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Measurement of Activity Coefficients at Infinite Dilution in Ionic Liquids Using the Dilutor Technique

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Activity coefficients at infinite dilution have been measured with the dilutor technique for 20 solutes (alkanes, alkenes, cyclic hydrocarbons, aromatic hydrocarbons, ketones, alcohols, and water) in the ionic liquids 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, and 1-ethyl-3-methylimidazolium ethylsulfate. The measurements were carried out in the temperature range between 293.15 K and 333.15 K. The selectivities at infinite dilution ($S_{ij}^{\infty} = \gamma_i^{\infty}/\gamma_j^{\infty}$) for the separation of aliphatics from aromatics and *n*-hexane from 1-hexene are presented and discussed. From the results it can be concluded that the ionic liquids investigated show different advantages compared to those of the entrainers actually used for the separation of aliphatic from aromatic hydrocarbons by extractive distillation or extraction.

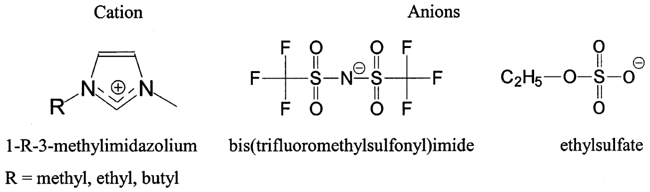
Introduction

Ionic liquids are a class of novel solvents with very interesting properties, such as low melting point (<100 °C), low viscosity, and in particular negligible vapor pressure. Because of their properties, ionic liquids are discussed as designer solvents which can be applied successfully for biphasic reactions or as selective solvents (entrainers) for different separation processes (e.g. extractive distillation, extraction,[1] and absorption).

In general, the phase equilibrium behavior and the excess properties of ionic liquids have not been systematically investigated. For a better understanding of their behavior and with respect to the development of thermodynamic models, reliable experimental data are required. But up to now only a limited number of phase equilibrium data are available.[2]

Therefore, systematic γ_i^{∞}, VLE,[14] and H^E measurements for the ionic liquids 1-methyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[MMIM]^+[(CF_3SO_2)_2N]^-$), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[EMIM]^+[(CF_3SO_2)_2N]^-$), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[BMIM]^+[(CF_3SO_2)_2N]^-$), and 1-ethyl-3-methylimidazolium ethyl sulfate ($[EMIM]^+[C_2H_5OSO_3]^-$) have been performed in the temperature range between 293.15 K and 353.15 K.

Activity coefficients at infinite dilution γ_i^{∞} (limiting activity coefficient) are important properties, which are used in particular for the selection of selective solvents (e.g. for extraction or extractive distillation) and for the reliable design of thermal separation processes,[3] since the removal of the last traces of impurities requires the largest separation effort.[3] To avoid an oversizing of the distillation column, reliable information about the separation factor at infinite dilution is required. Furthermore, more reliable g^E model or group interaction parameters can be obtained by fitting the required parameters simultaneously to vapor−liquid-equilibria (VLE), excess enthalpies (H^E), and limiting activity coefficients (γ_i^{∞}).



Activity coefficients at infinite dilution (γ_i^{∞}) can be determined by various methods: the retention time method (gas−liquid chromatography, GLC), ebulliometry, static methods, and the dilutor technique. The latter technique has the advantage that it can also be employed to determine γ_i^{∞} values in solvent mixtures.[4]

In this study activity coefficients at infinite dilution of 20 solutes in the temperature range between 293.15 K and 333.15 have been measured in four ionic liquids using the dilutor technique. The original idea of the dilutor technique was published by Fowlis and Scott[5] in 1963. They used the method for the calibration of chromatographic detectors to check their linearity and also for trace analysis. The first measurements of limiting activity coefficients using the dilutor technique were reported by Leroi et al.[6] in 1977. In this method, under isothermal conditions a highly diluted component is stripped from a solvent or solvent mixture with an inert gas stream. When an equilibrium stage is realized (in our case this was checked by variation of the carrier gas flow rate[7,8]) and the vapor phase composition in the measurement cell is recorded as a function of time, the limiting activity coefficient of the highly diluted component (solute) can be determined.

