J. Chem. Eng. Data **2005,** *50,* 1515−1519

Thermodynamic Properties of Mixtures Containing Ionic Liquids. 6. Activity Coefficients at Infinite Dilution of Hydrocarbons, Alcohols, Esters, and Aldehydes in 1-Methyl-3-octyl-imidazolium Tetrafluoroborate Using Gas−Liquid Chromatography

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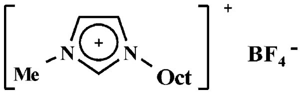
Activity coefficients at infinite dilution γ_i^∞ of alkanes, alkenes, and alkylbenzenes as well as of the linear and branched C_1-C_6 alcohols, esters, and aldehydes in the ionic liquid 1-methyl-3-octyl-imidazolium tetrafluoroborate were determined by gas chromatography using the ionic liquid as the stationary phase. The measurements were carried out at different temperatures between 302 K and 396 K. Data points (204) have been obtained for 51 solutes. From the temperature dependence of the limiting activity coefficients, partial molar excess enthalpies at infinite dilution $H_i^{E,\infty}$ of the solutes in the ionic liquid have been derived.

Introduction

"Green chemistry" (or clean technology) stands for the efforts made in reducing waste from an industrial chemical process to a minimum. It requires the rethinking and redesign of many current chemical processes. Ionic liquids are becoming recognized as novel solvents for green industrial chemistry. This work continues our study of the thermodynamic properties of mixtures containing ionic liquids.[1−4] Our interest in ionic liquids is focused on providing systematic data on activity coefficients in mixtures with organic solvents.

In this work, we extend our measurements of limiting activity coefficients γ_i^∞ in ionic liquids to the compound 1-methyl-3-octyl-imidazolium tetrafluoroborate ($C_{12}H_{23}BF_4N_2$)



having a molar mass of 279.2 and the common abbreviation [OMIM][BF_4].

Because ionic liquids have a negligible vapor pressure, the most suitable method for measuring limiting activity coefficients of volatile solutes in ionic liquids is the gas−liquid chromatographic method using the ionic liquid as the stationary phase. A series of hydrocarbons such as alkanes, alkenes, and alkylbenzenes as well as linear and branched C_1-C_6 alcohols, esters, aldehydes, and several common solvents (acetone, acetonitrile, and 1,4-dioxane) in the ionic liquid [OMIM][BF_4] have been studied over the temperature range of (302 to 396) K.

Experimental Procedure

Materials. The samples of solutes studied were of commercial origin. GC analysis gave a purity >99.9% in agreement with specifications stated by the suppliers. All chemicals were used without further purification. [OMIM][BF_4] was supplied by the research group of Professor Wasserscheid in Erlangen. Before use, the IL was subjected to vacuum evaporation at 333 K over 24 h to remove possible traces of solvents and moisture. The water concentration (<100 ppm) was determined by Karl Fischer titration. Chromosorb W/AW-DMCS 100/120 mesh was used as the solid support for the ionic liquid in the GC column. Before use, chromosorb was subjected to vacuum treatment with heating in order to remove traces of adsorbed moisture.

Experimental Procedure. Coating the solid support material with the ionic liquid was performed by dispersing a certain portion of chromosorb in a solution of the ionic liquid in dichloromethane followed by evaporation of the solvent using a rotating evaporator. The chromosorb was weighed before and after the coating process. The experiments were performed with a Varian-3600 gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. Nitrogen was used as the carrier gas. Two different GC columns (stainless steel) with lengths of 43 cm and 105 cm with an inside diameter of 0.40 cm have been used. The amounts of stationary phase (ionic liquid) were 3.99 mmol for the short column and 8.77 mmol for the longer one. The masses of the stationary phase were determined with a precision of ±0.0003 g. To avoid possible residual adsorption effects of the solutes on chromosorb, the amount of ionic liquid was about 60 mass % of the support material.

