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Experimental Study of Thermodynamic Properties of Mixtures Containing Ionic Liquid 1-Ethyl-3-methylimidazolium Ethyl Sulfate Using Gas−Liquid Chromatography and Transpiration Method

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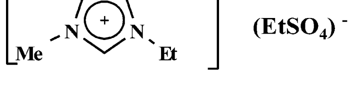
Activity coefficients at infinite dilution γ_i^∞ of 46 solutes such as alkanes, alkenes, alkylbenzenes, linear and branched C_1-C_6 alcohols, esters, aldehydes, cyclohexanone oxime, and ϵ-caprolactam in the ionic liquid (IL) 1-ethyl-3-methylimidazolium ethyl sulfate or [EMIM][EtSO$_4$] have been determined by gas chromatography using the IL as the stationary phase. The measurements were carried out at different temperatures between (302 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 ILs have been derived. Vapor−liquid equilibria (VLE) of binary mixtures containing water with [EMIM][EtSO$_4$] were studied using the transpiration method. VLE measurements were carried out over the broad concentration range at temperatures between (302.9 and 322.9) K. Activity coefficients γ_i of water in the [EMIM][EtSO$_4$] have been determined from the VLE data and are described formally by using the NRTL equation. Furthermore, activity coefficients in infinity dilution γ_i^∞ of water in the IL [EMIM]-[EtSO$_4$] have been derived by extrapolation to the infinite dilution of water.

Introduction

The use of room-temperature ionic liquids (ILs) as environmentally benign media for catalytic processes has widely been recognized and accepted.[1,2] Catalytic reactions of oximes into the corresponding lactams (Beckmann rearrangement) has long been an important subject for improvement, particularly with respect to commercial production of ϵ-caprolactam in which concentrated sulfuric acid is employed and a large amount of ammonium sulfate is produced as a byproduct. Great efforts have been put into the development of the ammonium sulfate-free processes. The Beckmann rearrangement was found to be efficiently progressed using ILs.[3−5] In this context, we decided to explore the applicability of some ILs for possible improvement of production of ϵ-caprolactam, especially on the stage of final drying of cyclohexanone oxime before catalytic conversion to ϵ-caprolactam. For this purpose, activity coefficients of water, cyclohexanone oxime, and ϵ-caprolactam in ILs are required.

Our general interest in ILs is focused on providing systematic data on activity coefficients in mixtures with organic solvents. This work continues our study of thermodynamic properties of mixtures containing ILs.[6−16] In this work, we extend our measurements of activity coefficients in infinite dilution γ_i^∞ in ILs to the compound 1-ethyl-3-methylimidazolium ethyl sulfate,



($C_7H_{14}N_2O_4S$) having the molar mass 236.29 and the common abbreviation [EMIM][EtSO$_4$]. At present, the IL [EMIM]-[EtSO$_4$] claims to be one of the cheapest on the market, and this IL is completely miscible with water, giving a chance of applying this IL for final drying of cyclohexanone oxime as mentioned above.

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 IL as stationary phase. Cyclohexanone oxime and ϵ-caprolactam and 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, and *N*,*N*-dimethylformamide) in [EMIM][EtSO$_4$] have been studied over the temperature range of (301.8 to 396.4) K.

In addition, vapor−liquid equilibrium (VLE) measurements of the water in [EMIM][EtSO$_4$] have been carried at temperatures between (302.9 and 322.9) K covering the broad range of binary concentrations using the transpiration method.[9,14] From the pressure data activity coefficients of water γ_i at different temperatures have been obtained. Furthermore, activity coefficients in infinity dilution γ_i^∞ of water in the IL [EMIM]-[EtSO$_4$] have been derived by extrapolation to $x_i = 0$.