The dilutor apparatus applied was constructed by Krummen as part of his diploma thesis. In studies already

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published[4,7,8] it has been shown that the achievement of one theoretical stage in the measurement cell depends on various factors such as the flow rate of the carrier gas and the filling level of the solvent in the cell. The equilibrium is reliably achieved for all investigated systems by consideration of these factors. It was already demonstrated that reliable and reproducible γ_i^∞ data can be obtained, using the dilutor technique, for pure solvents as well as solvent mixtures.[4] Measurements of γ_i^∞ in mixed solvents are of great interest because the addition of a solvent to an entrainer may have a considerable effect on the activity coefficient at infinite dilution and thus on the selectivity at infinite dilution ($S_{ij}^\infty = \gamma_i^\infty/\gamma_j^\infty$) and the capacity ($k_i^\infty = 1/\gamma_i^\infty$) of the entrainer.[9] While the selectivity mainly influences the number of separation stages, that is, the investment costs, the capacity determines the ratio of the entrainer to the feed flow; that is, the capacity has an important influence on the operating costs. Often an increase in selectivity leads to a decrease in capacity (solubility). Both selectivity and capacity of a solvent are important quantities for the economic realization of a separation process. An example is the separation of aromatic from aliphatic hydrocarbons, in which, often, small amounts of water are added to the entrainer, for example, *N*-methyl-2-pyrrolidone (NMP), to increase the selectivity.[4]

Experimental Section

The dilutor technique used to determine the activity coefficients at infinite dilution has already been described in a previous paper.[4]

The principle of the measurement is that a highly diluted component is stripped from the solvent (solvent mixture) by a constant inert gas flow. The variation of the solute concentration in the vapor phase is recorded with a gas chromatograph, whereby the flow of the inert gas, helium (Messer-Griesheim, purity 99.996%), can be controlled and measured by using a digital mass flow controller (Bronkhorst Hi-TEC; F-201C-RA-33V).

Since the vapor pressure of these ionic liquids is negligible in the temperature range covered, it is not necessary to saturate the gas with the solvent in a presaturation cell. This means that the amount of solvent in the measurement cell remains constant. This was also confirmed by weighing the cell before and after each measurement.

For the measurement, the measurement cell is filled with approximately 80 cm^3 of the ionic liquid (total cell volume approximately 100 cm^3), whereby the ionic liquid has been purified before by vacuum evaporation to remove the last traces of impurities. The water content (<100 ppm) was checked by Karl Fischer titration.[10] The measurement cell is weighed and installed in the dilutor apparatus, and the highly diluted component (solute) is injected into the measurement cell via a septum, whereby it is important that already at the beginning of the measurement the mole fraction of the solute (x_i) is smaller than 10^{-3}.

During the measurement (approximately 2 h), the solute is stripped from the cell by the carrier gas helium (typical flow rate 20 to 40 cm^3·min^{-1}). The gas leaving the measurement cell is analyzed periodically using a gas chromatograph (Hewlett-Packard; HP 6890). Since the injected solute is at infinite dilution, it is possible to study several solutes at the same time. They must only be separated on the GC column. The GC column (Porapak P, 80/100 mesh; diameter 3.175 mm (0.125 in.), length 1.5 m) allowed a satisfactory separation and permits a quantitative analysis of the injected solutes. A separation of the solutes from the ionic liquid is not necessary because of the negligible vapor pressure of the ionic liquids. The detection was carried out by using a flame ionization detector (FID); the signals are recorded by a computer. The decrease of the solute concentration (peak area) with time can then be used for the determination of the limiting activity coefficient. It has been found that at least 15% of the solute should be removed from the system during a single measurement, to guarantee reliable γ_i^∞ values.

Table 1. Density ρ for the Ionic Liquids in the Temperature Range from 20 to 80 °C (Investigated with an Anton Paar DMA 4500 Densimeter)

temp	ρ/g·cm^{-3}			
°C	[MMIM]$^+$ [(CF$_3$SO$_2$)$_2$N]$^-$	[EMIM]$^+$ [(CF$_3$SO$_2$)$_2$N]$^-$	[BMIM]$^+$ [(CF$_3$SO$_2$)$_2$N]$^-$	[EMIM]$^+$ [C$_2$H$_5$OSO$_3$]$^-$
20		1.5243	1.4425	1.2458
25	1.5700	1.5192	1.4377	1.2423
30	1.5648	1.5141	1.4329	1.2388
35	1.5596	1.5091	1.4280	1.2354
40	1.5544	1.5040	1.4232	1.2319
45	1.5493	1.4990	1.4185	1.2285
50	1.5441	1.4940	1.4137	1.2251
55	1.5390	1.4890	1.4090	1.2217
60	1.5339	1.4841	1.4043	1.2183
65	1.5289	1.4792	1.3996	1.2150
70	1.5238	1.4742	1.3949	1.2116
75	1.5188	1.4693	1.3903	1.2083
80	1.5138	1.4645	1.3856	1.2050

It should be mentioned that for the measurements with the dilutor technique only the variation of the relative peak areas is required. Since the measurements are carried out at infinite dilution, where the detector shows linear behavior, no calibration is necessary.

