol}^{-1}$ and −6.1 $\text{kJ}\cdot\text{mol}^{-1}$, respectively.[2] The similarity could be due to the common cation, and the relatively large values for hexane are probably again due to the van der Waals interaction between the hexane and the long alkyl chains of the cation. However, other published values of the $\Delta H_1^{E\infty}$ for another related IL with the same cation ($[3C_6C_{14}P][(C_2F_5)_3PF_6]$) are small, but positive.[1] For other ILs of different cation composition, for which data are available, it is our experience that large positive values of $\Delta H_1^{E\infty}$ were observed for hexane, and small negative values were observed for benzene.[4–7,25–27]

The selectivity, $S_{ij}{}^{\infty}$, values are given in Table 6 together with the literature values for a few other ILs and for a few solvents that are used in industry for the separation of aromatics from aliphatics. 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, hex-1-ene, or cyclohexane and j to benzene. The selectivity, $S_{ij}{}^{\infty} = 2.8$, for $[3C_6C_{14}P][Tf_2N]$ at $T = 308.15$ K is very small, compared to the value for sulfolane (18.63 for hexane/benzene)[7] or other ionic liquids, such as $[EMIM][Tf_2N]$ (22.5 for hexane/benzene).[5] This result highlights the important role of choosing the proper ionic liquid for separating organic liquids such as aromatics from aliphatic compounds by an extractive distillation. The small selectivity value obtained here indicates that the ionic liquid $[3C_6C_{14}P][Tf_2N]$ is not the best solvent for use in solvent extraction processes for separating aromatic compounds from aliphatic compounds. The results from this work show the influence of the cation's alkyl chain length on fundamental thermodynamic properties. An important observation found by comparing results from this work with related work from the literature is that the magnitude of γ_{13}^{∞} for hexane in ILs decreases with an increase in the length of the alkyl chain on the cation or the anion of the IL.[5] In this work, the selectivity value S_{ij}^{∞} depends very strongly on the van der Waals interaction of alkane and alkane chain on the cation of the ionic liquid.

Conclusions

Activity coefficients at infinite dilution for 18 various solutes in the ionic liquid trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide $[3C_6C_{14}P][Tf_2N]$ have been determined by gas−liquid chromatography at temperatures $T = (303.15, 308.15, 313.15, \text{and } 318.15)$ K. It was found that the investigated ionic liquid shows very low selectivity at infinite dilution for the separation of aromatic and aliphatic hydrocarbons. This IL is not the best one for use in solvent extraction processes for separating aromatic compounds from aliphatic compounds. This result shows again the influence of the cation's alkyl chain length.

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