According to Cruickshank et al.,[5] the following equation for the data treatment has been used

$$\ln \gamma_{i,3}^\infty = \ln\left(\frac{n_3 RT}{V_N p_1^0}\right) - \frac{B_{11} - V_1^0}{RT} p_1^0 + \frac{2B_{12} - V_1^\infty}{RT} J p_0 \quad (1)$$

where $\gamma_{i,3}^\infty$ is the activity coefficient of component i at infinite dilution in the stationary phase (index 3), p_1^0 is the vapor pressure of the pure liquid solute, n_3 is the number of moles of the stationary phase component (ionic liquid)

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10.1021/je050134y CCC: $30.25

on the column, and V_N is the standardized retention volume obtained by

$$V_N = JU_0(t_r - t_G)\frac{T_{col}}{T_f}\left[1 - \frac{p_{ow}}{p_o}\right] \tag{2}$$

where t_r is the retention time, t_G is the dead time, U_0 is the flow rate measured by a soap bubble flowmeter, T_{col} is the column temperature, T_f is the flowmeter temperature, p_{ow} is the saturation pressure of water at T_f, and p_o is the pressure at the column outlet.

The second and third terms in eq 1 are correction terms that arise from the nonideality of the mobile gaseous phase. B_{11} is the second virial coefficient of the solute, B_{12} is the mixed virial coefficient of the solute (1) with the carrier gas nitrogen (2), V_1^0 is the liquid molar volume of pure solute, and V_1^∞ is the partial molar volume of solute in the ionic liquid at infinite dilution.

The factor J appearing in eqs 1 and 2 corrects for the influence of the pressure drop along the column given by[6]

$$J = \frac{3(p_i/p_o)^2 - 1}{2(p_i/p_o)^3 - 1} \tag{3}$$

where p_i and p_o are the inlet and the outlet pressure of the GC column, respectively.

Outlet pressure p_o was kept equal to atmospheric pressure. The pressure drop $(p_i - p_o)$ was varied between (20.3 and 101.3) kPa, providing suitable retention times with sharp peaks. The pressure drop and the outlet pressure were measured using a membrane manometer with an uncertainty of ±0.2 kPa.

Volumes of the samples injected into the GC were (0.5 to 2) μL. No differences in retention times t_r were found by injecting individual pure components or their mixtures with both columns containing different masses of the ionic liquids, respectively. This fact indicates that different concentrations of the solute in the stationary phase caused by different ratios of the injected amounts of solute and the amount of stationary phase do not affect the results, and it can be concluded that in all cases the state of infinite dilution was realized to a high degree of approximation. Experiments were carried out at four to five temperatures (in steps of 10 °) between 302 K and 396 K. The temperature of the GC column was maintained constant to within ±0.01 K. At a given temperature, each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible to within (0.01 to 0.03) min. Absolute values of retention times varied between (3 and 30) min depending on the individual solute. At each temperature, values of the dead time t_G identical to the retention time of a nonretainable component were measured. Although our GC was equipped with a flame ionization detector, methane[1] was used as a nonretainable component under the assumtion that the effect of the solubility of methane in an ionic liquid is negligible. This assumption has been justified by the fact that we can attest to our experimental procedure with the reliable γ_i^∞ data of hexane, heptane, and benzene in hexadecane.[1]

To check the stability of the experimental conditions, such as the possible eluation of the stationary phase by the nitrogen stream, the measurements of retention times were repeated systematically every (2 to 3) days for three selected solutes. No changes in the retention times were observed during 3 months of continuous operation.

Data needed for calculating the correction terms in eq 1 have been obtained in the following way. Molar volumes of solutes V_1^0 were estimated using experimental values of their densities, and partial molar volumes of solute at infinite dilution V_1^∞ have been assumed to be equal to V_1^0. Values of B_{11} have been estimated according to Tsonopolous' method.[7] Critical parameters needed for the calculations were available from the literature.[7] If these data were not available, then values of the critical pressure P_c, the critical temperature T_c, and the critical volume T_c were estimated using Lydersen's method.[8] Acentric factors ω_i were calculated by Edminster's equation.[8] More details are given in the Supporting Information. Values of B_{12} have also been estimated according to Tsonopolous' method. The mixed critical properties P_{cij}, T_{cij}, V_{cij}, and Z_{cij} and mixed acentric factor ω_{ij} were calculated by equations given in the literature.[7,8]

Values of vapor pressures p_1^0 of pure solutes are of a crucial importance to the reliability of γ_i^∞. For alkanes, these values were calculated using parameters of the Cox equation recommended by Ruzicka and Majer.[9] For alkenes values of p_1^0 were calculated using parameters of the Cox equation recommended by Steele and Chirico.[10] Vapor pressures of pure alcohols were calculated using coefficients of Wagner's equation recommended by Ambrose and Walton.[11] A specification of the sources of vapor pressures of other solutes is given in Table 1.