Experimental Procedures

Materials. The samples of solutes studied were of commercial origin. GC analysis gave a purity >99.9 % in agreement with specifications stated by the suppliers. All chemicals were used without further purification. The [EMIM][EtSO$_4$] was supplied by Solvent Innovation, Germany (trade name ECOENG212). Its purity according specification was 99 %, with following

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certified amounts of impurities: $[\mathrm{Cl}^-] < 0.05$ mass fraction, water < 0.05 mass fraction. Prior to the 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 (< 0.01 mass fraction) was determined by Karl Fischer titration. Chromosorb W/AW-DMCS 100/120 mesh was used as solid support for the IL 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 IL 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 and 105) cm, respectively, with an inside diameter of 0.40 cm were used. The amounts of stationary phase (IL) were (4.20 to 4.46) mmol for the short column and 11.68 mmol for the longer one. The masses of the stationary phase were determined with a precision of ± 0.0003 g. In order to avoid possible residual adsorption effects of the solutes on chromosorb, the amount of IL was about (34.2 to 36.1) mass % of the support material.

According to Cruickshank et al.,[17] the following equation for the data treatment was used:

$$\ln \gamma_{i,3}^{\infty} = \ln\left(\frac{n_3RT}{V_{\mathrm{N}}p^{\circ}_{1}}\right) - \frac{B_{11} - V_1^0}{RT}p^{\circ}_{1} + \frac{2B_{12} - V_1^{\infty}}{RT}Jp_{\mathrm{o}} \qquad (1)$$

where $\gamma_{i,3}^{\infty}$ is the activity coefficient of component i at infinite dilution in the stationary phase (index 3), p°_{1} is the vapor pressure of the pure liquid solute, n_3 is the number of moles of the stationary phase component (IL) on the column, and V_{N} is the standardized retention volume obtained by

$$V_{\mathrm{N}} = JU_0(t_{\mathrm{r}} - t_{\mathrm{G}})\frac{T_{\mathrm{col}}}{T_{\mathrm{f}}}\left[1 - \frac{p_{\mathrm{ow}}}{p_{\mathrm{o}}}\right] \qquad (2)$$

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 the flowmeter temperature, p_{ow} is the saturation pressure of water at T_{f}, and p_{o} is the pressure at the column outlet.

The second and third terms in eq 1 are correction terms that arise from the nonideality of 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 IL 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[18]

$$J = \frac{3}{2}\frac{(p_{\mathrm{i}}/p_{\mathrm{o}})^2 - 1}{(p_{\mathrm{i}}/p_{\mathrm{o}})^3 - 1} \qquad (3)$$

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 at atmospheric pressure. The pressure drop ($p_{\mathrm{i}} - p_{\mathrm{o}}$) 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 ILs, 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 5) temperatures (in 10 deg steps) between (302 and 396) K [(412 to 427) K in the case of cyclohexanone oxime and ϵ-caprolactam)]. 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 and 30) min depending on the individual solute. At each temperature, values of the dead time t_{G} identical to the retention time of a non-retainable component were measured. While our GC was equipped with a flame-ionization detector, methane[6,7] 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]

In order 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.[19] Critical parameters needed for the calculations are presented in the Supporting Information. 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.[20] Acentric factors ω_i were calculated by the Edminster equation.[20] More details are given in the Supporting Information. Values of B_{12} have also been estimated according to Tsonopolous' method. The mixed critical properties $P_{\mathrm{c}ij}$, $T_{\mathrm{c}ij}$, $V_{\mathrm{c}ij}$, and $Z_{\mathrm{c}ij}$ and mixed acentric factor ω_{ij} were calculated by equations given in the literature.[19−20]

Values of vapor pressures p°_{1} 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.[21] For alkanes, values of p°_{1} were calculated using parameters of the Cox equation recommended by Steele and Chirico.[22] Vapor pressures of pure alcohols were calculated using coefficients of Wagner's equation recommended by Ambrose and Walton.[23] Specification of the sources of vapor pressures of other solutes was given in previous papers of this series.[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

