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Thermodynamic Properties of Mixtures Containing Ionic Liquids. 9. Activity Coefficients at Infinite Dilution of Hydrocarbons, Alcohols, Esters, and Aldehydes in Trimethyl-butylammonium Bis(trifluoromethylsulfonyl) Imide Using Gas−Liquid Chromatography and Static Method

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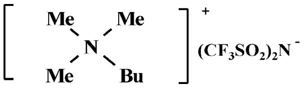
Activity coefficients at infinite dilution γ_i^∞ of solutes such as alkanes, alkenes, and alkylbenzenes as well as of the linear and branched C_1-C_6 alcohols, esters, and aldehydes in the ionic liquids trimethyl-butylammonium bis(trifluoromethylsulfonyl) imide $[Me_3BuN][NTf_2]$ have been determined by gas chromatography using the ionic liquids as stationary phase. The measurements were carried out at different temperatures between 302 K and 393 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. Vapor−liquid equilibria (VLE) of binary mixtures containing methanol, ethanol, and propan-1-ol in $[Me_3BuN][NTf_2]$ were studied by using a static method. VLE measurements were carried out covering the whole concentration range at four different temperatures between 298.15 K and 313.15 K. Activity coefficients γ_i of solutes in the ionic liquid and their osmotic coefficients ϕ_i in the $[Me_3BuN][NTf_2]$ have been determined from the VLE data and are described formally by using the NRTL equation. γ_i^∞ and $H_i^{E,\infty}$ for methanol, ethanol, and propan-1-ol in $[Me_3BuN][NTf_2]$ are derived from the both the GC and the static method.

Introduction

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 infinite dilution γ_i^∞ in ionic liquids to the compound trimethyl-butylammonium bis(trifluoromethylsulfonyl) imide ($C_9H_{18}N_2O_4S_2F_6$)



having the molar mass 396.33 and the common abbreviation $[Me_3BuN][NTf_2]$.

Since ionic liquids (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_6 alcohols, esters, aldehydes, and several common solvents (acetone, acetonitrile, trichloromethane, 1,4-dioxane, *N*-methylpyrrolidone, and *N*,*N*-dimethylformamide) in $[Me_3BuN][NTf_2]$ have been studied over the temperature range (302 to 393) K.

In addition, vapor pressure measurements of the three solutes methanol, ethanol, and propan-1-ol in the ionic liquid $[Me_3BuN][NTf_2]$ have been carried out over the whole range of binary concentrations. In contrast to previous work where VLE data of low volatile solutes in ILs were measured using the transpiration method,[10,11] in the present work the VLE data have been obtained by using a static vapor pressure method.[5] From the pressure data, activity coefficients γ_i at different temperatures have been obtained. Furthermore, activity coefficients in infinity dilution γ_i^∞ of methanol, ethanol, and propan-1-ol in the ionic liquid $[Me_3BuN][NTf_2]$ have been derived by extrapolation to $x_i = 0$ and compared with those obtained from the GC method.

Experimental Procedure

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 $[Me_3BuN][NTf_2]$ 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 more than 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 at high temperature in order to remove traces of adsorbed moisture.

GC Method: 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 carrier gas. A GC column (stainless steel) with length 43 cm with an inside diameter of 0.40 cm was used. The amount of stationary phase (ionic liquid)

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was 2.46 mmol. The mass of the stationary phase was determined gravimetrically 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 35 mass % of the support material.

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

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

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

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

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 flowmeter temperature; p_{ow} is 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 mobile gaseous phase. B_{11} is the second virial coefficient of the solute, and 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[13]

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

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 four to five 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 IL 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 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 Edminster 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}, and 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 alkanes 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 %.

Static Vapor Pressure Method: Experimental Procedure. The VLE measurements of binary solutions of [Me_3BuN][NTf_2] with (CH_3OH, or C_2H_5OH, or C_3H_7OH) have been performed by using a static method.[5] The experimental setup consisted of a bolted-top glass cell surrounded by a water bath. which was kept at constant temperature (± 0.02 K). The measuring cell is equipped with an injection port containing a septum. A special construction of the injection port allows evacuation of the injection port before and after injecting a liquid sample and prevents pressure fluctuation in the measuring cell during the injection procedure. The pressure was measured using a calibrated high accuracy sensor head (type 615A, MKS Baratron) connected to the signal conditioner (type 670A, MKS Baratron) attached to the top of the cell. The sensor head and the connecting line from the cell to the sensor were thermostated at 333.15 ± 0.01 K. This temperature is always kept above the temperatures of the measuring cell in order to avoid any condensation in the pressure head. The experimental uncertainties were ± 0.01 K for the temperature and ± 10 Pa for the pressure.