For the analysis, the following experimental information is required: the slope (a) of the natural logarithm of the peak areas of the solute i against time, the absolute temperature (T), the pressure in the measurement cell (P), the carrier gas flow rate (F_{He}), and the amount of the solvent. Equation 1 relates the activity coefficient of the solute i at infinite dilution to these properties

$$\gamma_i^\infty = -\frac{n_{solv}RT}{\varphi_i^s P_i^s\left(\dfrac{F_{He}(1 + P_{solv}^s/P)}{a} + V_g\right)} \qquad (1)$$

where R is the general gas constant and P_i^s is the saturation vapor pressure of the solute, which is calculated using a vapor pressure equation, for example, the Antoine equation. The saturation fugacity coefficients of the solute, φ_i^s, are calculated using second virial coefficients derived with the Soave−Redlich−Kwong equation of state according to Gmehling and Kolbe.[11] The saturation vapor pressure of the ionic liquids P_{solv}^s is negligible, that is, the ratio P_{solv}^s/P can be neglected in eq 1. The vapor volume in the measurement cell V_g is obtained from the amount and the density of the ionic liquid and the well-known cell volume. The densities of the ionic liquids were measured using a vibrating tube densimeter. The values are given in Table 1. The other pure component properties, that is, such as Antoine coefficients and second virial coefficients, are taken from the Dortmund Data Bank.[12] The values for φ_i^s are given in Table 2. The accuracy of these values is within ±0.5%.[13]

Apart from the flow rate F_{He}, which is corrected to the cell conditions, the slope a, the pressure P, and the temperature T in the measurement cell as well as the mass of the solvent are the experimental quantities required for

Table 2. Saturation Fugacity Coefficients φ_i^s for the Solutes Investigated at Temperature T

	φ_i^s				
solute i	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
n-pentane	0.970	0.962	0.953	0.943	0.932
n-hexane	0.987	0.982	0.976	0.969	0.962
n-heptane	0.994	0.991	0.988	0.984	0.979
cyclopentane	0.984	0.979	0.974	0.967	0.960
cyclohexane	0.992	0.989	0.985	0.981	0.976
1-pentene	0.967	0.958	0.949	0.938	0.926
1-hexene	0.985	0.980	0.974	0.967	0.959
1-heptene	0.993	0.991	0.987	0.983	0.978
cyclopentene	0.980	0.975	0.968	0.960	0.952
cyclohexene	0.992	0.990	0.986	0.982	0.978
benzene	0.994	0.991	0.988	0.984	0.980
toluene	0.996	0.995	0.993	0.990	0.987
acetone	0.977	0.971	0.965	0.957	0.949
2-butanone	0.990	0.986	0.982	0.977	0.971
2-pentanone	0.994	0.992	0.988	0.985	0.980
methanol	0.988	0.984	0.980	0.975	0.970
ethanol	0.992	0.989	0.985	0.981	0.976
2-propanol	0.994	0.991	0.988	0.984	0.979
1-propanol	0.998	0.996	0.994	0.992	0.989
water	0.999	0.998	0.997	0.996	0.995

Table 3. Infinite Dilution Activity Coefficients γ_i^∞ for Organic Solutes in 1-Methyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ($[MMIM]^+[(CF_3SO_2)_2N]^-$)

	γ_i^∞				
solute i	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
n-pentane		23.1	21.7	20.1	18.9
n-hexane		39.9	36.8	33.8	31.5
n-heptane		66.3	60.2	54.8	50.2
cyclopentane		13.8	13.0	12.2	11.4
cyclohexane		22.7	20.9	19.3	18.0
1-pentene		10.5	10.1	9.78	9.46
1-hexene		17.2	16.4	15.7	15.0
1-heptene		27.9	26.1	24.4	23.1
cyclopentene		6.55	6.37	6.20	6.05
cyclohexene		10.6	10.1	9.58	9.17
benzene	1.33	1.34	1.35	1.36	1.37
toluene	2.00	2.01	2.02	2.04	2.08
water		2.86	2.54	2.23	2.01

determining the γ_i^∞ values. The main source of error is the determination of the flow rate F_{He}. But the accuracy of F_{He} is better than ±0.85% (i.e. the measurement is within ±0.2 s over a volume of 20 cm^3 in the determination of the flow rate of the helium carrier gas with the help of a soap bubble flow meter). Thus, the relative error for measurements carried out using the dilutor technique is approximately ±2.5%.