Table 1. Experimental Results of γ_i^∞ for Different Solutes in the [EMIM][EtSO$_4$]: Temperature Ranges, Coefficients of Equation 5, Correlation Coefficients R^2, γ_i^∞ at 298 K Calculated Using Equation 5, and Values of $H_i^{E,\infty}$ Derived from Equation 6

solute *i*	temp range/K	*a*	*b*/K	R^2	γ_i^∞(298 K)	$H_i^{E,\infty}$/kJ·mol^{-1}
Alkanes						
1-octane	301.9−333.5	−1.17	1971.3	0.996	243.6	16.4
1-nonane	301.8−333.5	−0.20	1839.4	0.991	392.4	15.3
1-decane	301.8−333.5	1.83	1329.4	0.992	538.4	11.0
1-undecane	301.8−354.3	−0.09	1979.1	0.979	700.9	16.5
1-dodecane	323.0−364.8	1.15	1677.2	0.966	878.5	14.0
Alkenes						
1-hexene	301.9−344.0	4.79	−169.9	0.958	67.9	−1.4
1-heptene	301.9−344.0	2.59	619.2	0.995	106.0	5.1
1-octene	302.1−344.0	2.81	669.1	0.988	156.2	5.6
1-nonene	301.9−343.9	0.34	1515.3	0.994	226.4	12.6
1-decene	301.9−322.9	1.29	1362.9	0.993	353.6	11.3
1-undecene	301.9−354.3	2.37	1135.2	0.976	480.9	9.4
1-dodecene	312.5−354.3	2.88	1050.4	0.980	606.2	8.7
Cyclic Hydrocarbons						
cyclohexane	301.6−364.7	−3.17	2081.1	0.995	45.3	17.3
cyclohexene	301.6−343.8	−1.30	1308	0.993	21.8	10.9
Alkylbenzene						
benzene	301.8−364.7	0.06	315.7	0.958	3.1	2.6
toluene	312.3−364.7	0.60	363.3	0.981	6.2	3.0
ethyl benzene	354.3−385.7	0.18	720.6	0.997	13.5	6.0
propyl benzene	343.8−385.7	0.64	749.9	0.999	23.4	6.2
butyl benzene	343.7−396.1	0.76	890.8	0.997	42.4	7.4
pentyl benzene	354.3−396.1	1.01	981.0	0.995	73.6	8.2
Alcohols						
methanol	312.4−354.2	−1.94	330.2	0.994	0.43	2.7
ethanol	302.4−354.3	−1.92	536.6	0.992	0.89	4.5
1-propanol	322.8−375.4	−2.23	783.2	0.998	1.5	6.5
1-butanol	323.0−365.0	−1.67	709.8	0.981	2.0	5.9
1-pentanol	333.4−364.7	−1.34	758.3	0.986	3.3	6.3
1-hexanol	343.8−375.2	−1.39	912.7	0.995	5.3	7.6
isopropanol	302.5−343.9	−1.76	652.4	0.997	1.5	5.4
isobutanol	322.7−386.0	−1.54	655.0	0.996	1.9	5.4
sec-butanol	312.5−364.9	−1.55	687.8	0.989	2.1	5.7
tert-butanol	302.0−354.4	−1.34	614.0	0.996	2.1	5.1
tert-pentanol	302.0−354.4	−0.43	410.9	0.996	2.6	3.4
Aldehydes						
propanal	333.5−375.2	−0.31	324.8	0.981	2.2	2.7
butanal	322.8−385.9	0.65	191.9	0.996	3.6	1.6
pentanal	333.5−375.2	0.71	313.5	0.986	5.8	2.6
hexanal	312.2−333.4	2.04	121.9	0.999	11.6	1.01
heptanal	303.3−354.2	0.44	708.0	0.999	16.7	5.89
octanal	303.3−343.8	2.07	399.2	0.981	30.2	2.1
Esters						
methyl propanoate	322.9−375.3	−0.39	634.9	0.972	5.7	5.3
methyl butanoate	343.9−385.9	0.09	652.8	0.996	9.8	5.4
methyl pentanoate	333.6−385.9	−0.48	984.1	0.982	16.8	8.2
methyl hexanoate	301.7−343.9	1.11	572.6	0.991	20.7	4.8
methyl heptanoate	301.8−333.4	1.79	483.5	0.991	30.5	4.0
Solvents						
acetone	323.1−386.0	−0.04	173.3	0.95	1.7	1.4
acetonitrile	312.2−354.3	−0.63	132.3	0.981	0.83	1.10
1,4-dioxane	312.4−354.2	0.59	47.7	0.990	2.1	0.4
trichloromethane	301.6−354.2	1.97	−835.9	0.999	0.44	−7.0
ϵ-caprolactam	412.3−427.1				5.5[a]	
cyclohexanone oxime	417.2−427.5				0.49[a]	

