894 *J. Chem. Eng. Data* **2002,** *47,* 894−899

Thermodynamic Properties of Mixtures Containing Ionic Liquids. 2. Activity Coefficients at Infinite Dilution of Hydrocarbons and Polar Solutes in 1-Methyl-3-ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) Amide and in 1,2-Dimethyl-3-ethyl-imidazolium Bis(trifluoromethyl-sulfonyl) Amide 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, acetone, acetonitrile, ethyl acetate, alkyl ethers, and chloromethanes in the ionic liquids 1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide and 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide were determined by gas chromatography using the ionic liquids as the stationary phase. The measurements were carried out at different temperatures between 313 K and 363 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

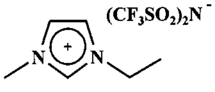
This work continues our study of thermodynamic properties of mixtures containing ionic liquids.[1,2] The study of ionic liquids has become the subject of an increasing number of scientific investigations.[3] Our interest in ionic liquids is focused on providing systematic data on activity coefficients 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.[1,2] Values of γ_i^∞ are useful, in particular, for the selection of solvents for extraction and extractive distillation. For example, values of γ_i^∞ can be used to calculate Henry's coefficient K_i defined by

$$K_i = \lim_{x_i \to 0} \frac{p_i}{x_i} = p_{i_0}\gamma_i^\infty \tag{1}$$

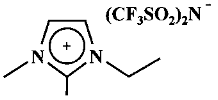
where p_i is the partial pressure of the solute and x_i its mole fraction in the liquid mixture. p_{i_0} is the vapor pressure of the pure liquid solute. Equation 1 allows approximate calculation of the partition of the solute between the liquid and the vapor phase at low values of x_i.

Understanding the thermodynamics of mixtures of ionic liquids with organic solvents exhibits a challenge for theoreticians dealing with statistical mechanics of electrolyte solutions. Therefore, experimental data of thermodynamic properties of mixtures consisting of ionic liquids and organic solvents are also of interest for testing theoretical concepts.

A diversity of ionic liquids are commercially available.[4] In this work we extend our measurements of γ_i^∞ in ionic liquids to the compounds 1-methyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide ($C_8H_{14}S_2O_4F_6N_3$) and 1,2-dimethyl-3-ethyl-imidazolium bis(trifluoromethyl-sulfonyl) amide ($C_9H_{16}S_2O_4F_6N_3$):



($C_8H_{14}S_2O_4F_6N_3$)



($C_9H_{16}S_2O_4F_6N_3$)

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, acetone, acetonitrile, ethyl acetate, alkyl ethers, and chloromethanes in the ionic liquids ($C_8H_{14}S_2O_4F_6N_3$) and ($C_9H_{16}S_2O_4F_6N_3$) has been studied over the temperature range (313 to 363) K.

Experimental Procedure

Materials. The samples of compounds studied were purchased from Aldrich and Merck. GC analysis gave a purity >99.9% in agreement with specifications stated by the suppliers. The ionic liquids ($C_8H_{14}S_2O_4F_6N_3$) and ($C_9H_{16}S_2O_4F_6N_3$) were donated by Dr. Peter Wasserscheid, RWTH Aachen, Germany. Before using, the sample of the ionic liquid was dissolved in excess of methanol and filtered. Then, it was subjected to vacuum evaporation to remove possible traces of solvents and moisture. The densities at 298.15 K of the purified sample of ($C_8H_{14}S_2O_4F_6N_3$) (1525.20 ± 0.20) $kg\cdot m^{-3}$ and (1480.20 ± 0.23) $kg\cdot m^{-3}$ of the ($C_9H_{16}S_2O_4F_6N_3$) were measured using the vibrating tube method. These values were checked regularly to test the chemical stability of the samples. Chromosorb W/AW-DMCS 100/120 mesh was used as solid support for the ionic liquid in the GC column. Before using,