To start an experimental series of measurements a certain amount of degassed IL was placed into the cell using a weighted syringe. The cell loaded with the IL is kept at room temperature

Table 1. Experimental Results of γ_i^∞ for Different Solutes in the [Me$_3$BuN][NTf$_2$]: 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*	temperature interval/K	*a*	*b*/K	R^2	$\gamma_{i\,(298\text{ K})}^\infty$	$H_i^{E,\infty}$/ kJ·mol^{-1}
Alkanes						
1-pentane	301.85−322.85	2.49	38.789	1.000	13.70	0.32
1-hexane	301.9−333.4	1.11	560.44	0.999	19.85	4.66
1-heptane	301.7−333.3	0.745	804.04	0.998	31.23	6.69
1-octane	301.7−333.3	0.808	906.89	1.000	46.98	7.54
1-nonane	301.7−375.0	0.500	1120.0	0.999	70.55	9.31
1-decane	302.2−354.1	0.445	1254.5	0.998	104.86	10.43
1-undecane	322.8−364.6	0.583	1317.4	0.998	154.67	11.58
1-dodecane	333.3−354.1	−0.715	1857.0	0.996	248.09	15.44
Alkenes						
1-pentene	301.9−312.4	0.45	407.5	0.999	6.17	3.39
1-hexene	305.9−364.55	0.78	469.93	0.998	10.60	3.91
1-heptene	306.8−354.1	0.34	737.41	0.999	16.69	6.13
1-octene	306.8−364.6	0.51	807.03	0.996	24.87	6.71
1-nonene	306.7−364.6	0.36	936.04	0.998	37.72	8.12
1-decene	306.2−354.1	0.59	1023.0	0.999	55.53	8.51
1-undecene	322.6−375.0	0.58	1149.0	0.996	87.88	9.55
1-dodecene	333.3−385.5	0.29	1353.4	0.999	124.9	11.25
Cyclic Hydrocarbons						
cyclohexane	301.0−333.3	−0.40	641.3	0.999	5.76	5.33
cyclohexene	312.1−354.2	−0.31	462.2	0.991	7.65	5.90
1,3-cyclohexadiene	306.0−364.6	−0.29	480.09	0.995	3.76	3.99
Alkylbenzene						
benzene	322.8−364.5	−0.39	209.45	0.962	1.37	1.74
toluene	322.8−364.5	0.28	89.18	0.999	1.78	0.74
ethyl benzene	322.9−354.3	0.16	280.36	0.964	3.01	2.33
propyl benzene	333.3−364.5	0.60	259.16	0.992	4.33	2.15
butyl benzene	333.3−375.0	0.75	336.1	0.996	6.5	2.79
pentyl benzene	354.1−385.5	0.65	503.24	0.991	10.39	4.18
Alcohols						
methanol	304.0−343.7	−3.17	1099.2	0.998	1.67	9.14
ethanol	322.9−343.7	−2.79	1078.1	1.000	2.29	8.96
1-propanol	301.8−333.4	−2.93	1192.2	1.000	2.91	9.91
1-butanol	302.6−343.7	−2.75	1221.5	1.000	3.85	10.16
1-pentanol	322.9−364.5	−2.60	1274.6	1.000	5.32	10.60
1-hexanol	343.7−385.6	−2.35	1285.5	1.000	7.1	10.69
2-propanol	302.6−354.1	−2.98	1167.0	0.999	2.54	9.70
iso-butanol	302.6−354.1	−2.64	1217.6	0.999	4.23	10.12
sec-butanol	333.2−375.0	−2.84	1190.8	0.998	3.16	9.9
tert-butyl alcohol	302.6−354.1	−2.71	1064.6	1.000	2.36	8.85
tert-pentanol	302.6−354.1	−1.93	864.19	1.000	2.64	7.19
cyclohexanol	343.7−385.6	−4.05	1816.5	0.995	7.74	15.10
Aldehydes						
propanal	301.7−343.6	−1.49	284.15	0.958	0.59	2.36
butanal	301.8−354.2	−0.65	132.4	0.992	0.81	1.1
pentanal	301.8−354.2	−0.52	321.32	0.980	1.74	2.67
hexanal	322.8−364.7	0.25	129.45	0.978	1.99	1.08
heptanal	354.2−396.0	−2.23	1008.7	0.993	3.17	8.39
octanal	364.6−396.0	0.69	210.01	0.988	4.02	1.75
Esters						
methyl propanoate	311.7−343.8	−0.48	130.97	0.992	0.96	1.09
methyl butanoate	311.7−364.5	−0.33	188.12	1.000	1.35	1.56
methyl pentanoate	322.8−364.6	−1.04	503.35	0.960	1.92	4.19
methyl hexanoate	343.7−375.0	−0.97	640.19	0.992	3.24	5.32
methyl heptanoate	343.6−385.5	−1.30	846.26	0.989	4.68	7.04
Polar Solvents						
acetone	301.9−343.8	−1.30	131.83	0.982	0.42	1.10
acetonitrile	301.8−343.8	−1.65	299.3	0.991	0.52	2.49
1,4-dioxane	343.8−354.3	−0.35	13.027	0.999	0.74	0.11
trichloromethane	301.8−333.3	0.25	−67.311	0.969	1.02	−0.56
N-methyl-pyrrolidone	312.35−375.15	−4.86	2990.2	1.000	175.49	24.86
N,*N*-dimethyl-formamide	375.15−396.15	−0.68	−208.4	0.960	0.25	−1.73

