Activity Coefficients at Infinite Dilution of Alkanes, Alkenes, and Alkyl Benzenes in 1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate Using Gas−Liquid Chromatography

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Activity coefficients at infinite dilution, γ_i^∞, have been determined for 17 organic solutes, alkanes, alkenes, and alkyl benzenes, in the ionic liquid 1-propyl-2,3-dimethylimidazolium tetrafluoroborate ([PDMIM][BF_4]) by the gas−liquid chromatographic method with the ionic liquid as the stationary phase. The measurements were carried out in the temperature range of 303.15 K to 363.15 K. The partial molar excess enthalpies at infinite dilution, $H_i^{E,\infty}$, were also determined for the solutes from the temperature dependence of the γ_i^∞ values.

Introduction

This work is a continuation of our studies on the determination of activity coefficients at infinite dilution by the gas−liquid chromatographic (GLC) method for ionic liquids.[1,2]

Experimental Section

The ionic liquid 1-propyl-2,3-dimethylimidazolium tetrafluoroborate ([PDMIM][BF_4]) was purchased from Hang Zhou Chemer Chemical Co., Ltd. Its purity was above 99 % (mass), with the following certified amounts of impurities: [Cl^-] < 500 ppm, water < 1000 ppm. The hydrocarbons provided by Beijing Chemical Reagents Company were analytical reagents. The solutes were used without further purification.

The GLC apparatus, column preparation, packing method, and experimental process in this work are the same as those described by Zhou.[1,2] In this work, dry nitrogen was used as the carrier gas, and ethanol was used as solvent to coat the ionic liquid onto the solid support.

The values of infinite dilution, γ_i^∞, were obtained by the equation proposed by Cruickshank et al.[3] and Everett.[4] For all solutes, values of the vapor pressure of the pure liquid solute (i), P_i^0, were calculated from the Antoine equation, with Antoine coefficients given by Boublik et al.,[5] which are given in Table 1. The liquid molar volumes of pure solute, V_i^0, were estimated using experimental values of their densities; the partial molar volumes of the solute, V_i^∞, have been assumed to be equal to V_i^0. Values of B_{11} and B_{12} have been estimated according to the Tsonopolous method[6] with an uncertainty of < ± 10 $cm^3 \cdot mol^{-1}$. The critical parameters needed for the calculations were available from the literature,[6] which are given in Table 2. The mixed critical properties, P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and mixed acentric factor ω_{ij} were calculated by using equations given in the literature.[6,7] The pressure drop was recorded by GC automatically with an uncertainty of ± 0.2 kPa. The errors in the γ_i^∞ were obtained from the law of propagation of errors. The uncertainties in the measured and derived quantities are listed in Table 3.

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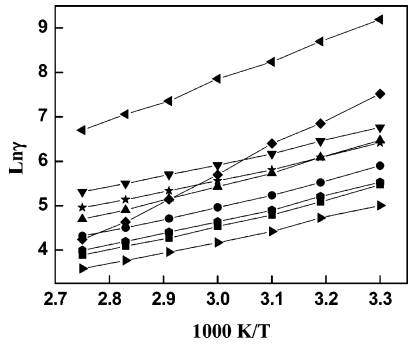

Figure 1. Plot of ln $\gamma_{i,3}^\infty$ vs 1/T for the solutes: ■, pentane; ●, hexane; ▲, heptane; ▼, octane; ◆, nonane; solid triangle pointing left, decane; solid triangle pointing right, cyclohexane; solid oval, methylcyclohexane; ★, 2,2,4-trimethylpentane.

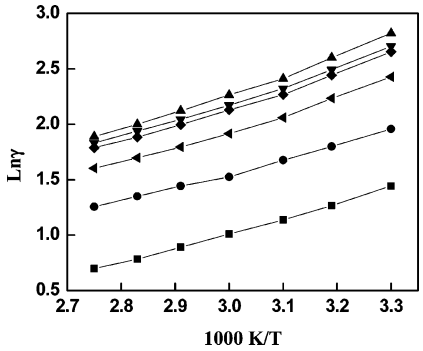

Figure 2. Plot of ln $\gamma_{i,3}^\infty$ vs 1/T for the solutes: ■, benzene; ●, toluene; ▲, ethyl benzene; ▼, *m*-xylene; ◆, *p*-xylene; solid triangle pointing left, *o*-xylene.