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10.1021/je0103115 CCC: $22.00

Table 1. Experimental Activity Coefficients γ_i^∞ at Infinite Dilution for Hydrocarbons in the Ionic Liquid ($C_8H_{14}S_2O_4F_6N_3$) as the Stationary Phase at Temperatures 313 to 343 K[a]

solute *i*	313 K	323 K	333 K	343 K
		Alkanes		
hexane	25.346 (313.9)	24.452 (323.3)	23.131 (333.7)	22.054 (344.1)
heptane	38.376 (313.9)	35.892 (323.3)	33.382 (333.7)	30.671 (344.1)
octane	58.470 (313.9)	54.060 (323.3)	49.449 (333.7)	45.084 (344.1)
nonane	91.891 (313.8)	81.198 (323.2)	73.387 (333.6)	65.772 (344.1)
decane	151.22 (313.9)	132.09 (323.3)	116.27 (333.8)	101.17 (344.2)
cyclohexane	14.239 (313.9)	13.421 (323.3)	12.694 (333.7)	11.765 (344.1)
2,2,4-trimethylpentane	36.141 (313.8)	34.000 (323.3)	31.102 (333.7)	28.907 (344.1)
		Alkenes		
cyclohexene	7.497 (313.8)	7.210 (323.3)	6.844 (333.7)	6.480 (344.1)
1-methylcyclohexene	12.25 (313.8)	11.76 (323.3)	11.138 (333.7)	10.674 (344.1)
styrene	1.664 (313.8)	1.668 (323.1)	1.673 (333.4)	1.680 (343.8)
α-methylstyrene[b]	3.035 (323.1)	3.235 (333.4)	3.494 (343.8)	3.832 (354.1)
		Alkylbenzenes		
benzene	1.177 (313.8)	1.179 (323.1)	1.179 (333.6)	1.181 (344.1)
toluene	1.735 (313.8)	1.753 (323.0)	1.762 (333.3)	1.776 (343.7)
ethylbenzene	2.836 (313.9)	2.814 (323.2)	2.795 (333.4)	2.768 (343.8)
o-xylene	2.396 (313.8)	2.414 (323.1)	2.433 (333.4)	2.451 (343.8)
p-xylene	2.704 (313.8)	2.718 (323.1)	2.733 (333.4)	2.743 (343.8)
m-xylene	2.735 (313.9)	2.741 (323.1)	2.744 (333.5)	2.750 (343.8)
isopropylbenzene	4.198 (313.8)	4.146 (323.1)	4.088 (333.4)	4.020 (343.8)
tert-butylbenzene	5.274 (313.8)	5.208 (323.1)	5.114 (333.4)	5.013 (343.8)

[a] Measured experimental temperatures are given in parentheses. [b] Values are measured in the temperature interval 323 to 354 K.

Table 2. Experimental Activity Coefficients γ_i^∞ at Infinite Dilution for Hydrocarbons in the Ionic Liquid ($C_9H_{16}S_2O_4F_6N_3$) as the Stationary Phase at Temperatures 313 to 343 K[a]