The validity of the experimental procedure has been checked by comparison of our measured values of γ_i^∞ for hexane, heptane, and benzene in hexadecane with those available in the literature.[1] The procedure of the experimental error estimation was described in our previous work.[1] Values of γ_i^∞ are estimated to be accurate to within ±3%.

As a rule, about 30% of an IL is considered to be enough to cover the solid support completely, so adsorption on the solid surface can be excluded.[1-3] However, in our recent paper we have compared our results for γ_i^∞ from the GC technique with those obtained from the static method by extrapolating the values of γ_i to infinite dilution.[29-31] Some discrepancies have been discovered between the two methods when highly polar molecules such as methanol and ethanol have been studied in cases where the covering grade of the solid support was less than 50%.[31] This fact has been taken into consideration in this work, and we used a solid support covered with 60% of an IL. However, the discrepancy in the γ_i^∞ for methanol is still apparent because of residual adsorption effects with the solid support as well as most probably with the walls of tubing in the GC.

Results and Discussion

The values of γ_i^∞ of different solutes in [OMIM][BF$_4$] obtained at different temperatures are listed in Table 1. Altogether, 204 data points for 51 solutes have been obtained in the temperature range of (302 to 396) K. The complete set of data is available in the Supporting Information. The values of γ_i^∞ have been approximated by the linear regression

$$\gamma_i^\infty = a + bT \tag{4}$$

Coefficients a and b, correlation coefficients R^2, and the values of $\gamma_{i(298K)}^\infty$ calculated with these coefficients are also given in Table 1. The quality of the linear regression was very good because the correlation coefficients lie between 0.98 and 0.99.

Table 1. Experimental Results of γ_i^∞ for Different Solutes in [OMIM][BF$_4$]: Temperature Ranges, Coefficients of Equation 4, Correlation Coefficients R^2, γ_i^∞ at 298 K Calculated Using Equation 4, and Values of $H_i^{E,\infty}$ Derived from Equation 5