Results and Discussion

The values of γ_i^∞ of different solutes in [PDMIM][BF_4] obtained over a temperature range of 303.15 K to 363.15 K were listed in Table 4. The results of γ_i^∞ were correlated with temperature by the following equation

$$\ln \gamma_i^\infty = a + \frac{b}{(T/\mathrm{K})} \tag{1}$$

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Table 1. Vapor Pressure P_i^0 of the Solutes (i) from T = 303.15 K to 363.15 K

	P_i^0/kPa						
solutes (i)	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15	T/K = 353.15	T/K = 363.15
			Alkanes				
pentane	82.0	116	159	214	283	367	480
hexane	24.9	37.3	54.1	76.4	105	143	189
heptane	7.79	12.3	18.9	28.1	40.5	57.1	78.6
octane	2.46	4.14	6.69	10.5	15.9	23.1	33.4
nonane	0.782	1.41	2.41	4.03	6.31	9.81	14.5
decane	0.245	0.473	0.865	1.51	2.52	4.06	6.33
2,2,4-trimethylpentane	8.33	13.0	19.5	28.6	43.5	56.8	77.4
cyclohexane	16.2	24.6	36.3	51.9	72.5	99.0	132
methylcyclohexane	7.83	12.2	18.4	27.0	38.6	53.9	73.6
			Alkenes				
cyclohexene	16.0	22.6	35.4	48.1	70.4	92.7	129
styrene	1.08	1.89	3.18	5.14	8.02	12.1	17.8
			Alkyl Benzenes				
benzene	15.9	24.3	36.2	52.2	73.5	101	136
toluene	4.89	7.89	12.3	18.6	27.2	38.9	54.3
ethylbenzene	1.68	2.87	4.69	7.40	11.3	16.8	24.3
o-xylene	1.78	2.04	3.40	5.44	8.43	12.7	18.6
m-xylene	1.49	2.55	4.18	6.63	10.2	15.2	22.0
p-xylene	1.55	2.27	4.34	6.94	10.5	15.6	22.7

Table 2. Critical Constants Z_c, T_c, P_c, and V_c and Acentric Factors ω of the Solutes and the Carrier Gas Used in the Calculation of the Virial Coefficients

solute (i)	Z_c	T_c/K	P_c/bar	V_c/cm^3·mol^{-1}	ω
		Alkanes			
pentane	0.268	470	33.7	311	0.252
hexane	0.264	508	30.3	368	0.30
heptane	0.261	540	27.4	428	0.350
octane	0.259	569	24.9	492	0.399
nonane	0.252	595	22.9	555	0.445
decane	0.256	618	21.1	624	0.49
cyclohexane	0.273	554	40.7	308	0.211
methylcyclohexane	0.268	572	34.7	368	0.235
2,2,4-trimethylpentane	0.266	544	25.7	470	0.304
		Alkenes			
cyclohexene	0.27	560	42.9	292	0.210
styrene	0.274	647	39.4	374	0.257
		Alkyl Benzenes			
benzene	0.268	562	49.0	256	0.210
toluene	0.264	592	41.1	316	0.264
ethyl benzene	0.263	617	36.1	374	0.304
o-xylene	0.263	630	37.3	370	0.312
m-xylene	0.259	617	35.4	375	0.327
p-xylene	0.259	616	35.1	378	0.322
nitrogen	0.290	126	33.5	89.5	0.0400

Table 3. Uncertainties in the Measured and Derived Quantities

parameters	uncertainty
$t_r - t_G$	± 3.3 %
U_0	± 0.5 %
P_i	± 0.6 %
P_o	± 0.02 %
J	± 1 %
P_i^0	± 0.01 % to ± 0.25 %
n_3	± 0.5 %
$\gamma_{i,3}^{\infty}$	± 4 %

According to the Gibbs−Helmholtz equation, the value for the partial molar excess enthalpy at infinite dilution, $H_i^{E,\infty}$, can be obtained from the slope of a straight line derived from eq 1.

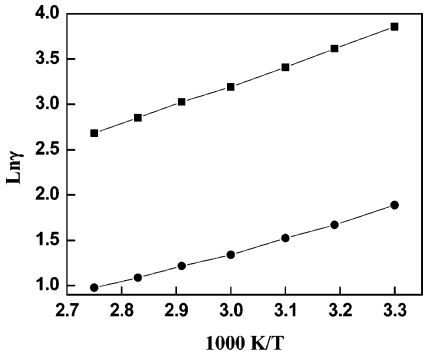

Figure 3. Plot of ln $\gamma_{i,3}^{\infty}$ vs 1/T for the solutes: ■, cyclohexene; ●, styrene.

The coefficients a and b, the correlation coefficient R^2, the standard deviation σ of the fitted equation, γ_i^{∞} at 298.15 K calculated using eq 1, and values of $H_i^{E,\infty}$ derived from eq 1 are listed in Table 5. The plots of measured ln γ_i^{∞} vs 1/T values are given in Figures 1 to 3, which showed a fairly good fitting quality of eq 1.

The selectivity S_{ij}^{∞} is defined below[8]

$$S_{ij}^{\infty} = \frac{\gamma_{i,3}^{\infty}}{\gamma_{j,3}^{\infty}} \tag{2}$$

The values of selectivity, S_{ij}^{∞}, for the separation of a hexane (i)/benzene (j) mixture at T = 298.15 K using different ILs and some very polar solvents obtained from the literature[9,10] and from this work are presented in Table 6. The results indicated that [PDMIM][BF_4] is an ideal extraction solvent for separation of the hexane and benzene binary system.

