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Articles

Thermodynamic Properties of Mixtures Containing Ionic Liquids. 5. Activity Coefficients at Infinite Dilution of Hydrocarbons, Alcohols, Esters, and Aldehydes in 1-Methyl-3-butyl-imidazolium Bis(trifluoromethyl-sulfonyl) Imide Using Gas−Liquid Chromatography

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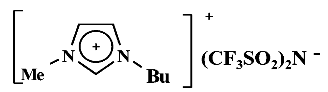
Activity coefficients at infinite dilution (γ_i^∞) of alkanes, alkenes, and alkylbenzenes as well as of the linear and branched C_1-C_7 alcohols, esters, and aldehydes in the ionic liquids 1-methyl-3-butyl-imidazolium bis(trifluoromethyl-sulfonyl) imide were determined by gas chromatography using the ionic liquid as stationary phase. The measurements were carried out at different temperatures between 302 K and 385 K. 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 liquids have been derived.

Introduction

This work continues our study of 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. Activity coefficients at infinite dilution of a solute i (γ_i^∞) can be used to quantify the volatility of the solute as well as to provide information about the intermolecular energy between solvent and solute. Values of γ_i^∞ can be used to calculate Henry's coefficients. They are also useful, in particular, for the selection of solvents for extraction and extractive distillation.

In this work we extend our measurements of γ_i^∞ in ionic liquids (IL) to the compound 1-methyl-3-butyl-imidazolium bis(trifluoromethyl-sulfonyl) imide ($C_{10}H_{15}S_2O_4F_6N_3$):



having the molar mass 419.3 and the common abbreviation [BMIM][NTf$_2$].

Since ILs 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 stationary phase. A series of hydrocarbons such as alkanes, alkenes, and alkylbenzenes as well as linear and branched C_1-C_7 alcohols, esters, aldehydes, and several common solvents (acetone, acetonitrile, *N*-methylpyrrolidone, and 1,4-dioxane) in the ionic liquid [BMIM][NTf$_2$] have been studied over the temperature range (302 to 385) K.

Experimental Procedures

Materials. The samples of solutes studied were of commercial origins. GC analysis gave a purity > 99.9 % in agreement with specifications stated by the suppliers. All chemicals were used without further purification. The [BMIM][NTf$_2$] was supplied by the research group of Prof. Wasserscheid in Erlangen. Prior to experiments, the IL was subjected to vacuum evaporation at 333 K for > 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 solid support for the ionic liquid in the GC column. The chromosorb had been subjected to vacuum treatment with heating in order to remove traces of adsorbed moisture.

Experimental Procedures. 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 carrier gas. Two different GC columns (stainless steel) with length 43 cm and 105 cm, respectively, with an i.d. of 0.40 cm were used. The amounts of stationary phase (ionic liquid) were 2.62 mmol for the short column and 7.22 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,

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the amount of ionic liquid was about (27 to 60) mass % of the support material.

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

$$\ln \gamma_{i,3}^{\infty} = \ln\left(\frac{n_3RT}{V_N p_1{}^0}\right) - \frac{B_{11} - V_1{}^0}{RT} p_1{}^0 + \frac{2B_{12} - V_1^{\infty}}{RT} J p_0 \quad (1)$$

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

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

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 flowmeter temperature; p_{ow} is saturation pressure of water at T_f; p_o is the pressure at the column outlet.

The second and third term in eq 1 are correction terms that arise from the non-ideality of 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]

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

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

The outlet pressure p_o was kept equal to the 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 probes 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. 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 4 to 5 temperatures (in 10 deg steps) between 302 K and 385 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 within (0.01 to 0.03) min. Absolute values of retention times varied between (3 to 30) min depending on the individual solute. At each temperature values of the dead time t_G identical to the retention time of a non-retainable component were measured. While our GC was equipped with a flame-ionization detector, methane[1] was used as the non-retainable component under the assumtion that the effect of solubility of methane in ionic liquid is negligible. This assumption has been justified by attestation of our experimental procedure with the reliable data on γ_i^{∞} 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 of 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; partial molar volumes of solute at infinite dilution V_1^{∞} have been assumed to be equal of $V_1{}^0$. 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, values of the critical pressure (P_c), the critical temperature (T_c), and the critical volume (V_c) were estimated using Lydersen's method.[8] Acentric factors (ω_i) were calculated by Edminster 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}, 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 for 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] Specification of the sources of vapor pressures of other solutes is given in the 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 within ±3 %.