Results and Discussion

The values of the activity coefficients at infinite dilution for the solutes investigated in the ionic liquids for the various temperatures are listed in Tables 3−6.

Surprisingly, it was found that aliphatic hydrocarbons, in contrast to aromatic hydrocarbons, show strong deviations from Raoult's law in the presence of the investigated ionic liquids. This effect can be used for separation processes such as extractive distillation or extraction.[1] For the selection of entrainers, it is important to know the selectivity at infinite dilution ($S_{ij}^\infty = \gamma_i^\infty/\gamma_j^\infty$) and the capacity ($k_i^\infty = 1/\gamma_i^\infty$) for the separation problem studied.[9] Table 7 shows the various selectivities at infinite dilution and the capacities for the separation of aliphatic from aromatic hydrocarbons for the systems cyclohexane/benzene, cyclohexene/benzene, *n*-heptane/toluene, and *n*-hexane/benzene and additionally for the separation of *n*-hexane from 1-hexene for the investigated ionic liquids.

Table 4. Infinite Dilution Activity Coefficients γ_i^∞ for Organic Solutes in 1-Ethyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ($[EMIM]^+[(CF_3SO_2)_2N]^-$)

	γ_i^∞			
solute i	293.15 K	303.15 K	313.15 K	323.15 K
n-pentane	18.5	17.4	16.3	15.4
n-hexane	30.1	27.9	25.9	24.2
n-heptane	48.0	43.8	40.2	37.1
cyclopentane	10.7	10.1	9.60	9.10
cyclohexane	17.0	15.6	14.5	13.5
1-pentene	8.40	8.17	7.96	7.75
1-hexene	13.2	12.7	12.2	11.8
1-heptene	21.0	19.8	18.8	17.9
cyclopentene	5.41	5.26	5.12	4.99
cyclohexene	8.59	8.10	7.74	7.38
benzene	1.18	1.19	1.20	1.21
toluene	1.82	1.81	1.81	1.81
acetone	0.403	0.404	0.410	0.423
2-butanone	0.544	0.556	0.571	0.586
2-pentanone	0.703	0.724	0.743	0.763
methanol	1.54	1.40	1.30	1.21
ethanol	2.14	1.93	1.77	1.62
2-propanol	2.45	2.20	1.96	1.79
1-propanol	2.63	2.39	2.19	2.02
water	3.68	3.17	2.83	2.54

Table 5. Infinite Dilution Activity Coefficients γ_i^∞ for Organic Solutes in 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide ($[BMIM]^+[(CF_3SO_2)_2N]^-$)

	γ_i^∞			
solute i	293.15 K	303.15 K	313.15 K	323.15 K
n-pentane	10.3	9.78	9.26	8.73
n-hexane	15.1	14.2	13.5	12.7
n-heptane	22.2	20.7	19.4	18.2
cyclopentane	6.22	5.94	5.67	5.43
cyclohexane	9.18	8.64	8.17	7.73
1-pentene	5.11	5.04	4.98	4.92
1-hexene	7.55	7.34	7.15	6.97
1-heptene	11.2	10.7	10.2	9.81
cyclopentene	3.57	3.48	3.40	3.33
cyclohexene	5.38	5.15	4.90	4.68
benzene	0.872	0.881	0.892	0.903
toluene	1.22	1.24	1.26	1.28
water	3.95	3.43	3.01	2.64

Table 6. Infinite Dilution Activity Coefficients γ_i^∞ for Organic Solutes in 1-Ethyl-3-methylimidazolium Ethylsulfate ($[EMIM]^+[C_2H_5OSO_3]^-$)