under vacuum for ca. 12 h (until the pressure sensor indicates zero point). Exactly known amounts of the degassed solvent were injected stepwise into the thermostated equilibrium cell with the help of special glass injectors. Phase equilibrium was reached in each step by using a magnetic stirrer with a Teflon-coated magnet inside the cell. The vapor phase consists exclusively of the solvent, and equilibration in the cell is a rapid process. A constant pressure is reached within 15 min. Equilibrium pressure readings are registered in 10 min intervals. The method was checked[9] by measuring the vapor pressure of pure methanol[19] as well as the vapor−liquid equilibrium of the binary mixture (benzene + tetradecane), where reliable VLE data exist in the literature.[20] The experiments were carried out in the temperature range $T = (298.15\text{ to }313.15)$ K. The experimental

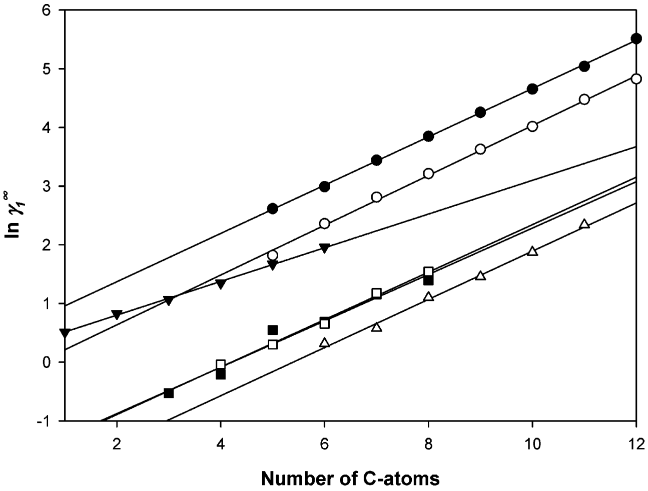

Figure 1. Values of $\ln \gamma_i^\infty$ as function the number of carbon atoms for different classes of solutes in [Me$_3$BuN][NTf$_2$] at 298.15 K: ●, alkanes; ○, alkenes; △, alkylbenzenes; ▼, alcohols; ■, aldehydes; □, esters.

vapor pressure is assessed to be reliable to within ± 1 % according to the test measurements.

Results and Discussion

GC Method. The values of γ_i^∞ of different solutes in [Me$_3$BuN][NTf$_2$] obtained at different temperatures are listed in Table 1. Altogether 256 data points for 55 solutes have been obtained in the temperature range (302 to 393) 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 γ_i^∞(298 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 0.96 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 slightly 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 than those obtained for alkanes and alkenes.