solute *i*	313 K	323 K	333 K	343 K
		Alkanes		
hexane	25.267 (313.7)	23.642 (324.1)	22.328 (333.6)	21.119 (344.1)
heptane	37.397 (313.7)	34.299 (324.2)	31.692 (333.6)	29.702 (344.0)
octane	55.416 (313.7)	49.825 (324.2)	45.709 (333.6)	42.007 (344.0)
nonane	84.900 (313.6)	76.051 (323.0)	68.213 (333.4)	61.129 (343.9)
decane	131.509 (313.7)	117.029 (322.9)	102.057 (333.3)	90.614 (343.7)
cyclohexane	14.859 (313.6)	13.734 (323.0)	12.656 (333.5)	11.659 (343.9)
2,2,4-trimethylpentane	35.490 (313.7)	32.625 (324.2)	30.450 (333.5)	28.766 (343.9)
		Alkenes		
cyclohexene	7.691 (313.7)	7.198 (324.2)	6.870 (333.5)	6.516 (343.9)
1-methylcyclohexene	12.433 (313.7)	11.708 (324.2)	11.194 (333.5)	10.627 (343.9)
styrene	1.490 (313.8)	1.502 (323.1)	1.514 (333.4)	1.531 (343.7)
α-methylstyrene[b]	2.978 (333.3)	3.218 (343.6)	3.510 (354.1)	3.874 (364.4)
		Alkylbenzenes		
benzene	1.097 (313.7)	1.100 (323.0)	1.101 (333.3)	1.105 (343.7)
toluene	1.647 (313.7)	1.657 (323.0)	1.663 (333.4)	1.672 (343.7)
ethylbenzene	2.814 (313.7)	2.789 (323.0)	2.748 (333.4)	2.717 (343.7)
o-xylene	2.210 (313.7)	2.219 (323.0)	2.238 (333.3)	2.245 (343.7)
p-xylene	2.572 (313.7)	2.569 (323.0)	2.564 (333.3)	2.556 (343.6)
m-xylene	2.623 (313.7)	2.620 (323.1)	2.614 (333.3)	2.610 (343.7)
isopropylbenzene	4.353 (313.7)	4.235 (323.0)	4.162 (333.3)	4.061 (343.6)
tert-butylbenzene	5.594 (313.8)	5.434 (323.1)	5.281 (333.4)	5.166 (343.7)

[a] Measured experimental temperatures are given in parentheses. [b] Values are measured in the temperature interval 333 to 363 K.

chromosorb was subjected to vacuum treatment with heating 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 “Carlo Erba Strumentazione−4130” gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard 3390A integrator. Nitrogen was used as a carrier gas. Two different GC columns with lengths of 100 and 240 cm, respectively, with an inside diameter of 0.40 cm have been used. The masses of the stationary phase (ionic liquid) were about 1 g for the short column and about 2.7 g for the longer one. The masses of the stationary phase were determined with a precision of ±0.0005 g. To avoid possible residual adsorption effects of the solutes on chromosorb, the amount of ionic liquid was about 30 mass % of the support material. Columns were filled with help of an ultrasound vibrator to provide uniform packing of the material in the column.

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

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

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

$$V_N = J U_0 (t_r - t_G) \frac{T_{col}}{T_f}\left[1 - \frac{p_{ow}}{p_o}\right] \qquad (3)$$

Table 3. Experimental Activity Coefficients γ_i^∞ at Infinite Dilution for Polar Solutes in the Ionic Liquid ($C_8H_{14}S_2O_4F_6N_3$) as the Stationary Phase at Temperatures 313 to 343 K[a]