	γ_i^∞				
solute i	293.15 K	303.15 K	313.15 K	323.15 K	333.15 K
n-hexane		106	92.6	81.5	72.0
n-heptane		227	195	168	145
cyclopentane		29.5	27.0	24.7	22.8
cyclohexane		56.7	50.8	46.1	41.9
1-hexene		48.2	44.2	40.6	37.9
1-heptene		92.5	83.0	75.0	68.4
cyclopentene		13.4	12.9	12.4	11.9
cyclohexene		23.0	21.8	20.7	19.7
benzene	2.70	2.73	2.76	2.80	2.83
toluene	5.21	5.28	5.35	5.41	5.48

A comparison of the values given in Tables 3−7 with the values in Table 8, in which the γ_i^∞ values, selectivities at infinite dilution, and capacities for NMP and NMP + water systems from the literature are given, shows that the γ_i^∞ values of the nonaromatic hydrocarbons (cyclohexane, *n*-hexane, *n*-heptane) in the ionic liquids are essentially higher than those for NMP. Even for NMP + water mixtures, the γ_i^∞ values are essentially smaller than those for the ionic liquids investigated. The γ_i^∞ values for aromatic compounds are similar in NMP (NMP + water

Table 7. Selectivities and Capacities at Infiite Dilution for the Ionic Liquids for Different Separation Problems

	T	$[MMIM]^+[(CF_3SO_2)_2N]^-$		$[EMIM]^+[(CF_3SO_2)_2N]^-$		$[BMIM]^+[(CF_3SO_2)_2N]^-$		$[EMIM]^+[C_2H_5OSO_3]^-$	
separation problem	°C	S_{12}^∞	k_2^∞	S_{12}^∞	k_2^∞	S_{12}^∞	k_2^∞	S_{12}^∞	k_2^∞
cyclohexane (1)/benzene (2)	20			14.4	0.847	10.5	1.15		
	30	16.9	0.746	13.1	0.840	9.81	1.14	20.8	0.366
	40	15.5	0.741	12.1	0.833	9.16	1.12	18.4	0.362
	50	14.2	0.735	11.2	0.826	8.56	1.11	16.5	0.357
	60	13.1	0.730					14.8	0.353
cyclohexene (1)/benzene (2)	20			7.28	0.847	6.17	1.15		
	30	7.91	0.746	6.81	0.840	5.85	1.14	8.42	0.366
	40	7.48	0.741	6.45	0.833	5.49	1.12	7.90	0.362
	50	7.04	0.735	6.10	0.826	5.18	1.11	7.39	0.357
	60	6.69	0.730					6.96	0.353
n-heptane (1)/toluene (2)	20			26.4	0.549	18.2	0.820		
	30	33.0	0.498	24.2	0.552	16.7	0.806	43.0	0.189
	40	29.8	0.495	22.2	0.552	15.4	0.794	36.4	0.187
	50	26.9	0.490	20.5	0.552	14.2	0.781	31.1	0.185
	60	24.1	0.481					26.5	0.182
n-hexane (1)/benzene (2)	20			25.5	0.847	17.3	1.15		
	30	29.8	0.746	23.4	0.840	16.1	1.14	38.8	0.366
	40	27.3	0.741	21.6	0.833	15.1	1.12	33.6	0.362
	50	24.9	0.735	20.0	0.826	14.1	1.11	29.1	0.357
	60	23.0	0.730					25.4	0.353
n-hexane (1)/1-hexene (2)	20			2.29	0.076	2.00	0.132		
	30	2.32	0.058	2.20	0.079	1.93	0.136	2.20	0.021
	40	2.24	0.061	2.12	0.082	1.88	0.140	2.10	0.023
	50	2.16	0.064	2.05	0.085	1.82	0.144	2.01	0.025
	60	2.10	0.067					1.90	0.026

Table 8. Experimental γ_i^∞ Values for the Solvents NMP and NMP + 3% and + 6% (w/w) Water as Well as the Selectivities and Capacities at Infinite Dilution for Different Separation Problems