solute *i*	*T* interval/K	*a*	*b*/°C	R^2	γ_i^∞(298 K)	$H_i^{E,\infty}$/kJ·mol^{-1}	solute *i*	*T* interval/K	*a*	*b*/°C	R^2	γ_i^∞(298 K)	$H_i^{E,\infty}$/kJ·mol^{-1}
						Alkanes							
1-pentane	302.6−333.4	9.85	−0.0311	0.989	9.07	3.1	1-nonane	323.0−364.8	31.2	−0.1154	0.993	28.4	4.9
1-hexane	302.6−333.4	13.4	−0.0412	0.994	12.4	3.1	1-decane	333.4−375.3	40.0	−0.1438	0.970	36.4	5.3
1-heptane	302.6−333.4	18.1	−0.0858	0.999	16.0	5.0	1-undecane	344.1−375.2	70.8	−0.3962	0.997	60.9	11.7
1-octane	302.6−354.3	24.5	−0.0983	0.980	22.0	4.6	1-dodecane	344.1−375.2	91.6	−0.5485	0.986	77.9	13.3
						Alkenes							
1-pentene	302.0−343.8	4.76	0.0127	0.986	5.08	−2.0	1-nonene	312.6−375.3	18.7	−0.0900	0.985	16.5	7.2
1-hexene	302.0−333.3	7.39	−0.0132	0.975	7.06	1.6	1-decene	312.6−375.3	24.6	−0.1271	0.986	21.4	7.9
1-heptene	302.0−364.7	10.6	−0.0317	0.991	9.76	3.4	1-undecene	344.1−375.3	29.5	−0.1481	0.996	25.8	9.6
1-octene	312.2−364.7	14.2	−0.0454	0.995	13.1	3.8	1-dodecene	344.1−375.3	37.7	−0.2012	0.997	32.7	10.8
						Cyclic Hydrocarbons							
cyclohexane[a]	302.6−333.3	9.10	−0.0415	0.997	8.06	4.8	1,3-cyclohexadiene[b]	322.9−354.3	2.85	−0.0065	0.995	2.69	2.5
cyclohexene[b]	302.6−354.3	5.25	−0.0167	0.989	4.83	3.4							
						Alkylbenzene							
benzene[c]	322.9−364.7	1.23	−0.0014	0.986	1.19	1.2	propyl benzene[e]	364.9−396.3	4.29	−0.0178	0.997	3.85	9.0
toluene[d]	323.1−354.4	1.80	−0.0130	0.993	1.54	8.7	butyl benzene[e]	364.9−396.3	5.73	−0.0253	0.992	5.10	10.2
ethyl benzene[a]	323.1−354.4	2.55	−0.0106	0.997	2.29	5.5	pentyl benzene[e]	364.9−396.3	7.63	−0.0361	0.997	6.73	11.7
						Alcohols							
methanol	301.9−333.5	1.22	−0.0062	0.992	1.07	5.5	2-propanol[f]	343.7−375.2	1.74	−0.0095	0.993	1.51	11.2
ethanol	301.9−333.5	2.22	−0.0186	0.993	1.75	11.3	iso-butanol[f]	343.7−375.2	2.09	−0.0121	0.982	1.79	12.7
1-propanol	313.0−364.7	2.67	−0.0196	0.993	2.18	13.8	*sec*-butanol[f]	343.7−375.2	1.93	−0.0105	0.990	1.67	11.1
1-butanol	364.7−396.2	2.80	−0.0191	0.999	2.32	32.2	*tert*-butyl alcohol[f]	343.7−375.2	1.65	−0.0075	0.996	1.45	8.9
1-pentanol	364.7−396.2	2.82	−0.0178	0.998	2.38	24.0	tert-pentanol[g]	343.7−375.2	1.79	−0.0085	0.988	1.58	8.7
1-hexanol	364.7−396.2	3.01	−0.0170	0.999	2.58	17.5	cyclohexanol[h]	385.6−396.0	2.38	−0.0143	0.999	2.02	13.1
						Aldehydes							
propanal[i]	301.7−354.1	0.94	−0.0034	0.991	0.85	4.0	hexanal[l]	322.7−354.1	2.48	−0.0081	0.990	2.28	4.0
butanal[j]	301.7−354.1	1.23	−0.0039	0.986	1.13	3.4	heptanal[m]	333.2−385.5	3.01	−0.0183	0.994	2.55	10.2
pentanal[k]	301.7−354.1	2.23	−0.0062	0.998	2.07	3.0	octanal[l]	354.1−375.0	5.12	−0.0313	0.999	4.34	17.2
						Esters							
methyl propanoate[n]	302.9−333.5	1.55	−0.0045	0.996	1.43	2.8	methyl hexanoate[o]	323.2−375.4	3.57	−0.0173	0.991	3.14	7.3
methyl butanoate[n]	302.9−333.5	1.93	−0.0052	0.999	1.80	2.6	methyl heptanoate[o]	343.8−375.4	4.38	0.0239	0.997	3.78	11.1
methyl pentanoate[o]	323.2−375.4	2.67	−0.0133	0.999	2.33	8.1							
						Polar Solvents							
acetone[i]	301.6−333.2	0.89	−0.0045	0.972	0.78	5.5	1,4-dioxane[q]	323.0−343.6	0.92	−0.0025	0.999	0.86	2.8
acetonitrile[p]	312.3−343.6	0.70	−0.0032	0.996	0.62	5.4							

[a] Data from ref 12. [b] Data from ref 13. [c] Data from ref 14. [d] Data from ref 15. [e] Data from ref 16. [f] Data from ref 17. [g] Data from ref 18. [h] Data from ref 19. [i] Data from ref 20. [j] Data from ref 21. [k] Data from ref 22. [l] Data from ref 23. [m] Data from ref 24. [n] Data from ref 25. [o] Data from ref 26. [p] Data from ref 27. [q] Data from ref 28.

Table 2. Comparison of Values of γ_i^∞ at 298 K Dereived in This Work with Those Obtained by the Static Method[30a]

	γ_i^∞ this work	ref 30
benzene	1.34	1.19
methanol	0.69	1.07
ethanol	1.76	1.75
propanol	2.15	2.18

[a] See the text.