solute *i*	313 K	323 K	333 K	343 K
Alcohols				
methanol	1.131 (313.7)	1.050 (323.1)	0.951 (333.5)	0.872 (343.9)
ethanol	1.525 (313.8)	1.411 (323.2)	1.290 (333.6)	1.187 (344.1)
1-propanol	2.088 (313.9)	1.895 (323.3)	1.737 (333.8)	1.594 (344.2)
1-butanol	2.945 (313.8)	2.679 (323.0)	2.393 (333.4)	2.162 (343.7)
1-pentanol	4.311 (313.8)	3.780 (323.1)	3.315 (333.4)	2.967 (343.8)
isopropyl alcohol	1.931 (313.8)	1.768 (323.2)	1.581 (333.6)	1.447 (344.0)
tert-butyl alcohol	1.896 (313.9)	1.739 (323.3)	1.603 (333.8)	1.484 (344.2)
sec-butanol	2.424 (313.9)	2.187 (323.2)	1.983 (333.4)	1.813 (343.8)
tert-pentanol	2.216 (313.7)	2.051 (323.0)	1.910 (333.3)	1.790 (343.7)
cyclohexanol[b]	3.006 (323.1)	2.791 (333.4)	2.608 (343.8)	2.435 (354.1)
1-hexanol[b]	5.254 (323.1)	4.576 (333.4)	4.086 (343.8)	3.691 (354.1)
Polar Organics				
acetonitrile	0.435 (313.7)	0.429 (323.0)	0.425 (333.3)	0.419 (343.7)
acetone	0.399 (313.8)	0.406 (323.2)	0.412 (333.6)	0.415 (344.0)
ethyl acetate	0.886 (313.8)	0.900 (323.0)	0.910 (333.3)	0.924 (343.7)
methyl *tert*-butyl ether	2.416 (313.9)	2.413 (323.3)	2.405 (333.7)	2.396 (344.1)
methyl *tert*-amyl ether	3.856 (313.9)	3.849 (323.3)	3.830 (333.7)	3.823 (344.1)
Chloromethanes				
dichloromethane	0.891 (313.8)	0.882 (323.2)	0.869 (333.6)	0.862 (344.0)
trichloromethane	0.972 (313.8)	0.989 (323.2)	1.011 (333.6)	1.029 (344.1)
tetrachloromethane	3.248 (313.8)	3.218 (323.2)	3.186 (333.6)	3.150 (344.0)

[a] Measured experimental temperatures are given in parentheses. [b] Values are measured in the temperature interval 323 to 354 K.

Table 4. Experimental Activity Coefficients γ_i^∞ at Infinite Dilution for Polar Solutes in the Ionic Liquid ($C_9H_{16}S_2O_4F_6N_3$) as the Stationary Phase at Temperatures 313 to 343 K[a]

solute *i*	313 K	323 K	333 K	343 K
Alcohols				
methanol	1.460 (313.7)	1.323 (323.1)	1.190 (333.6)	1.076 (344.0)
ethanol	2.043 (313.7)	1.825 (323.0)	1.648 (333.3)	1.490 (343.7)
1-propanol	2.759 (313.7)	2.484 (323.0)	2.197 (333.3)	1.985 (343.7)
1-butanol	3.892 (313.7)	3.425 (323.0)	3.010 (333.4)	2.689 (343.7)
1-pentanol	5.783 (313.7)	4.949 (323.0)	4.250 (333.3)	3.728 (343.6)
isopropyl alcohol	2.522 (313.7)	2.273 (323.1)	2.028 (333.4)	1.801 (344.0)
tert-butyl alcohol	2.431 (313.7)	2.199 (323.0)	1.966 (333.3)	1.806 (343.7)
sec-butanol	3.123 (313.7)	2.773 (323.0)	2.467 (333.4)	2.229 (343.7)
tert-pentanol	2.881 (313.7)	2.627 (323.0)	2.411 (333.3)	2.222 (343.7)
cyclohexanol	4.137 (313.7)	3.712 (323.0)	3.467 (333.3)	3.179 (343.6)
1-hexanol[b]	5.790 (333.3)	5.039 (343.6)	4.463 (354.1)	4.021 (364.4)
Polar Organics				
acetonitrile	0.462 (313.7)	0.453 (323.0)	0.449 (333.3)	0.440 (343.7)
acetone	0.462 (313.7)	0.464 (323.0)	0.468 (333.3)	0.469 (343.7)
ethyl acetate	1.068 (313.7)	1.069 (323.0)	1.070 (333.4)	1.070 (343.7)
methyl *tert*-butyl ether	2.870 (313.7)	2.825 (323.0)	2.759 (333.5)	2.692 (344.0)
methyl *tert*-amyl ether	4.667 (313.7)	4.553 (323.1)	4.446 (333.4)	4.343 (344.0)
Chloromethanes				
dichloromethane	0.909 (313.6)	0.892 (323.0)	0.879 (333.4)	0.858 (343.9)
trichloromethane	0.958 (313.7)	0.976 (323.0)	0.989 (333.3)	1.006 (343.7)
tetrachloromethane	3.388 (313.6)	3.337 (323.0)	3.258 (333.5)	3.182 (344.0)