	T	NMP				NMP + 3% (w/w) water				NMP + 6% (w/w) water			
separation problem	°C	γ_1^∞	γ_2^∞	S_{12}^∞	k_2^∞	γ_1^∞	γ_2^∞	S_{12}^∞	k_2^∞	γ_1^∞	γ_2^∞	S_{12}^∞	k_2^∞
cyclohexane (1)/benzene (2)	30	8.06^a	1.04^a	7.75	0.962	12.7^b	1.36^b	9.34	0.735	20.1^b	1.92^b	10.5	0.521
	40	7.40^a	1.05^a	7.05	0.952	11.5^b	1.40^b	8.21	0.714	17.8^b	1.93^b	9.22	0.518
	50	6.80^a	1.05^a	6.48	0.952	10.5^b	1.44^b	7.29	0.694	16.2^b	1.94^b	8.35	0.515
	60	6.32^a	1.06^a	5.96	0.943	9.61^b	1.47^b	6.54	0.680	14.5^b	1.99^b	7.29	0.503
cyclohexene (1)/benzene (2)	30	4.17^c	1.04^a	4.01	0.962	6.41^c	1.36^b	4.71	0.735	9.81^c	1.92^b	5.11	0.521
	40	3.97^c	1.05^a	3.78	0.952	6.07^c	1.40^b	4.34	0.714	9.14^c	1.93^b	4.74	0.518
	50	3.82^c	1.05^a	3.64	0.952	5.80^c	1.44^b	4.03	0.694	8.57^c	1.94^b	4.42	0.515
	60	3.69^c	1.06^a	3.48	0.943	5.50^c	1.47^b	3.74	0.680	8.10^c	1.99^b	4.07	0.503
n-heptane (1)/toluene (2)	30	14.9^c	1.33^c	11.2	0.752	26.7^c	1.91^c	14.0	0.524	45.9^c	2.63^c	17.5	0.380
	30	13.7^c	1.33^c	10.3	0.752	23.7^c	1.95^c	12.2	0.513	40.3^c	2.70^c	14.9	0.370
	50	12.4^c	1.35^c	9.19	0.741	21.4^c	1.95^c	11.0	0.513	35.6^c	2.75^c	12.9	0.364
	60	11.5^c	1.37^c	8.39	0.730	19.4^c	1.97^c	9.85	0.508	31.6^c	2.81^c	11.2	0.356
n-hexane (1)/benzene (2)	30	13.1^a	1.04^a	12.6	0.962	21.1^b	1.36^b	15.5	0.735	34.8^b	1.92^b	18.1	0.521
	30	11.8^a	1.05^a	11.2	0.952	19.1^b	1.40^b	13.6	0.714	31.4^b	1.93^b	16.3	0.518
	50	10.9^a	1.05^a	10.4	0.952	17.4^b	1.44^b	12.1	0.694	27.9^b	1.94^b	14.4	0.515
	60	10.0^a	1.06^a	9.43	0.943	15.9^b	1.47^b	10.8	0.680	25.1^b	1.99^b	12.6	0.503
n-hexane (1)/1-hexene (2)	30	13.1^a	6.59^a	1.99	0.152	21.1^b	10.6^b	1.99	0.094	34.8^b	16.9^b	2.06	0.059
	30	11.8^a	6.23^a	1.89	0.161	19.1^b	9.89^b	1.93	0.101	31.4^b	15.5^b	2.03	0.065
	50	10.9^a	6.02^a	1.81	0.166	17.4^b	9.27^b	1.88	0.108	27.9^b	14.2^b	1.96	0.070
	60	10.0^a	5.68^a	1.76	0.176	15.9^b	8.67^b	1.83	0.115	25.1^b	13.2^b	1.90	0.076

[a] Published in refs 7 and 8. [b] Published in ref 4. [c] Unpublished data, ref 17.

mixtures) and in the ionic liquids; that is, the presence of ionic liquids leads to an evident increase of the selectivity compared to those for NMP or NMP + water systems. For the system *n*-hexane/1-hexene, comparable selectivities are obtained for NMP and the ionic liquids.

In Figures 1−4 the selectivities at infinite dilution of the four binary systems for ionic liquids and NMP and respectively NMP + water are shown as a function of temperature. It can be seen that in all cases the selectivities of the ionic liquids are evidently higher than those for NMP or NMP + water. For the imidazolium compounds with bis(trifluoromethylsulfonyl)imide as anion, the selectivity increases with decreasing length of the alkyl chain for the different separation problems. Furthermore, it can be seen that, by changing the anion from $[(CF_3SO_2)_2N]^-$ to $[C_2H_5OSO_3]^-$, the highest selectivity for the separation of cyclohexane/benzene, cyclohexene/benzene, *n*-heptane/toluene, and *n*-hexane/benzene is obtained. For the separation problem cyclohexane/benzene, a selectivity increase of 168% at 303.15 K compared with the case of the entrainer NMP is observed for $[EMIM]^+[C_2H_5OSO_3]^-$. This means that ionic liquids are ideal entrainers for the separation of aliphatic from aromatic hydrocarbons.