Table 2. Experimental Vapor Pressure Values of Investigated Solutions

	298.15 K		303.15 K		308.15 K		313.15 K	
x_1	p/Pa	γ_1	p/Pa	γ_1	p/Pa	γ_1	p/Pa	γ_1
xCH$_3$OH + (1 − x)[Me$_3$BuN][NTf$_2$]								
0.0000	0	1.279	0	1.219	0	1.147	0	1.120
0.0850	1980	1.328	2411	1.274	2823	1.205	3419	1.171
0.1093	2502	1.339	3040	1.287	3658	1.219	4379	1.183
0.1308	2923	1.347	3608	1.297	4315	1.230	5171	1.192
0.2069	4799	1.367	5917	1.323	7202	1.261	8650	1.219
0.2166	5034	1.368	6230	1.325	7561	1.264	9102	1.222
0.2539	5963	1.371	7386	1.331	8945	1.273	10746	1.229
0.2973	7051	1.369	8729	1.333	10553	1.279	12748	1.234
0.4400	10047	1.328	12605	1.304	15457	1.263	18703	1.222
0.5989	12676	1.232	16044	1.218	19893	1.194	24271	1.163
0.6450	13302	1.198	16902	1.186	20913	1.166	25631	1.140
0.7410	14489	1.125	18386	1.118	22840	1.106	28317	1.090
0.8624	15756	1.044	20028	1.041	25170	1.037	31522	1.031
0.9046	16118	1.023	20583	1.021	26007	1.019	32503	1.016
0.93664	16409	1.011	20997	1.010	26561	1.009	33321	1.008
0.96865	16750	1.003	21546	1.003	27400	1.002	34573	1.002
1.0000	16958	1.000	21880	1.000	27960	1.000	35450	1.000
xC$_2$H$_5$OH + (1 − x)[Me$_3$BuN][NTf$_2$]								
0.0000	0	2.378	0	2.199	0	1.983	0	1.815
0.0575	1097	2.225	1369	2.061	1625	1.864	1910	1.706
0.1524	2222	2.019	2678	1.874	3184	1.705	3872	1.562
0.1651	2420	1.995	2913	1.852	3461	1.687	4235	1.546
0.2540	3652	1.845	4555	1.720	5423	1.575	6280	1.447
0.3305	4665	1.737	5748	1.625	7000	1.497	7947	1.379
0.4141	5486	1.637	6839	1.539	8218	1.427	9774	1.320
0.5078	6226	1.538	7889	1.457	9677	1.361	11885	1.267
0.5919	6771	1.458	8652	1.391	10769	1.311	13488	1.229
0.6555	7219	1.399	9215	1.343	11596	1.275	14490	1.203
0.7041	7616	1.352	9736	1.307	12248	1.249	15212	1.185
0.7364	7731	1.320	9991	1.282	12607	1.230	15701	1.173
0.7969	7825	1.256	10227	1.230	13127	1.193	16569	1.149
0.8705	7837	1.165	10364	1.156	13501	1.138	17338	1.112
0.94893	7854	1.052	10430	1.053	13690	1.053	17790	1.051
0.96847	7857	1.025	10439	1.027	13723	1.028	17856	1.029
1.0000	7876	1.000	10468	1.000	13768	1.000	17928	1.000
xC$_3$H$_7$OH + (1 − x)[Me$_3$BuN][NTf$_2$]								
0.0000	0	3.888	0	3.625	0	3.248	0	3.112
0.0223	247	3.723	316	3.478	382	3.137	492	3.003
0.0336	332	3.644	422	3.408	514	3.083	644	2.951
0.0785	710	3.356	905	3.152	1125	2.883	1424	2.758
0.1456	1193	2.994	1535	2.830	1941	2.626	2504	2.512
0.1742	1355	2.860	1750	2.710	2223	2.529	2839	2.419
0.1841	1416	2.816	1824	2.670	2305	2.497	2951	2.389
0.2518	1772	2.543	2289	2.427	2917	2.295	3770	2.199
0.2937	1977	2.396	2567	2.295	3280	2.184	4200	2.096
0.3317	2134	2.274	2802	2.187	3615	2.091	4598	2.010
0.3857	2330	2.117	3082	2.046	4012	1.969	5122	1.898
0.4575	2519	1.931	3364	1.879	4410	1.823	5654	1.764
0.5025	2594	1.825	3478	1.783	4583	1.737	5955	1.687
0.5622	2665	1.694	3587	1.665	4766	1.630	6259	1.590
0.62471	2702	1.566	3658	1.549	4895	1.523	6471	1.494
0.65725	2715	1.502	3686	1.490	4940	1.469	6550	1.445
0.78237	2737	1.274	3737	1.275	5041	1.267	6723	1.260
0.87331	2747	1.125	3755	1.130	5076	1.127	6775	1.128
0.91542	2 750	1.066	3 755	1.070	5 076	1.069	6 782	1.071
1.0000	2786	1.000	3826	1.000	5199	1.000	6986	1.000

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:

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

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 $\ln \gamma_i^\infty$ 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]

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

Table 3. Vapor Pressure of Pure Solutes p^*, Second Virial Coefficient B_s of Vapor Solute and Molar Volume V_s^* of Liquid Solute at Different Temperatures

T	p^*	B_s	V_s^*
K	Pa	$m^3 \cdot mol^{-1}$	$m^3 \cdot mol^{-1}$
		CH_3OH	
298.15	16958	$-2172.5 \cdot 10^{-6}$	$4.075 \cdot 10^{-5}$
303.15	21880	$-1942.3 \cdot 10^{-6}$	$4.099 \cdot 10^{-5}$
308.15	27960	$-1746.6 \cdot 10^{-6}$	$4.124 \cdot 10^{-5}$
313.15	35450	$-1579.0 \cdot 10^{-6}$	$4.150 \cdot 10^{-5}$
		C_2H_5OH	
298.15	7878	$-1723.5 \cdot 10^{-6}$	$5.868 \cdot 10^{-5}$
303.15	10467	$-1598.8 \cdot 10^{-6}$	$5.901 \cdot 10^{-5}$
308.15	13765	$-1485.5 \cdot 10^{-6}$	$5.933 \cdot 10^{-5}$
313.15	17906	$-1382.50 \cdot 10^{-6}$	$5.967 \cdot 10^{-5}$
		C_3H_7OH	
298.15	2786	$-4290.0 \cdot 10^{-6}$	$7.514 \cdot 10^{-5}$
303.15	3826	$-4013.9 \cdot 10^{-6}$	$7.553 \cdot 10^{-5}$
308.15	5199	$-3713.3 \cdot 10^{-6}$	$7.592 \cdot 10^{-5}$
313.15	6986	$-3401.1 \cdot 10^{-6}$	$7.631 \cdot 10^{-5}$