As a rule, the amount of about 30 % of IL is considered to be enough to cover completely the solid support, so adsorption on the solid surface can be excluded.[1−3] However, this time we have had the opportunity to compare our results for γ_i^{∞} from the GC technique with those obtained from the static method by extrapolating values of γ_i to infinite dilution.[30] As can be seen from the Table 2, there are some discrepancies between two methods for highly polar molecules such as methanol and ethanol by lower covering grade of the solid support. We assume that the reason is a preferred adsorption of the polar methanol on small parts of the surface of the supporting material, which are not completely covered by the ionic liquid at mass percentage of 27 % as well as by residual adsorption on the tubing surface in detector. This fact should be taken into consideration for future measurements of γ_i^{∞} of polar compounds.

Results and Discussion

The values of γ_i^{∞} of different solutes in [BMIM][NTf$_2$] obtained at different temperarures are listed in Table 1.

Table 1. Experimental Results for the Different Solutes in the [BMIM][NTf$_2$]: Temperature Ranges, Coefficients of Eq 4, Correlation Coefficients R^2, γ_i^∞ at 298 K Calculated Using Eq 4, and Values of $H_i^{E,\infty}$ Derived from Eq 5

solute i	temperature interval K	a	b K	R^2	$\gamma_{i\,(298\text{ K})}^\infty$	$H_i^{E,\infty}$ kJ·mol^{-1}
Alkanes						
1-pentane	302.0−333.6	29.15	−0.0639	0.983	10.1	6.0
1-hexane	302.0−333.6	45.57	−0.1012	0.995	15.4	6.3
1-heptane	302.0−333.6	72.61	−0.1664	0.994	23.0	7.1
1-octane	302.0−333.6	112.2	−0.2630	0.990	33.8	7.7
1-nonane	302.0−333.6	174.5	−0.4188	0.991	49.6	8.5
1-decane	312.3−354.3	204.2	−0.4685	0.995	64.5	9.0
1-undecane	312.3−354.3	306.5	−0.7173	0.995	92.6	9.9
1-dodecane	322.8−354.3	422.6	−0.9904	0.997	127.3	10.9
Alkenes						
1-pentene	301.9−333.7	10.43	−0.0182	0.989	5.00	3.3
1-hexene	301.9−333.7	16.44	−0.0294	0.996	7.67	3.5
1-heptene	301.9−333.6	25.71	−0.0480	0.998	11.4	3.8
1-octene	301.9−333.6	41.01	−0.0812	0.997	16.8	4.5
1-nonene	301.9−333.6	65.01	−0.1352	0.996	24.7	5.1
1-decene	312.2−354.3	98.50	−0.2150	0.999	34.4	7.4
1-undecene	312.2−354.3	157.5	−0.3584	0.996	50.6	8.7
1-dodecene	312.2−354.3	244.6	−0.5736	0.996	73.6	9.9