From the γ_i^∞ values and the VLE measurements[14] it can be concluded that the ionic liquids form a large miscibility gap with aliphatic hydrocarbons. This large miscibility gap (without the addition of water as in the case of NMP) can directly be used for the separation of aromatic from aliphatic hydrocarbons by liquid−liquid extraction. Besides the miscibility gap, there are different further requirements for the extractant such as (i) high selectivity, (ii) high capacity, (iii) a low solubility of the extractant in the raffinate phase, (iv) a simple separation of the extract and

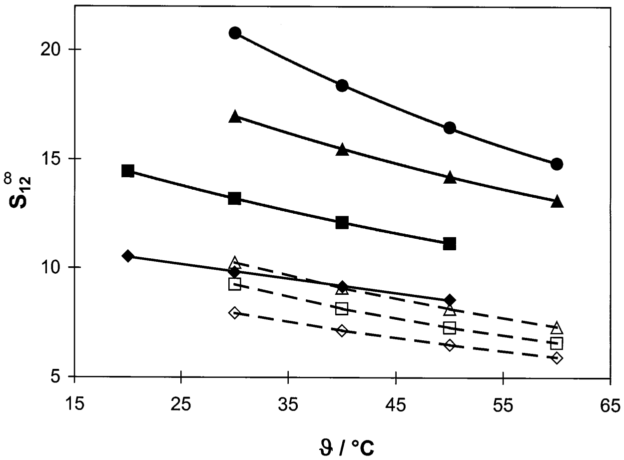

Figure 1. Comparison of the selectivities at infinite dilution S_{12}^{∞} of various solvents for the separation problem cyclohexane (1)/benzene (2): (◆) [BMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$ (this work); (■) [EMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$ (this work); (▲) [MMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$ (this work); (●) [EMIM]$^+$[C$_2$H$_5$OSO$_3$]$^-$ (this work); (◇) NMP;[4] (□) NMP + 3% (w/w) water;[4] (△) NMP + 6% (w/w) water.[4]

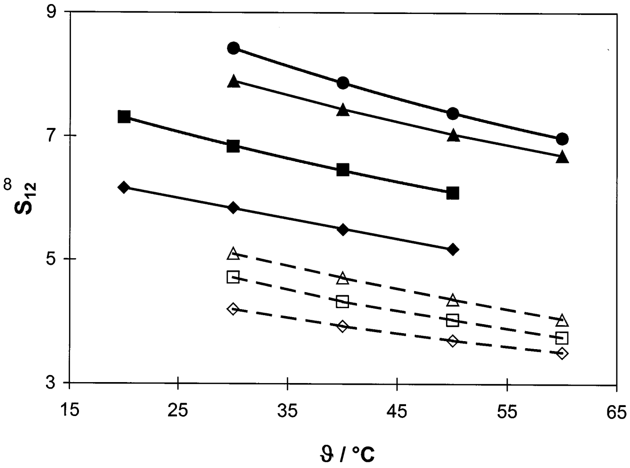

Figure 2. Comparison of the selectivities at infinite dilution S_{12}^{∞} of various solvents for the separation problem cyclohexene (1)/benzene (2): (◆) [BMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (■) [EMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (▲) [MMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (●) [EMIM]$^+$[C$_2$H$_5$OSO$_3$]$^-$; (◇) NMP; (□) NMP + 3% (w/w) water; (△) NMP + 6% (w/w) water.

the raffinate phase, (v) low viscosity, (vi) high chemical and thermal stability, (vii) low vapor pressure, and (viii) a sufficient density difference.

Nearly all these requirements for the entrainer for liquid−liquid extraction are fulfilled by the investigated ionic liquids. However, up to now, knowledge about the thermal and chemical stabilities of ionic liquids is limited.

A description of the industrial application of ionic liquids for the separation of aliphatic from aromatic hydrocarbons by extractive distillation and extraction is given in a patent application.[1]

Figure 5 shows the natural logarithm of the activity coefficients as a function of the inverse absolute temperature for three alkanes in the ionic liquid [EMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$. For the small temperature range covered, a linear relationship is observed. For these alkanes the γ_i^{∞} increases with the chain length; that is, the solubility (x_i) of the alkanes in the ionic liquids decreases from *n*-pentane to *n*-heptane.