[a] Measured e7.5rimental temperatures are given in parentheses. [b] Values are measured in the temperature interval 333 to 363 K.

where t_r is the retention time, t_G is the dead time, and 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 term in eq 2 are correction terms which 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[6]

$$J = \frac{3(p_i/p_o)^2 - 1}{2(p_i/p_o)^3 - 1} \tag{4}$$

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 a precision of ±0.2 kPa.

Volumes of the samples injected into the GC probes were (0.5 to 2) mL. No differences in retention times t_r were found by injecting individual pure components or their mixtures with both columns containing 1 g and 2.7 g 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

Table 5. Experimental Results for the Hydrocarbons in the ($C_8H_{14}S_2O_4F_6N_3$): Coefficients of Eq 5, Correlation Coefficient R^2, γ_i^∞ at 298 K Calculated Using Eq 5 and Values of $H_i^{E,\infty}$ Derived from Eq 6, Including Estimated Experimental Uncertainty

solute *i*	*a*	*b* (K)	R^2	γ_i^∞ 298 K	$H_i^{E,\infty}$ (J·mol^{-1})
Alkanes					
hexane	1.6276	505.16	0.9939	27.1	4200 ± 160
heptane	1.1194	794.76	0.9964	42.3	6608 ± 230
octane	1.1121	929.21	0.9983	65.3	7725 ± 260
nonane	0.7673	1176.0	0.9979	104	9777 ± 330
decane	0.4963	1419.6	0.9993	175	11803 ± 390
cyclohexane	0.5212	671.03	0.9935	15.5	5579 ± 180
2,2,4-trimethylpentene	1.0165	808.41	0.9959	39.9	6721 ± 230
Alkenes					
cyclohexene	0.3589	520.92	0.9939	8.04	4331 ± 150
1-methylcyclohexene	0.9212	497.73	0.9978	13.1	4138 ± 150
styrene	0.6183	−34.378	0.9842	1.65	−285.8 ± 11
α-methylstyrene[a]	3.7569	−858.18	0.9881	2.36	−7135 ± 260
Alkylbenzenes					
benzene	0.2000	−11.680	0.9612	1.17	−97.1 ± 5
toluene	0.8139	−82.201	0.9858	1.72	−683.5 ± 31
ethylbenzene	0.7675	86.364	0.9936	2.87	718.a1 ± 31
o-xylene	1.1351	−81.941	1.000	2.37	−681.3 ± 32
p-xylene	1.1603	−51.875	0.9961	2.68	−431.3 ± 20
m-xylene	1.0662	−18.829	0.9641	2.73	−156.6 ± 8
isopropylbenzene	0.9413	155.10	0.9945	4.29	1289 ± 62
tert-butylbenzene	1.0802	183.44	0.9902	5.42	1525 ± 70

[a] For the temperature interval 323 to 354 K.

Table 6. Experimental Results for the Hydrocarbons in the ($C_9H_{16}S_2O_4F_6N_3$): Coefficients of Eq 5, Correlation Coefficient R^2, γ_i^∞ at 298 K Calculated Using Eq 5, and Values of $H_i^{E,\infty}$ Derived from Eq 6, Including Estimated Experimental Uncertainty