Table 4. Parameters of the NRTL Equation

T	$g_{12}-g_{22}$	$g_{21}-g_{11}$	α
K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	
	[Me_3BuN][NTf_2] + CH_3OH		
298.15	14.4371	−8.7766	0.0739247
303.15	16.5879	−10.5958	0.0611245
308.15	17.5388	−11.5650	0.0564698
313.15	17.1496	−11.6591	0.0547772
	[Me_3BuN][NTf_2] + C_2H_5OH		
298.15	10.1683	1.0862	0.550942
303.15	10.1726	1.0994	0.604492
308.15	9.9069	1.0652	0.689704
313.15	9.4340	1.0696	0.820402
	[Me_3BuN][NTf_2] + C_3H_7OH		
298.15	8.0361	1.5344	0.456086
303.15	8.3361	1.5185	0.475931
308.15	8.3059	1.3299	0.491408
313.15	8.3703	1.4014	0.523682

chain length. For trichloromethane and *N*,*N*-dimethylformamide $H_i^{E,\infty}$ becomes negative.

Static Method. Experimental vapor pressures p of binary mixtures of [Me_3BuN][NTf_2] with (CH_3OH, or C_2H_5OH, or C_3H_7OH) measured at T = (298.15 to 313.15) K are listed in Table 2.

Binary mixtures of IL with nonelectrolyte components belong to the class of electrolyte solutions covering the whole range of composition including the pure liquid electrolyte. Since there exist no reliable theoretical models for the Gibbs energy of mixing of this kind of mixtures, we have tried to describe the results of activity coefficients using purely empirical expressions that are well-known in thermodynamics of nonelectrolyte mixtures. It turned out[5] that the NRTL equation gives the best empirical description of the activity coefficients. Equation 6 has been used to determine activity coefficients γ_1 from experimental data of partial pressures p_1 including the vapor pressure of the pure solutes p_{10}:

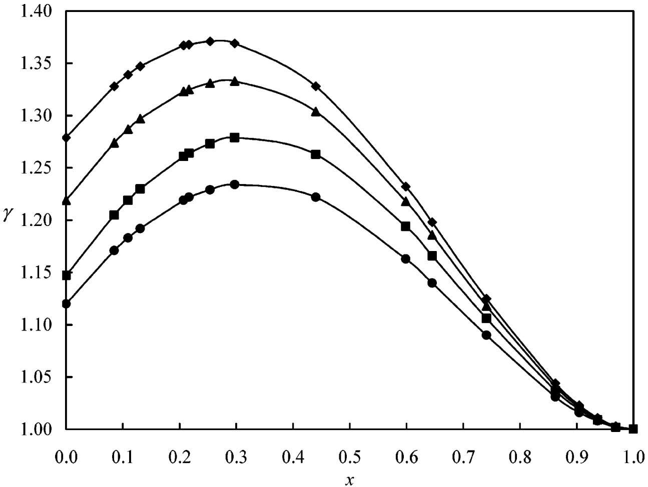

Figure 2. Plot of activity coefficient γ of methanol in CH_3OH + [Me_3-BuN][NTf_2] mixture vs mole fraction x of CH_3OH: ♦, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K; points and solid lines, eq 8.

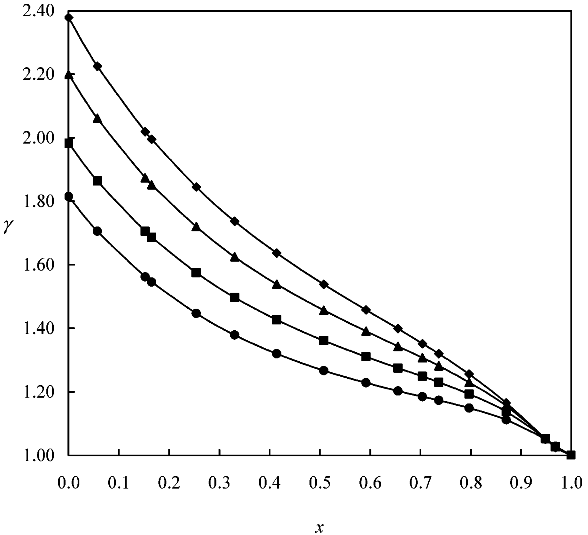

Figure 3. Plot of activity coefficient γ of ethanol in C_2H_5OH + [Me_3-BuN][NTf_2] mixture vs mole fraction x of C_2H_5OH: ♦, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K; points and solid lines, eq 8.