[a] Results are referred to the T_{av} of the measured temperature range.

literature.[6,7] An agreement of the activity coefficients γ_i^∞ for these compounds within to ± 3 % has been observed. Experimental results of γ_i^∞ for different solutes in the [EMIM][EtSO$_4$] are presented in Table 1.

VLE Measurements of the Binary Mixtures (Water + IL). The VLE measurements of binary solutions of [EMIM][SO$_4$] with water have been performed by using a transpiration method at three temperatures: (302.9, 312.9, and 322.9) K. The transpiration method has been described earlier.[9,14] In general, about (0.3 to 0.6) g of the IL was weighted in a glass flask together with a certain amount of the water in order to obtain a desired mole fraction of the liquid phase. About 4.3 g of glass beads (having a size of 1 mm) was added to the content of the glass flask. Glass beads coated with the initial mixture were placed in the saturation tube quantitatively. At constant temperature (± 0.1 K), a nitrogen stream was passed through the saturator, and the transported amount of gaseous water was collected in a cold trap at 228 K. We carried out the experiments in the flow rate interval of (2.4 to 6.0) dm^3·h^{-1}, which has ensured that transporting gas was in saturated equilibrium with the coexisting liquid phase in the saturation tube. Due to the negligible vapor pressure of the IL, the vapor phase consists exclusively of water. The mass of water collected in the trap within a certain time interval is determined gravimetrically (± 0.0001 g). Assuming that Dalton's law of partial pressures applied to the nitrogen stream saturated with the water is valid in the temperature range studied [(302.9 to 322.9) K], values of $p^{\text{sat}}_{\text{water}}$ were calculated:

$$p^{\text{sat}}_{\text{water}} = m_{\text{water}}RT_{\text{a}}/VM_{\text{water}} \qquad V = V_{\text{N2}} + V_{\text{water}} \qquad (V_{\text{N2}} \gg V_{\text{water}}) \tag{4}$$

where R = 8.31447 J·K^{-1}·mol^{-1}; m_{water} is the mass of transported water, and M_{water} is its molar mass and V_{water} is its volume contribution to the gaseous phase. V_{N2} is the volume of transporting gas, and T_{a} is the temperature of the soap bubble meter. The volume of transporting gas V_{N2} was determined from the flow rate and time measurements. The flow rate was maintained constant using a high-precision needle valve (Hoke). The accuracy of the volume V_{N2} measurements from the flow rate was assessed to be ± (0.02 to 0.03) %. Since the method is a dynamic one, extreme care has to be taken to ensure that thermodynamic equilibrium conditions have been fulfilled by adjusting the gas flow. If the amount of water swept from saturator and condensed in the trap is small as compared to its contents in the liquid phase inside the saturator, the change of concentration in the liquid mixture is negligible during such an experiment, and the partial pressure of the water can be assigned to the known composition of the liquid mixture being in thermodynamic equilibrium with the vapor phase. This method was carefully checked earlier by comparing results obtained by the transpiration method for binary systems where reliable VLE data exist in the literature.[9,14] The agreement was within (1 to 3) %.

Measurements of vapor pressures covering the broad range of concentrations of water (1) + IL (2) mixtures have been performed. Partial pressures of the water are presented in Table 2; the partial pressure of the IL was not detectable. We checked the system under study for the reproducibility of the data, which was found to be within (3 to 5) %. Real gas corrections arising from interactions of the vapor with the carrier gas were considered negligible within the range of the experimental uncertainties.