solute *i*	*a*	*b* (K)	R^2	γ_i^∞ 298 K	$H_i^{E,\infty}$ (J·mol^{-1})
Alkanes					
hexane	1.1873	640.52	0.9997	27.3	5325 ± 240
heptane	0.9763	829.36	0.9978	41.1	6895 ± 310
octane	0.8627	988.18	0.9993	61.8	8216 ± 370
nonane	0.7275	1164.7	0.9998	96.2	9683 ± 440
decane	0.5778	1350.0	0.9996	152	11224 ± 490
cyclohexane	−0.0475	861.49	0.9998	16.4	7162 ± 320
2,2,4-trimethylpentene	1.1561	755.86	0.9963	38.7	6284 ± 280
Alkenes					
cyclohexene	0.1643	587.77	0.9988	8.25	4887 ± 220
1-methylcyclohexene	0.7435	557.16	0.9996	13.3	4632 ± 210
styrene	0.6986	−94.159	0.9931	1.47	−782.9 ± 39
α-methylstyrene[a]	4.1479	−1021.2	0.9934	1.94	−8490 ± 400
Alkylbenzenes					
benzene	0.1750	−25.922	0.9763	1.09	−215.5 ± 11
toluene	0.6645	−51.794	0.9921	1.64	−431 ± 21
ethylbenzene	0.6259	128.57	0.9927	2.87	1069 ± 50
o-xylene	0.9859	−60.616	0.9789	2.19	−504 ± 24
p-xylene	0.8737	22.433	0.9630	2.58	186 ± 14
m-xylene	0.9062	18.252	0.9843	2.63	152 ± 22
isopropylbenzene	0.6956	242.69	0.9921	4.49	2018 ± 95
tert-butylbenzene	0.8016	288.27	0.9927	5.81	2397 ± 110

[a] For the temperature interval 333 to 363 K.

approximation. Experiments were carried out at four temperatures between 313 K and 363 K. The temperature of the GC column was maintained constant to within ±0.05 K. At a given temperature each experiment was repeated at least twice to check the reproducibility. Retention times were generally reproducible within 0.01−0.03 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 nonretainable component were measured. While our GC was equipped with a flame-ionization detector, methane[1] was used as the nonretainable component under the assumption that the effect of solubility of methane in an 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 6−8 h for three selected solutes. No changes of the retention times were observed during 80 h of continuous operation.

Data needed for calculating the correction terms in eq 1 have been obtained in the following way. For all solutes with exception of α-methyl-styrene,[7] hexanol,[8] methyl *tert*-butyl ether,[9] and methyl *tert*-amyl ether[10] values of p_1^0 were taken from the Antoine constants given by Boublik et al.[11]

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 to V_1^0.

Table 7. Experimental Results for the Polar Solutes in the ($C_8H_{14}S_2O_4F_6N_3$): Coefficients of Eq 5, Correlation Coefficient R^2, γ_i^{∞} at 298 K Calculated Using Eq 5, and Values of $H_i^{E,\infty}$ Derived from Eq 6, Including Estimated Experimental Uncertainty

solute i	a	b (K)	R^2	γ_i^{∞} 298 K	$H_i^{E,\infty}$ (J·mol^{-1})
		Alcohols			
methanol	−2.8581	936.54	0.9978	1.26	7787 ± 360
ethanol	−2.4327	896.39	0.9995	1.69	7453 ± 350
1-propanol	−2.3119	955.76	0.9990	2.32	7946 ± 360
1-butanol	−2.4844	1119.4	0.9994	3.34	9307 ± 420
1-pentanol	−2.8422	1349.1	0.9988	4.95	11217 ± 480
1-hexanol [a]	−2.3716	1300.4	0.9980	6.43	10812 ± 450
isopropyl alcohol	−2.6607	1042.1	0.9985	2.17	8664 ± 390
tert-butyl alcohol	−2.1364	870.77	0.9995	2.10	7240 ± 340
sec-butanol	−2.4495	1045.8	0.9992	2.72	8695 ± 400
tert-pentanol	−1.6527	767.13	0.9986	2.42	6378 ± 310
cyclohexanol[a]	−1.2941	773.86	0.9998	3.45	6434 ± 310
		Polar Organics			
acetonitrile	−1.2532	132.01	0.9932	0.444	1097 ± 50
acetone	−0.4574	−144.0	0.9743	0.391	−1197 ± 50
ethyl acetate	0.3462	−146.37	0.9923	0.867	−1217 ± 50
methyl *tert*-butyl ether	0.7865	30.203	0.9592	2.43	251.1 ± 13
methyl *tert*-amyl ether	1.2451	32.945	0.9582	3.87	273.9 ± 13
		Chloromethanes			
dichloromethane	−0.5030	121.50	0.9906	0.905	1010 ± 45
trichloromethane	0.6310	−207.14	0.9996	0.941	−1722 ± 50
tetrachloromethane	0.8325	108.57	0.9974	3.23	903 ± 40