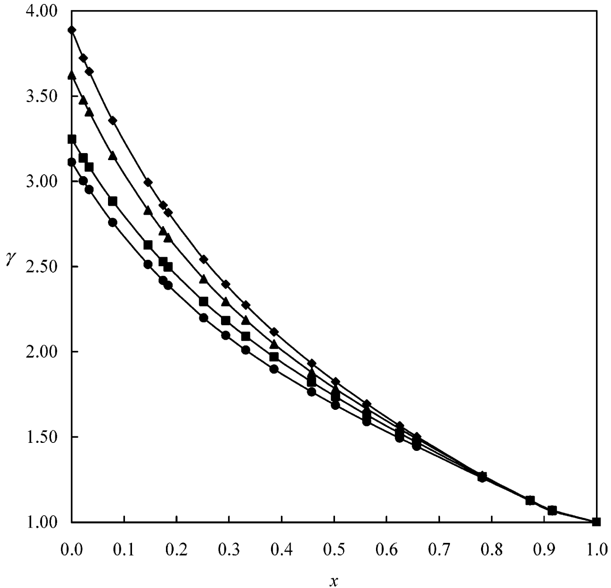

Figure 4. Plot of activity coefficient γ of propanol in C_3H_7OH + [Me_3-BuN][NTf_2] mixture vs mole fraction x of C_3H_7OH: ♦, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K; points and solid lines, eq 8.

$$p_1\frac{\phi_1}{\varphi_{10}} = p_{10}x_1\gamma_1^{\mathrm{NRTL}} \tag{6}$$

Corrections due to fugacity coefficients φ_1 and φ_{10} have been accounted for by

$$\frac{\varphi_1}{\varphi_{10}} = \exp[-(V_1 - B_{11})(p_1 - p_{10})/RT] \tag{7}$$

The second virial coefficients B_{11} of the alcohols have been taken from ref 21, and the molar liquid volumes V_1 are from ref 22. These data are presented in Table 3. It turned out that the eq 7 is only a small correction for the values of γ_1 that is within ± 1 %. The expression for $\ln \gamma_1$ is

$$\ln \gamma_1^{\mathrm{NRTL}} = x_2^2\left[\tau_{21}\left(\frac{G_{21}}{x_1 + x_2G_{21}}\right)^2 + \frac{\tau_{12}G_{12}}{(x_2 + x_1G_{12})^2}\right] \tag{8}$$

with $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $\tau_{ij} = (g_{ij}-g_{jj})/RT$ and $\alpha_{ij} = \alpha_{ji} = \alpha$ (i, j = 1, 2; $i \neq j$). Table 4 contains the parameters α_{ij} and $(g_{ij}-g_{jj})$ obtained by fitting γ_1^{NRTL} to the experimental VLE data. The plots of eq 8 of IL with alcohols versus the mole fractions x_1 of solvent are shown in Figures 2 to 4.

The activity of the solvent, a_s, and osmotic coefficients, ϕ, were calculated from the experimental vapor pressure values using the following equations:

$$\ln a_s = \ln(p/p^*) + (B_s - V_s^*)(p - p^*)/RT \tag{9}$$

$$\phi = -\ln a_s/(\nu m M_s) \tag{10}$$

where p and p^* are the vapor pressures of the solution and pure solvent, respectively; B_s and V_s^* are the second virial coefficient of solvent vapor and molar volume of pure liquid solvent, respectively; ν is the sum of stoichiometric numbers of anion and cation ($\nu_- + \nu_+$); m is molality of salt; and M_s is the molecular weight of solvent, respectively. The second term on the right-hand side of eq 9 takes into account the nonideality of the solvent vapor using the virial equation. The obtained values for a_s and ϕ are tabulated in Table 5. The values of p^*, B_s, and V_s^* required for calculations were taken from refs 19−21 and are shown in Table 3. The plots of eq 10 of IL with alcohols versus the molality of solvent are shown in Figures 5 to 7.

Values of γ_1 decrease with temperature for all mixtures (except for the mixture methanol + [Me_3BuN][NTf_2]). In case

Table 5. Calculated Activity of Solutes a_s and Osmotic Coefficients ϕ of the Investigated Solutions

