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Thermodynamic Properties of Mixtures Containing Ionic Liquids. 8. Activity Coefficients at Infinite Dilution of Hydrocarbons, Alcohols, Esters, and Aldehydes in 1-Hexyl-3-methylimidazolium Bis(trifluoromethylsulfonyl) Imide Using Gas−Liquid Chromatography

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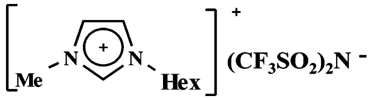
Activity coefficients at infinite dilution γ_i^∞ of alkanes, alkenes, and alkylbenzenes as well as of the linear and branched C_1-C_6 alcohols, esters, and aldehydes in the ionic liquids 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide have been determined by gas chromatography using the ionic liquids as stationary phase. The measurements were carried out at different temperatures between 301 K and 396 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

Replacing volatile organic compounds by less polluting solvents is an aspect of major interest in the field of “green chemistry”. Ionic liquids (ILs) appear to be an alternative because of their negligible vapor pressure. This work continues our study of thermodynamic properties of mixtures containing ionic liquids.[1−11] 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 activity coefficients in infinity dilution γ_i^∞ in ILs to the compound 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ($C_{12}H_{19}S_2O_4F_6N_3$),



having the molar mass 447.3 and the common abbreviation [HMIM][NTf_2].

Since ILs have a negligible vapor pressure, the most suitable method for measuring limiting activity coefficients of volatile solutes in ILs 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_6 alcohols, esters, aldehydes, and several common solvents (acetone, acetonitrile, trichloromethane, and 1,4-dioxane) in the ionic liquid [HMIM][NTf_2] have been studied over the temperature range (301 to 396) K.

Experimental Section

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 [HMIM][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 has been 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 IL 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 inside diameter of 0.40 cm were used. The amounts of stationary phase (ionic liquid) were 3.36 mmol for the short column and 7.61 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 48 mass percent of the support material.

According to Cruickshank et al.,[12] the following equation for the data treatment was used:

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

where $\gamma_{i,3}^\infty$ is the activity coefficient of component *i* at infinite

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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

$$V_N = JU_0(t_r - t_G)\frac{T_{col}}{T_f}\left[1 - \frac{p_{0w}}{p_0}\right] \tag{2}$$

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 flowmeter temperature, p_{0w} is saturation pressure of water at T_f, and p_0 is the pressure at the column outlet.

The second and third term in eq 1 are correction terms that arise from the nonideality of mobile gaseous phase. B_{11} is the second virial coefficient of the solute, B_{12} 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[13]

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

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

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, 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 4 to 8 temperatures (in 10 deg steps) between 301 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 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 non-retainable component under the assumption 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 elution 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 several 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.[14] Critical parameters needed for the calculations were available from the literature.[14] 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.[15] Acentric factors ω_i were calculated by Edmister equation.[15] 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.[14,15]

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.[16] For hydrocarbons values of p_1^0 were calculated using parameters of the Cox equation recommended by Steele and Chirico.[17] Vapor pressures of pure alcohols were calculated using coefficients of Wagner's equation recommended by Ambrose and Walton.[18] Specification of the sources of vapor pressures of other solutes was given in the previous papers of this series.[8,9]

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 to ± 3 %.

Results and Discussion

The values of γ_i^∞ of different solutes in [HMIM][NTf$_2$] obtained at different temperatures are listed in Table 1. Altogether 269 data points for 52 solutes have been obtained in the temperature range (301 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

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

The coefficients a and b, the correlation coefficients R^2, and the values of $\gamma_{i\,(298\ \mathrm{K})}^\infty$ 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 0.96 and 0.99.

The activity coefficients of the linear *n*-alkanes, *n*-alkenes, alkylbenzenes, aldehydes, and esters increase with increasing chain length. 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 slightly increase with increasing chain length. The branching of the alkane skeleton (e.g., 2-propanol