[a] For the temperature interval 323 to 354 K.

Table 8. Experimental Results for the Polar Solutes in the ($C_9H_{16}S_2O_4F_6N_3$): Coefficients of Eq 5, Correlation Coefficient R^2, γ_i^{∞} at 298 K Calculated Using Eq 5, and Values of $H_i^{E,\infty}$ Derived from Eq 6, Including Estimated Experimental Uncertainty

solute i	a	b (K)	R^2	γ_i^{∞} 298 K	$H_i^{E,\infty}$ (J·mol^{-1})
		Alcohols			
methanol	−3.0881	1087.9	0.9999	1.65	9045 ± 420
ethanol	−2.8840	1127.6	0.9991	2.30	9375 ± 420
1-propanol	−2.7985	1196.6	0.9994	3.14	9949 ± 440
1-butanol	−2.8852	1330.4	0.9994	4.47	11061 ± 500
1-pentanol	−3.2922	1581.4	0.9989	6.74	13148 ± 550
1-hexanol[a]	−2.5163	1422.3	0.9986	7.70	11825 ± 500
isopropyl alcohol	−2.8879	1197.1	0.9991	2.88	9953 ± 440
tert-butyl alcohol	−2.5619	1081.7	0.9981	2.74	8993 ± 410
sec-butanol	−2.7301	1212.5	0.9991	3.55	10081 ± 440
tert-pentanol	−1.9084	929.76	0.9992	3.20	7730 ± 350
cyclohexanol	−1.5349	924.3	0.9910	4.56	7685 ± 350
		Polar Organics			
acetonitrile	−1.2947	163.47	0.9881	0.471	1359 ± 70
acetone	−0.5852	−58.634	0.9603	0.459	−487.5 ± 30
ethyl acetate	0.0861	−6.3527	0.8978	1.07	−52.8 ± 4
methyl *tert*-butyl ether	0.3293	228.13	0.9908	2.97	1896 ± 95
methyl *tert*-amyl ether	0.7260	255.37	0.9997	4.83	2123 ± 100
		Chloromethanes			
dichloromethane	−0.7329	200.05	0.9899	0.935	1663 ± 85
trichloromethane	0.5105	−173.39	0.9965	0.935	−1441 ± 80
tetrachloromethane	0.5030	225.75	0.9896	3.50	1877 ± 90

[a] For the temperature interval 333 to 363 K.

Values of B_{11} have been estimated according to Tsonopolous' method.[12] Critical parameters needed for the calculations were available from the literature.[12] If these data were not available, values of the critical pressure P_c, the critical temperature T_c, and the critical volume T_c were estimated using Lydersen's method.[13] Acentric factors w_i were calculated by the Edminster equation.[13]

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 w_{ij} were calculated by equations given in the literature.[12,13]

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 for the experimental error estimation was described in our previous work.[1] Values of $\gamma^{\infty}{}_i$ are estimated to be accurate within ±3%.

Results and Discussion

The values of γ_i^{∞} of different solutes in ($C_8H_{14}S_2O_4F_6N_3$) and ($C_9H_{16}S_2O_4F_6N_3$) obtained at different temperarures are listed in Tables 1−4. They have been approximated by the linear regression:

$$\ln(\gamma^{\infty}{}_i) = a + \frac{b}{T} \qquad (5)$$

The coefficients a and b, the correlation coefficients R^2, and the values of γ_i^{∞} 98 K calculated with these coefficients are given in Tables 5−8. The quality of the linear regression was very good because the correlation coefficients lie between 0.97 and 0.99. The results obtained for both ionic liquids are similar for all solvents.