Special Test Measurements of Pure Water and the Binary Mixture (Water + TEG) Using Transpiration Method. In order to test the ability of the transpiration method to provide reliable results in experiments with water, vapor pressure measurements of pure water as well as VLE measurements of binary mixtures of water with triethyleneglycol (TEG) have been performed by using a transpiration method. In the latter case, we have modeled the experimental conditions for investigation of binary mixtures (water + very high boiling compound) where reliable experimental data for activity coefficients were already available from the literature. Such experience is required before commencing study of mixtures containing ILs. The conditions for these preliminary experiments were exactly the same as described above for mixtures (water + IL). Results of our measurements for vapor pressures of pure water are compared in the Table 3 with those well-established in the literature.[24] It can be seen from this table that vapor pressure measurements on pure water are reliable within (1 to 3) %.

The VLE measurements of binary solutions of water with TEG have been performed by using a transpiration method at three temperatures of (310.0, 313.0, and 316.0) K. Activity coefficients for this system have been evaluated and recommended by Twu et al.[25] recently. Comparison with our results presented in Table 4 show an agreement with recommended activity coefficients within (3 to 5) %.

Table 2. VLE in the System H_2O (1) + [EMIM][EtSO$_4$] (2)

T/K	x_1	p_1^{exp}/Pa	p_1^{NRTL}/Pa	γ_1^{NRTL}
302.9	0	0	0	0.23
	0.278	345	345	0.30
	0.424	639	638	0.37
	0.572	1070	1094	0.47
	0.613	1199	1265	0.50
	0.620	1439	1294	0.51
	0.832	2711	2676	0.79
	0.853	2600	2868	0.82
	0.959	3834	3840	0.98
	1	4095	4095	1.00
312.9	0	0	0	0.26
	0.480	1533	1524	0.45
	0.501	1555	1638	0.46
	0.54	1893	1877	0.49
	0.551	2054	1947	0.50
	0.810	4702	4519	0.79
	0.874	5045	5444	0.88
	0.888	5317	5656	0.90
	0.953	6907	6591	0.98
	1	7072	7072	1.00
322.9	0	0	0	0.20
	0.284	1036	1071	0.31
	0.302	1128	1173	0.32
	0.440	2434	2214	0.41
	0.463	2561	2433	0.43
	0.518	3237	3049	0.49
	0.542	3115	3356	0.51
	0.647	4832	5013	0.64
	0.669	5074	5424	0.67
	0.783	8315	7988	0.84
	0.858	9884	9878	0.95
	0.941	11626	11519	1.01
	1	12141	12141	1.00

Table 3. Comparison of the Vapor Pressures of Pure Water p_{exp} Measured in This Work with Those p_{lit} Available from the Literature[24]

T/K	p_{exp}/Pa	p_{lit}/Pa	Δ^a/%
302.8	4095	4146	−1.2
305.9	5003	4951	1.1
312.8	7072	7256	−2.5
322.7	12452	12202	2.1
322.9	12141	12327	−1.5
328.0	15552	15911	−2.3

[a] $\Delta = 100(p_{\text{exp}} - p_{\text{lit}})/p_{\text{exp}}$.

Table 4. Comparison of Activity Coefficients γ_{exp} of H_2O in Solution [TEG + H_2O] Measured in This Work with Those γ_{lit} Available from the Literature[25]

x_{TEG}	γ_{exp}	γ_{calc}	Δ^a/%
	T = 310.0 K		
0.248	0.787	0.775	1.5
0.332	0.745	0.766	−2.8
	T = 313.0 K		
0.375	0.745	0.766	−2.8
0.535	0.767	0.736	4.0
	T = 316.0 K		
0.248	0.787	0.786	0.1
0.444	0.736	0.761	−3.4
0.624	0.688	0.726	−5.5

[a] $\Delta = 100(\gamma_{\text{exp}} - \gamma_{\text{lit}})/\gamma_{\text{exp}}$.