Cyclic Hydrocarbons						
cyclohexane[a]	301.9−333.6	25.84	−0.0554	0.998	9.32	5.6
cyclohexene[b]	301.9−333.6	11.85	−0.0220	0.998	5.29	3.8
1,3-cyclohexadiene[b]	301.9−333.6	4.44	−0.0061	0.998	2.62	2.0
Alkylbenzenes						
benzene[c]	322.8−354.5	1.15	−0.0009	0.993	0.88	1.0
toluene[d]	312.2−343.7	3.64	−0.0075	0.992	1.40	5.6
ethyl benzene[a]	354.2−385.6	3.30	−0.0036	0.993	2.23	2.1
propyl benzene[e]	354.2−385.6	5.20	−0.0066	0.996	3.23	2.7
butyl benzene[e]	354.2−385.6	8.18	−0.0118	0.996	4.66	3.5
pentyl benzene[e]	354.2−385.6	12.36	−0.0192	0.999	6.64	4.1
Alcohols						
methanol	312.2−354.2	4.10	−0.0094	0.981	1.30	8.8
ethanol	312.2−343.7	5.82	−0.0132	0.997	1.88	9.3
1-propanol	312.2−354.2	9.98	−0.0245	0.993	2.68	12.6
1-butanol	312.1−343.6	10.26	−0.0245	0.992	2.96	9.8
1-pentanol	354.0−385.6	8.13	−0.0167	0.994	3.15	9.7
1-hexanol	354.0−385.6	10.41	−0.0215	0.992	4.00	9.9
1-heptanol	354.0−385.6	94.78	−0.3000	0.991	5.33	10.7
2-propanol[f]	312.2−343.7	6.96	−0.0164	0.994	2.07	9.2
isobutanol[f]	312.1−343.6	10.51	−0.0256	0.992	2.88	10.8
sec-butanol[f]	312.1−343.6	8.63	−0.0206	0.990	2.49	9.8
tert-butyl alcohol[f]	312.1−343.6	6.07	−0.0140	0.990	1.90	8.3
tert-pentanol[g]	312.5−344.0	5.56	−0.0120	0.993	1.98	6.6
cyclohexanol[h]	354.3−385.8	9.49	−0.0206	0.991	3.35	12.5
Aldehydes						
propanal[i]	312.3−343.8	0.59	−0.0003	0.999	0.50	0.49
butanal[j]	312.3−343.8	0.71	−0.0001	0.990	0.68	0.11
pentanal[k]	312.3−343.8	2.02	−0.0021	0.998	1.39	1.4
hexanal[l]	322.8−375.1	1.15	0.0011	0.997	1.48	−0.78
heptanal[m]	354.3−385.7	3.87	−0.0069	0.997	1.81	6.0
octanal[l]	354.3−385.7	2.01	0.0017	0.997	2.52	−0.73
Esters						
methyl propanoate[n]	312.3−343.7	0.86	−0.0002	0.997	0.80	0.24
methyl butanoate[n]	312.3−343.7	1.12	−0.0002	0.994	1.06	0.18
methyl pentanoate[o]	354.3−385.7	2.92	−0.0047	0.999	1.52	4.6
methyl hexanoate[o]	354.3−385.7	4.32	−0.0070	0.999	2.23	4.6
methyl heptanoate[o]	354.3−385.7	5.90	−0.0103	0.999	2.83	5.6
Polar Solvents						
acetone[i]	312.3−343.7	0.31	0.0002	0.981	0.37	−0.42
acetonitrile[p]	312.3−343.7	0.84	−0.0012	0.999	0.48	2.4
N-methylpyrrolidone[q]	312.4−343.9	600.7	−1.600	0.994	123.7	19.3
1,4-dioxane[r]	312.4−343.9	0.49	0.0001	0.999	0.52	−1.1

[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. [r] Data from ref 29.