A more accurate treatment for infinite dilution activity coefficient measurement by GC was discussed in the work of Nutelet and Jaubert,[11] and the retention mechanism of neutral organic compounds on the polar liquid stationary phase was investigated by Ali and Poole.[12] On the basis of their analysis,

Table 4. Experimental Activity Coefficients at Infinite Dilution for Various Solutes in the Ionic Liquid 1-Propyl-2,3-dimethylimidazolium Tetrafluoroborate as the Stationary Phase at Temperatures of 303.15 K to 363.15 K

solutes (*i*)	T/K = 303.15	T/K = 313.15	T/K = 323.15	T/K = 333.15	T/K = 343.15	T/K = 353.15	T/K = 363.15
			Alkanes				
pentane	236.7	162.0	120.5	92.81	71.52	59.77	48.47
hexane	364.4	250.5	187.0	142.7	111.0	90.25	75.11
heptane	644.7	441.1	307.8	227.4	173.8	134.6	109.5
octane	864.8	634.4	475.1	369.4	299.1	244.2	202.9
nonane	1843	944.0	602.3	297.0	170.4	102.6	69.5
decane	9813	5975	3788	2579	1566	1164	814.2
cyclohexane	149.2	112.8	83.3	64.7	52.2	43.2	36.1
methylcyclohexane	251.5	182.6	134.3	103.2	82.1	66.1	54.2
2,2,4-trimethylpentane	611.6	439.9	333.4	259.6	208.6	169.7	142.0
			Alkenes				
cyclohexene	47.24	37.13	30.18	24.34	20.65	17.31	14.62
styrene	6.606	5.314	4.587	3.817	3.378	2.967	2.653
			Alkyl Benzenes				
benzene	4.239	3.551	3.123	2.745	2.436	2.193	2.011
toluene	7.082	6.048	5.351	4.594	4.323	3.861	3.514
ethylbenzene	16.81	13.50	11.16	9.630	8.356	7.396	6.616
o-xylene	11.33	9.341	7.855	6.793	6.022	5.455	4.970
m-xylene	14.93	12.11	10.21	8.773	7.734	6.948	6.253
p-xylene	14.22	11.50	9.645	8.414	7.367	6.576	5.980

Table 5. Coefficients of Equation 1, *a* and *b*, Correlation Coefficient R^2, γ_i^∞ at 298.15 K Calculated Using Equation 1, Values of $H_i^{E,\infty}$ Derived from Equation 1, and Standard Deviation σ

solute *i*	*a*	*b* / K	R^2	$\gamma_{i\ 298.15K}^{\infty}$[a]	$H_i^{E,\infty}$[b] / kJ·mol^{-1}	σ
			Alkane			
pentane	−4.07	2874	0.998	262.3	23.89	0.0411
hexane	−3.67	2885	0.998	406.0	23.99	0.0384
heptane	−4.34	3264	0.999	740.6	27.14	0.0350
octane	−2.02	2653	0.999	971.9	22.06	0.0266
nonane	−12.7	6118	0.999	2490	50.87	0.0654
decane	−5.93	4580	0.999	$1.247 \cdot 10^3$	38.08	0.0347
cyclohexane	−3.68	2625	0.999	168.1	21.82	0.0288
methylcyclohexane	−3.78	2813	0.999	285.7	23.39	0.0246
2,2,4-trimethylpentane	−2.42	2667	0.999	682.1	22.17	0.0283
			Alkene			
cyclohexene	−3.21	2138	0.999	52.50	17.78	0.0100
styrene	−3.62	1662	0.998	7.060	13.82	0.0210
			Alkyl Benzenes			
benzene	−3.07	1362	0.9987	4.473	11.32	0.0145
toluene	−2.28	1278	0.9975	7.437	10.63	0.0193
ethylbenzene	−2.81	1696	0.9975	17.79	14.10	0.0256
o-xylene	−2.55	1582	0.9967	15.74	13.15	0.0266
m-xylene	−2.58	1576	0.9967	14.97	13.10	0.0276
p-xylene	−2.58	1509	0.9962	11.96	12.55	0.0284

[a] Range of uncertainties is within ± 4 %. [b] Range of uncertainties is within ± 6 %.

Table 6. Selectivities, S_{ij}^{∞}, at Infinite Dilution of Various Solvents for the Hexane (*i*)/Benzene (*j*) Separation at T = 298.15 K

solvents	S_{ij}^{∞}
sulfolane[a]	30.5
dimethylsulfoxide[a]	22.7
diethylene glycol[a]	15.4
N-methyl-2-pyrrolidinone[a]	12.5
aniline[a]	11.2
[MMIM][BTI][b]	27
[EMIM][$EtOSO_3$][a]	41.4
[BMIM][BTI][b]	15
[HMIM][PF_6][a]	21.6
[HMIM][BF_4][a]	23.1
[BMIM][BF4][c]	63.7
[MBPY][BF_4][b]	18
[OMIM][Cl][b]	9
[PDMIM][BF_4][d]	90.77

[a] Ref 9. [b] Ref 10. [c] Ref 1. [d] This work.

the values of γ_i^∞ reported in this work might have a tendency of underestimation.

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