The activity coefficients of the linear *n*-alkanes increase with increasing chain length. Cyclization or branching of the alkane skeleton (e.g., cyclohexane or 2,2,4-trimethylpentane) reduces the value of γ_i^∞ in comparison to the corresponding linear alkanes (e.g., hexane and octane). Introduction of the double bond in the six-membered ring (cyclohexene) also causes a diminishing of γ_i^∞.

Values of γ_i^∞ for benzene and the alkylbenzenes are distinctly lower in comparison with those of the alkanes and alkenes. However, similarly as with the alkanes, γ_i^∞ values increase with increasing size of the alkyl group. No significant effect due to the branching of the alkane chain in alkylbenzenes was observed.

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 acetonitrile and the acetone are distinctly lower in comparison to those of the ester and ethers. Values of γ_i^∞ of dichloromethane and trichloromethane are very similar, but introducing the fourth chlorine atom in tetrachloromethane increases it γ_i^∞ substantially. This behavior indicates that solutes have higher solubilities in the ionic liquid the more polar the solute is probably due to the preferred attractive interaction of polar molecules with the ions of the solvent. It is interesting to compare these results with results obtained for the ionic liquid 4-methyl-*n*-butyl-pyridinium tetrafluoroborate ($C_{10}H_{16}BF_4N$) and the same solutes.[1,2] The values of γ_i^∞ are in general distinctly higher in this ionic liquid even though the general dependence on chain length, branching, or polarity shows the same trends as in the case with the two ionic liquids studied in the present work. This might have to do with the smaller anion tetrafluoroborate BF_4^- which gives rise to a stronger Coulomb interaction in this ionic liquid. Dissolution of a neutral molecule in the ionic liquid containing the tetrafluoroborate anion requires more interactional energy to be broken than in the case of the ionic liquids with the larger bis(trifluoromethyl-sulfonyl) amide ion.

According to the Gibbs−Helmholtz equation, 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:

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial(1/T)}\right) = \frac{H_i^{E,\infty}}{R} \tag{6}$$

where R is the gas constant. The values of $H_i^{E,\infty}$ for the compounds studied are also listed in Tables 5−8. The results are similar for the two ionic liquids.

$H_i^{E,\infty}$ is positive and increases with increasing chain length of the linear alkanes. The introduction of double bonds decrease the positive values of $H_i^{E,\infty}$. For molecules containing the aromatic ring, $H_i^{E,\infty}$ becomes negative; however, increasing the size of alkyl groups in the aromatic ring compensates for this effect and in the case of isopropylbenzene and *tert*-butylbenzene $H_i^{E,\infty}$ is again positive.

Values of $H_i^{E,\infty}$ are positive and increase slightly with increasing chain length of the linear alkanols up to 1-pentanol. Branching of the alkyl chain in alkanols decreases slightly the positive values of $H_i^{E,\infty}$ compared to the linear isomers. For acetone, ethyl acetate, and in particular trichloromethane $H_i^{E,\infty}$ becomes negative. This is most probably due to the high polarizibility of the chlorine atoms and the special strength of ion-induced dipole interactions.

A quantitative interpretation of the results of γ_i^∞ and $H_i^{E,\infty}$ has to be given in terms of an extended theory of electrolyte solutions which accounts for ionic as well as for polar and nonpolar interactions. In this respect the results obtained in this work as well as in the previous ones provide a basis for such theoretical investigations.

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Received for review November 26, 2001. Accepted February 20, 2002. One of us (D.K.) gratefully acknowledges a research scholarship from the DAAD (Deutscher Akademischer Austauschdienst).

JE0103115