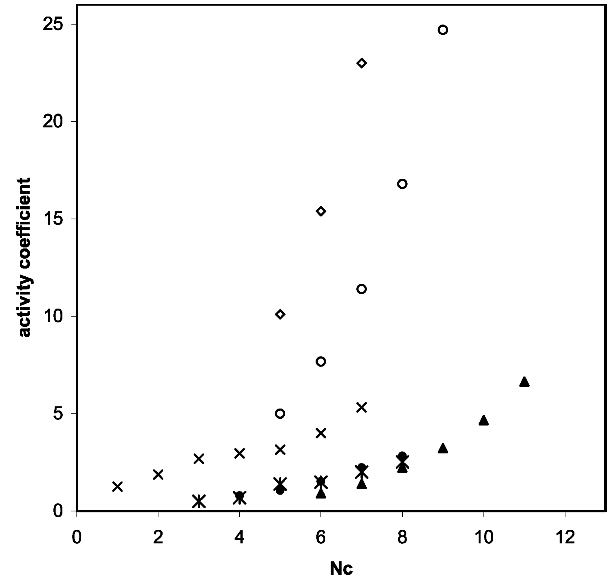

Figure 1. γ_i^∞ as function the number of carbon atoms (N_c) for different classes of solutes in [BMIM][NTf$_2$] at 298.15 K. ◇, alkanes; ○, alkenes; ▲, alkylbenzenes; ×, alcohols; × with a slash through it, aldehydes; ●, esters.

Table 2. Values of γ_i^∞ at 298 K with the Ionic Liquid Mass Percentage

	γ_i^∞	ionic liquid mass percentage		
solute *i*	from ref 30	27 %	50 %	60 %
benzene	0.64	0.84	0.85	0.86
methanol	0.95	1.57	1.30	1.30
ethanol	1.82	2.05	1.80	1.88
propanol	2.71	2.88	2.75	2.68

Altogether 212 data points for 53 solutes have been obtained in the temperature range (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:

$$\gamma_i^\infty = a + \frac{b}{T} \tag{4}$$

The coefficients a and b, the correlation coefficient R^2, and the values of $\gamma^\infty_{i\,(298\text{ K})}$ 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.

The activity coefficients of the linear *n*-alkanes, *n*-alkenes, alkylbenzenes, aldehydes, and esters increase with increasing chain length (see Figure 1). Cyclization of the alkane skeleton (e.g., cyclohexane) reduces the value of γ_i^∞ in comparison to the corresponding linear alkanes (e.g., hexane). Introduction of the double bond in the six-membered ring (cyclohexene, cyclohexadiene) also causes a decrease of γ_i^∞. This indicates a better solubility of molecules with double bonds in the ionic liquid due to their higher polarizability.

Values of γ_i^∞ for benzene and the alkylbenzenes are distinctly lower in comparison with those of the alkanes and alkenes. However, as with alkanes, 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 the corresponding linear alcohol. Values of γ_i^∞ of aldehydes and esters are distinctly lower in comparison with those of the alkanes and alkenes.

Table 3. Comparison of Values of γ_i^∞ at 298 K Derived in This Work with Those Measured by the Dilutor Technique[37] and the Static Method[30]

	γ_i^∞ at 298 K		
solute *i*	this work	ref 37	ref 30
1-pentane	10.1	10.0	
1-hexane	15.4	14.7	
1-heptane	23.0	21.4	
cyclohexane	9.3	8.9	
1-pentene	5.0	5.1	
1-hexene	7.7	7.5	
1-heptene	11.4	11.0	
cyclohexene	5.3	5.3	
benzene	0.88	0.86	0.64
toluene	1.4	1.2	

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

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

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

$H_i^{E,\infty}$ is positive and increases with increasing chain length of the linear alkanes. The introduction of double bonds lower the positive values of $H_i^{E,\infty}$. Values of $H_i^{E,\infty}$ are positive and increase slightly with increasing chain length of the linear alkanols. For acetone and some aldehydes, $H_i^{E,\infty}$ becomes negative. This is most probably due to the high polarizibility of the oxygen atoms and the special strength of ion-induced dipole interactions.

In the meantime the gaschromatographic method of determining values of γ_i^∞ and $H_i^{E,\infty}$ in ILs has become a well-established procedure that has successfully been applied for various systems.[33−36] The dilutor technique is known as an equivalent procedure,[37−39] and comparison of both techniques has revealed acceptable agreement. (see Table 3).

Acknowledgment

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Supporting Information Available:

Table of factors of solutes and carrier gas used in calculation of virial coefficients and table of experimental activity coefficients at infinity dilution. This material is available free of charge via the Internet at http://pubs.acs.org.

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