Results and Discussion

GC Method. The values of γ_i^∞ of different solutes in [EMIM][EtSO$_4$] obtained at different temperatures are listed in

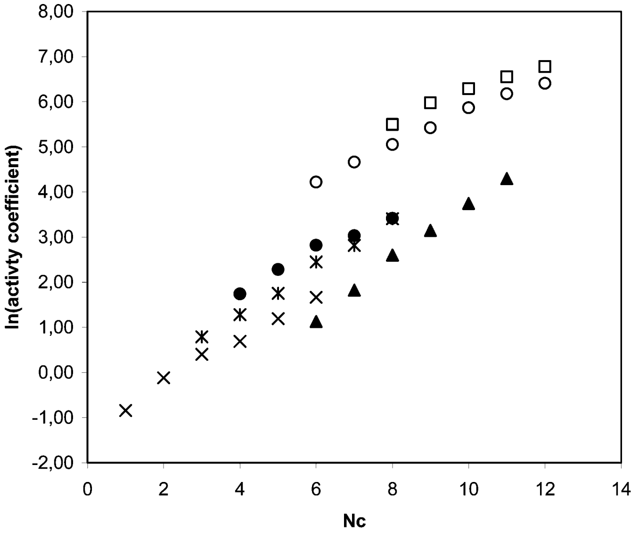

Figure 1. Values of $\ln(\gamma_i^\infty)$ as function the number of carbon atoms for different classes of solutes in [EMIM][EtSO$_4$] at 298 K. □, alkanes; ○, alkenes; ▲, alkylbenzenes; ×, alcohols; ∗, aldehydes; ●, esters.

Table 1. Altogether 226 data points for 46 solutes have been obtained in the temperature range of (302 to 396) K. The complete set of data is available in the Supporting information. The values of γ_i^∞ have been approximated by the linear regression:

$$\ln \gamma_i^\infty = a + \frac{b}{T} \tag{5}$$

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 in most cases lie between 0.95 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 IL 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., isopropanol or *tert*-butanol) hardly impact 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. This general behavior resembles the results obtained with other ILs.[7−15]

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

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

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 6 and direct calorimetric data is possible.[15]

Table 5. Parameters of the NRTL Equation

T/K	$g_{12}-g_{22}$/kJ·mol^{-1}	$g_{21}-g_{11}$/kJ·mol^{-1}	α
	[EMIM][EtSO$_4$] + H$_2$O		
302.95	4.313	−5.555	0.5
312.95	4.531	−5.408	0.5
322.95	11.173	−5.700	0.5

Values of $H_i^{E,\infty}$ are positive and decrease slightly with increasing chain length of the linear alkanes and alkenes. Values of $H_i^{E,\infty}$ of linear alcohols, aldehydes, and esters are positive and do not change with increasing chain length. For acetone, 1,4-dioxane, trichloromethane, and *N*,*N*-dimethylformamide $H_i^{E,\infty}$ becomes negative.

Data Correlation of Binary System (Water + IL) Using the NRTL Equation. Experimental vapor pressures of binary mixtures of [EMIM][EtSO$_4$] with water are listed in Table 2. There exist no reliable theoretical models for the Gibbs energy of mixing of mixtures containing ILs, thus 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[9,14] that the NRTL equation gives the best empirical description of the activity coefficients. Equation 7 has been used to determine activity coefficients γ_1 from experimental data of partial pressures p_1 including the vapor pressure of the pure water $p°_1$:

$$p_1 = p°_1 x_1 \gamma_1^{\mathrm{NRTL}} \tag{7}$$

with

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

where $G_{ij} = \exp(-\alpha_{ij}\tau_{ij})$, $\tau_{ij} = (g_{ij} - g_{jj})/RT$ and $\alpha_{ij} = \alpha_{ji} = \alpha$ (i, j = 1, 2; $i \neq j$). It turned out that the parameter α had also to be fitted separately for each system and temperature to obtain an optimized description of activity coefficients. Table 5 contains the parameters α_{ij} and ($g_{ij} - g_{jj}$) obtained by fitting γ_1^{NRTL} to the experimental VLE data. Figure 2 shows the experimental results for the partial pressures of the water mixed with [EMIM][EtSO$_4$] in comparison with the calculated results of the NRTL model according to eq 7 with parameters taken from Table 5. The NRTL equation is able to fit all the results within the experimental uncertainties. The scattering of the experimental data is about ± 5 % of the maximal pressure of the pure water.