	298.15 K		303.15 K		308.15 K		308.15 K	
x_1	a_s	ϕ	a_s	ϕ	a_s	ϕ	a_s	ϕ
$x\mathrm{CH_3OH} + (1 - x)[\mathrm{Me_3BuN}][\mathrm{NTf_2}]$								
0.96865	0.987918	0.188	0.984994	0.234	0.980354	0.307	0.975793	0.379
0.93664	0.968100	0.240	0.960311	0.300	0.950892	0.373	0.941190	0.449
0.9046	0.951179	0.238	0.941683	0.286	0.931419	0.338	0.918552	0.404
0.8624	0.930117	0.228	0.916691	0.274	0.901969	0.325	0.891373	0.362
0.7410	0.856291	0.224	0.842624	0.247	0.819805	0.287	0.802341	0.318
0.6450	0.786973	0.220	0.775518	0.234	0.751649	0.263	0.727451	0.293
0.5989	0.750357	0.218	0.736648	0.232	0.715497	0.254	0.689435	0.282
0.4400	0.596131	0.208	0.580317	0.219	0.557670	0.235	0.533116	0.253
0.2973	0.419486	0.189	0.403099	0.198	0.382045	0.210	0.364723	0.220
0.2539	0.355102	0.182	0.341441	0.189	0.324195	0.198	0.307828	0.207
0.2166	0.300028	0.172	0.288263	0.178	0.274299	0.185	0.261001	0.192
0.2069	0.286082	0.169	0.273848	0.175	0.261341	0.181	0.248110	0.188
0.1308	0.174541	0.136	0.167288	0.139	0.156895	0.144	0.148643	0.148
0.1093	0.149458	0.121	0.141015	0.125	0.133067	0.128	0.125938	0.132
0.0850	0.118331	0.103	0.111893	0.106	0.102752	0.110	0.098388	0.112
$x\mathrm{C_2H_5OH} + (1 - x)[\mathrm{Me_3BuN}][\mathrm{NTf_2}]$								
0.96847	0.997349	0.041	0.997343	0.041	0.996974	0.047	0.997290	0.042
0.94893	0.996971	0.028	0.996489	0.033	0.994596	0.050	0.993641	0.059
0.8705	0.994825	0.017	0.990227	0.033	0.980977	0.065	0.968637	0.107
0.7969	0.993310	0.013	0.977225	0.045	0.954018	0.093	0.926069	0.151
0.7364	0.981444	0.026	0.954823	0.065	0.916513	0.122	0.877977	0.183
0.7041	0.966925	0.040	0.930609	0.086	0.890607	0.139	0.850863	0.193
0.6555	0.916784	0.083	0.881111	0.121	0.843529	0.163	0.810803	0.201
0.5919	0.860166	0.110	0.827585	0.139	0.783761	0.178	0.755154	0.206
0.5078	0.791241	0.122	0.754981	0.147	0.704750	0.183	0.665998	0.212
0.4141	0.697568	0.129	0.654948	0.152	0.599022	0.184	0.548345	0.216
0.3305	0.593525	0.131	0.550862	0.150	0.510615	0.169	0.446297	0.203
0.2540	0.464980	0.133	0.436873	0.144	0.395957	0.161	0.353006	0.181
0.1651	0.308392	0.119	0.279690	0.129	0.253002	0.139	0.238324	0.145
0.1524	0.283201	0.116	0.257166	0.125	0.232792	0.134	0.217940	0.140
0.0575	0.139929	0.062	0.131577	0.064	0.118920	0.067	0.107623	0.071
$x\mathrm{C_3H_7OH} + (1 - x)[\mathrm{Me_3BuN}][\mathrm{NTf_2}]$								
0.91542	0.987141	0.075	0.981556	0.108	0.976519	0.138	0.971063	0.171
0.87331	0.986069	0.052	0.981556	0.069	0.976519	0.088	0.970070	0.112
0.78237	0.982497	0.034	0.976879	0.045	0.969836	0.059	0.962691	0.073
0.65725	0.974637	0.026	0.963627	0.038	0.950547	0.052	0.938136	0.066
0.62471	0.969993	0.027	0.956351	0.040	0.941951	0.054	0.926919	0.068
0.5622	0.956772	0.031	0.937896	0.044	0.917302	0.060	0.896805	0.075
0.5025	0.931399	0.039	0.909557	0.052	0.882319	0.068	0.853594	0.086
0.4575	0.904589	0.046	0.879907	0.058	0.849230	0.074	0.810774	0.095
0.3857	0.836996	0.060	0.806514	0.073	0.773043	0.087	0.735008	0.104
0.3317	0.766853	0.071	0.733575	0.083	0.696957	0.097	0.660276	0.111
0.2937	0.710631	0.077	0.672308	0.089	0.632684	0.103	0.603444	0.114
0.2518	0.637174	0.082	0.599769	0.093	0.562966	0.105	0.541974	0.112
0.1841	0.509483	0.082	0.478289	0.090	0.445256	0.099	0.424699	0.105
0.1742	0.487588	0.082	0.458940	0.089	0.429468	0.097	0.408641	0.102
0.1456	0.429415	0.078	0.402696	0.084	0.375144	0.091	0.360583	0.094
0.0785	0.255779	0.063	0.237663	0.067	0.217696	0.071	0.205356	0.073
0.0336	0.119683	0.040	0.110909	0.042	0.099553	0.044	0.092969	0.045
0.0223	0.089055	0.030	0.083064	0.031	0.074001	0.032	0.071040	0.033