The activity coefficients of the linear *n*-alkanes, *n*-alkenes, alkylbenzenes, aldehydes, and esters increase with increasing chain length (Figure 1). Cyclization of the alkane skeleton (e.g., cyclohexane) reduces the value of γ_i^∞ in comparison to that of the corresponding linear alkanes (e.g., hexane). The introduction of the double bond in the six membered ring (cyclohexene, cyclohexadiene) also causes a decrease in γ_i^∞.

Values of γ_i^∞ for benzene and the alkylbenzenes are distinctly lower in comparison with those of the alkanes and alkenes. However, similar to the trend in the γ_i^∞ values for the alkanes, the γ_i^∞ values increase with increasing size of the alkyl group.

The activity coefficients of the linear *n*-alkanols increase with increasing chain length. The branching of the alkane skeleton (e.g., 2-propanol or *tert*-butyl alcohol) reduces the value of γ_i^∞ in comparison to that of the corresponding linear alcohol.

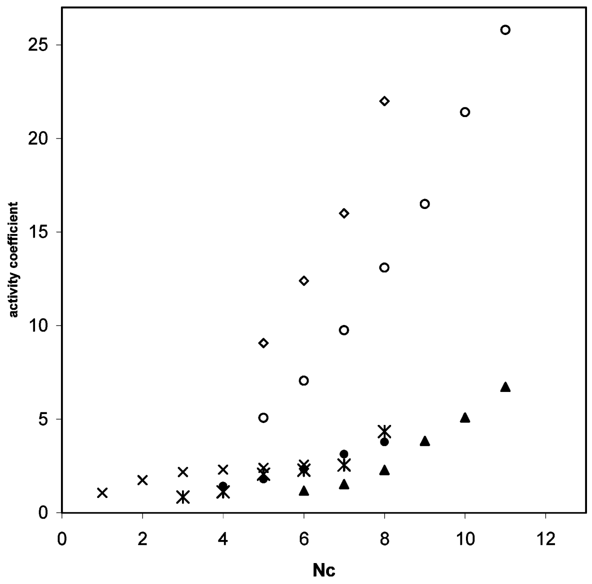

Figure 1. γ_i^∞as a function of the number of carbon atoms (Nc) for different classes of solutes in [OMIM][BF$_4$] at 298.15 K. ◇, Alkanes; ○, alkenes; ▲, alkylbenzenes; ×, alcohols; *, aldehydes; ●, esters.

Values of γ_i^∞ of aldehydes and esters are distinctly lower in comparison with those of the alkanes and alkenes.

The value for the partial molar excess enthalpy at infinite dilution $H_i^{\mathrm{E},\infty}$ can be directly obtained from the slope of a straight line derived from eq 5

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right) = \frac{H_i^{\mathrm{E},\infty}}{R} \qquad (5)$$

where R is the gas constant. The values of $H_i^{\mathrm{E},\infty}$ for the compounds studied are also listed in Table 1. The uncertainties in $H_i^{\mathrm{E},\infty}$ are estimated to be not better than ±10% because of the small slope of the ln γ_i^∞ versus $1/T$ plots. This is confirmed by comparison of $H_i^{\mathrm{E},\infty}$ of the diverse systems with direct calorimetric results.[31,32]

$H_i^{\mathrm{E},\infty}$ is positive and increases slightly with increasing chain length of the linear alkanes. The introduction of double bonds does not lower the positive values of $H_i^{\mathrm{E},\infty}$ significantly. Values of $H_i^{\mathrm{E},\infty}$ are positive and also increase slightly with increasing chain length of the linear alkanols.

In the meantime, the gas-chromatographic method of determining values of γ_i^∞ and $H_i^{\mathrm{E},\infty}$ in ILs has become a well-established procedure that has successfully been applied to various systems.[33−37] The dilutor technique is known as an equivalent procedure,[38−40] and a comparison of both techniques has revealed acceptable agreement.

Acknowledgment

We are grateful to Professor P. Wasserscheid (Technical University of Erlangen, Germany) for supplying the ionic liquid [OMIM][BF_4].

Supporting Information Available:

Critical constants and acentric factors of the solutes and the carrier gas used in the calculation of the virial coefficients. Experimental activity coefficients at infinite dilution for solutes in ionic liquid [OMIM][BF_4] as the stational phase at temperatures of 302 to 396 K. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review April 6, 2005. Accepted April 29, 2005. We are grateful to the German Science Foundation (DFG) for financial support.

JE050134Y