Activity coefficients in infinity dilution γ_i^∞ of water in the IL [EMIM][EtSO$_4$] have been derived (Table 2) by extrapolation to $x_i = 0$. Values of γ_i^∞ are on the level (0.20 to 0.26) in the temperature range studied and these values are very close to those of methanol. However, it was not possible to obtain the temperature dependence of γ_i^∞ for water with sufficient accuracy because uncertainty of extrapolating the VLE data to the infinite dilution is too large in order to obtain a reasonable value of γ_i^∞.

Comparison of the Infinite Dilution Activity Coefficients and Excess Enthalpies at Infinite Dilution from GC Method and Dilutor Method. Experimental data for γ_i^∞ and $H_i^{E,\infty}$ for

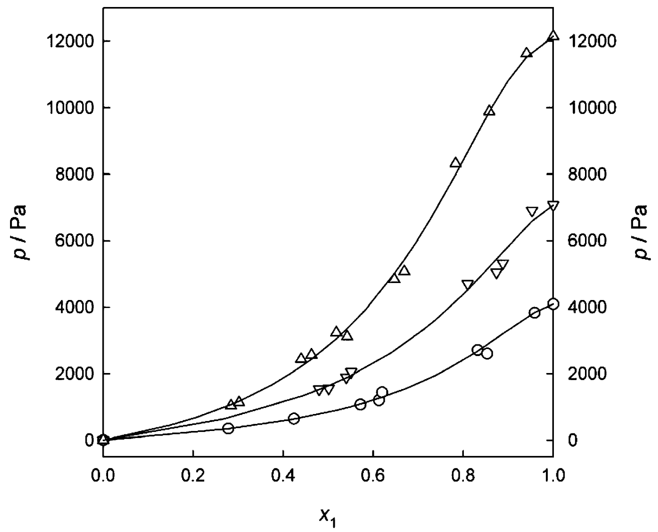

Figure 2. Partial pressure data of water in the mixture with [EMIM][EtSO$_4$] as function of x_1 (water) at ○, 303 K; ▽, 313 K; △, and 323 K.

Table 6. Comparison of Values of γ_i^∞ and $H_i^{E,\infty}$ of Alkanes. Alkenes. and Alkylbenzenes at 298 K in [EMIM][EtSO$_4$] Derived in This Work from GC Method and Those from Dilutor Technique[26]

	γ_i^∞ at 298 K		$H_i^{E,\infty}$ at 298 K	
solute *i*	GC	dilutor[26]	GC	dilutor[26]
1-hexene	67.9	50.4	16.2	6.8
1-heptene	106.0	97.8	15.6	8.5
cyclohexane	45.3	59.9	17.3	8.4
cyclohexene	21.8	23.7	10.9	4.3
benzene	3.1	2.71	2.6	−1.0
toluene	6.2	5.25	3.1	−1.0

several alkanes and alkenes in [EMIM][EtSO$_4$] have been measured in the temperature range of (293 to 333) K using dilutor technique recently.[26] These values were extrapolated to 298 K and are compared with our results in the Table 6. Present GC results for γ_i^∞ of alkene and cyclohexane agree moderately with the results obtained by dilutor techniques (see Table 6). The possible explanation for this fact could be very short retention times of the first members of the homologues series by GC method. However, agreement of γ_i^∞ for benzene and toluene is substantial better indicating consistency of results derived for these two compounds from GC and dilutor techniques. Comparison of the $H_i^{E,\infty}$ from GC and dilutor methods is also given in the Table 6. It makes oneself conspicuous that values derived by using the GC technique are about twice higher than those from dilutor method and such disagreement is hardly explainable even taking into account the relatively large uncertainty of $H_i^{E,\infty}$ from the GC method.

Supporting Information Available:

Two tables showing the critical constants and acentric factors of solutes and carrier gas used in calculation of virial coefficients and the 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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