Table 1. Experimental Results of γ_i^∞ for Different Solutes in the [HMIM][NTf$_2$] Temperature Ranges, Coefficients of Equation 4, Correlation Coefficients R^2 and γ_i^∞ at 298 K Calculated Using Equation 4, and Values of $H_i^{E,\infty}$ Derived from Equation 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	302.0−344.0	−1.41	979.6	0.952	6.5	8.1
1-hexane	301.9−343.8	0.62	443.1	0.988	8.2	3.7
1-heptane	301.0−343.8	0.34	625.6	0.998	11.4	5.2
1-octane	301.0−343.8	0.46	683.3	0.993	15.6	5.7
1-nonane	307.1−322.9	0.37	828.0	0.991	23.2	6.9
1-decane	307.1−333.4	0.45	895.2	0.980	31.7	7.4
1-undecane	312.4−354.3	0.46	985.0	0.992	43.3	8.2
1-dodecane	333.4−354.3	0.69	999.4	0.976	56.8	8.3
			Alkenes			
1-pentene	302.0−333.5	1.98	−232.0	0.966	3.3	−1.9
1-hexene	302.0−344.5	0.35	352.9	0.991	4.6	2.9
1-heptene	302.0−354.4	0.54	397.8	0.989	6.5	3.3
1-octene	302.0−354.4	0.73	438.3	0.997	9.0	3.6
1-nonene	312.3−364.6	0.63	593.7	0.998	13.7	4.9
1-decene	312.3−364.6	0.82	610.5	0.975	17.7	5.1
1-undecene	322.7−375.1	0.10	950.5	0.998	26.7	7.9
1-dodecene	333.2−375.0	−0.36	1203.0	0.988	39.2	10.0
			Cyclic Hydrocarbons			
cyclohexane	301.0−333.3	−0.40	641.3	0.999	5.8	5.3
cyclohexene	301.9−343.8	−0.31	462.2	0.999	3.5	3.8
1,3-cyclohexadiene	312.1−354.3	−0.29	276.0	0.989	1.9	2.3
			Alkylbenzenes			
benzene	301.7−343.8	−0.32	21.0	0.980	0.78	0.2
toluene	307.1−343.9	0.36	−98.3	0.963	1.0	−0.8
ethyl benzene	322.9−354.3	0.25	60.4	0.964	1.6	0.5
propyl benzene	333.4−385.7	0.25	163.7	0.966	2.2	1.4
butyl benzene	354.3−385.7	0.54	163.8	0.989	3.0	1.4
pentyl benzene	364.7−385.7	1.14	30.0	0.997	3.4	0.3
			Alcohols			
methanol	302.0−354.5	−2.72	939.2	0.999	1.5	7.8
ethanol	302.0−354.5	−3.33	1210.1	0.999	2.1	10.1
1-propanol	312.5−354.5	−3.64	1375.2	0.999	2.6	11.4
1-butanol	322.7−354.2	−2.63	1080.8	0.998	2.7	9.0
1-pentanol	333.3−375.0	−2.62	1133.5	0.998	3.3	9.4
1-hexanol	354.1−396.0	−2.38	1115.4	0.999	3.9	9.3
2-propanol	301.7−354.1	−3.14	1143.8	0.999	2.0	9.5
isobutanol	301.7−333.4	−3.12	1214.0	0.998	2.6	10.1
sec-butanol	301.7−333.4	−3.21	1200.0	0.999	2.3	10.0
tert-butyl alcohol	301.7−333.4	−3.10	1094.6	0.999	1.8	9.1
tert-pentanol	301.7−364.6	−2.16	808.0	0.998	1.7	6.7
cyclohexanol	354.1−396.0	−3.58	1482.0	0.989	4.0	12.3
			Aldehydes			
propanal	301.8−333.4	−1.13	103.9	0.984	0.46	0.9
butanal	301.8−333.4	−0.65	31.5	0.977	0.58	0.3
pentanal	301.8−375.0	−0.48	179.2	0.987	1.1	1.5
hexanal	333.2−375.0	0.59	−135.6	0.999	1.14	−1.1
heptanal	343.6−396.0	−1.59	584.7	0.991	1.45	4.9
octanal	354.1−396.0	0.98	−119.7	0.981	1.78	−1.0
			Esters			
methyl propanoate	322.8−354.1	−0.28	−34.5	0.996	0.67	−0.3
methyl butanoate	322.8−354.2	0.06	−64.2	0.967	0.86	−0.5
methyl pentanoate	322.8−354.2	−0.52	182.5	0.988	1.1	1.5
methyl hexanoate	343.7−385.7	−1.02	464.1	0.995	1.7	3.9
methyl heptanoate	354.2−385.7	−1.34	639.9	0.999	2.2	5.3
			Polar Solvents			
acetone	301.8−354.3	−0.62	−128.9	0.999	0.35	−1.0
acetonitrile	312.3−354.3	−1.61	257.6	0.988	0.47	2.1
1,4-dioxane	375.2−396.2	−0.01	−1202.0	0.999	0.02	−10.0
trichloromethane	301.8−344.0	0.16	−170.3	0.948	0.66	−1.4

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.

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 eq 5:

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

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 and taking into account the experimental uncertainty of the γ_i^∞ values. This is also confirmed by results of $H_i^{E,\infty}$ for systems where a comparison between the results obtained by eq 5 and direct calorimetric data is possible.[10]

$H_i^{E,\infty}$ are positive and hardly change with increasing chain length of the linear alkanes. The introduction of double bonds slightly lower the positive values of $H_i^{E,\infty}$. Values of $H_i^{E,\infty}$ of linear alcohols are positive and do not change with increasing chain length. For dioxane, 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.

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Supporting Information Available:

Two tables showing critical constants and acentric factors of the solutes and 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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