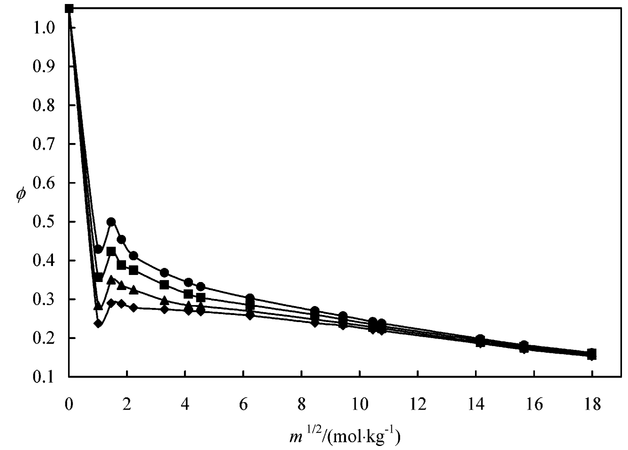

Figure 5. Plot of osmotic coefficient ϕ of CH_3OH + $[Me_3BuN][NTf_2]$ mixture vs molality $m^{1/2}$ of CH_3OH: ♦, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

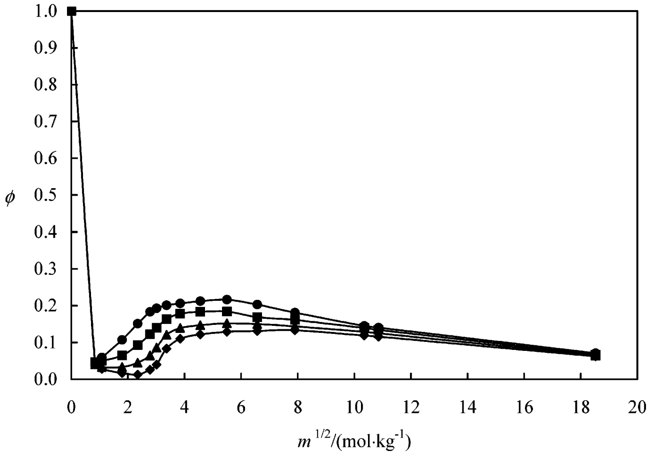

Figure 6. Plot of osmotic coefficient ϕ of C_2H_5OH + $[Me_3BuN][NTf_2]$ mixture vs molality $m^{1/2}$ of C_2H_5OH: ♦, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

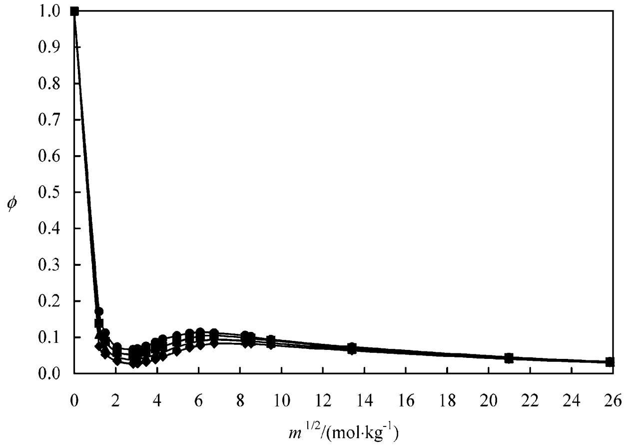

Figure 7. Plot of osmotic coefficient ϕ of C_3H_7OH + $[Me_3BuN][NTf_2]$ mixture vs molality $m^{1/2}$ of C_3H_7OH: ♦, 298.15 K; ▲, 303.15 K; ■, 308.15 K; ●, 313.15 K.

of methanol + $[Me_3BuN][NTf_2]$ γ_1 passes a maximum at high mole fractions of the solvents. Such a behavior is similar to the results obtained for $[BMIM][NTf_2]$ investigated in our previous work.[5]

Table 6. Comparison of Values of γ_i^∞ and $H_i^{E,\infty}$ of Methanol, Ethanol, and Propan-1-ol at 298 K in $[Me_3BuN][NTf_2]$ Derived in This Work from GC Method and Static Method

	γ_i^∞ at 298 K		$H_i^{E,\infty}$ at 298 K	
solute *i*	GC	static	GC	static
methanol	1.67	1.28	8.7	7.1
ethanol	2.29	2.38	9.0	14.2
propan-1-ol	2.91	3.89	9.9	12.1

Comparison of the Infinite Dilution Activity Coefficients and Excess Enthalpies at Infinite Dilution from GC Method and Static Method. Values of γ_i^∞ in $[Me_3BuN][NTf_2]$ at 298 K extrapolated from the present VLE results agree only very moderately with the results obtained by GC techniques (see Table 6) indicating no completely consistency for all three systems. The deviation in case of methanol arises most probably from some inherent problems involved with methanol by using the GC technique, discussed in ref 9. The deviation in case of pronane-1-ol arises most probably from an insufficient extrapolation based on VLE data with mole fractions not small enough to justify an extrapolation within the uncertainty of experimental error of the GC method.

Values of $H_i^{E,\infty}$ in $[Me_3BuN][NTf_2]$ at 298 K extrapolated from the present VLE results are still in acceptable agreement with the results obtained by GC techniques (see Table 6) considering the estimated experimental error sources.

Supporting Information Available:

Two tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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