A comparison of γ_i^{∞} values for *n*-hexane as a function of the inverse temperature in four different imidazolium derivatives is shown in Figure 6. It can be seen that the structure and respectively the length of the alkyl chain at the imidazolium ring have an essential influence on the γ_i^{∞} values. The γ_i^{∞} values diminish with increasing length of the alkyl chain. Furthermore, the variation of the counteranion ([(CF$_3$SO$_2$)$_2$N]$^-$ → [C$_2$H$_5$OSO$_3$]$^-$) results in an increase of the γ_i^{∞} values. By variation of the cation and the anion of the ionic liquid, the solubilities of the solutes ($x_i \approx 1/\gamma_i^{\infty}$) can be influenced. Large γ_i^{∞} values lead to a solubility decrease and result in a miscibility gap, as required, for example, for the use of ionic liquids as extractant in liquid−liquid extraction.

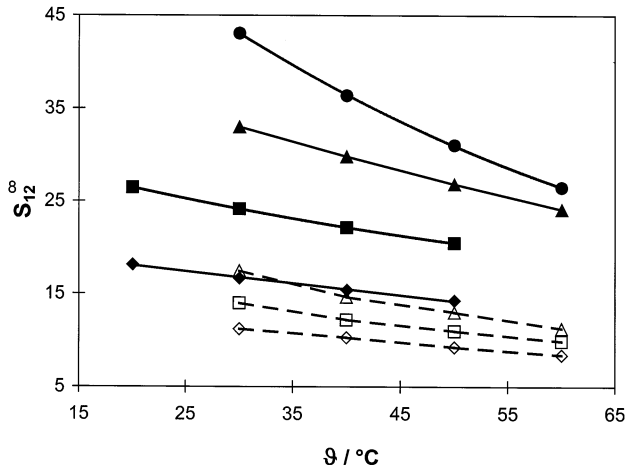

Figure 3. Comparison of the selectivities at infinite dilution S_{12}^{∞} of various solvents for the separation problem *n*-heptane (1)/toluene (2): (◆) [BMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (■) [EMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (▲) [MMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (●) [EMIM]$^+$[C$_2$H$_5$OSO$_3$]$^-$; (◇) NMP; (□) NMP + 3% (w/w) water; (△) NMP + 6% (w/w) water.

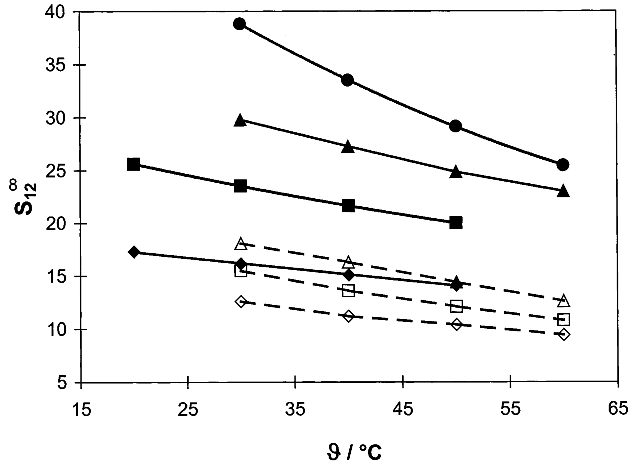

Figure 4. Comparison of the selectivities at infinite dilution S_{12}^{∞} of various solvents for the separation problem *n*-hexane (1)/benzene (2): (◆) [BMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (■) [EMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (▲) [MMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$; (●) [EMIM]$^+$[C$_2$H$_5$OSO$_3$]$^-$; (◇) NMP; (□) NMP + 3% (w/w) water; (△) NMP + 6% (w/w) water.

The ketones show small γ_i^{∞} values in the ionic liquid [EMIM]$^+$[(CF$_3$SO$_2$)$_2$N]$^-$ (see Table 4). These values indicate a strong interaction between the ionic liquid and the ketones.

The choice of the optimal temperature is also important for the application of selective solvents in, for example, extraction processes. The temperature dependence can be described using excess enthalpy information. Furthermore, experimental H_i^{E} data can be used to confirm the observed experimental temperature dependence of γ_i^{∞}. According to the Gibbs−Helmholtz equation, the values for the partial

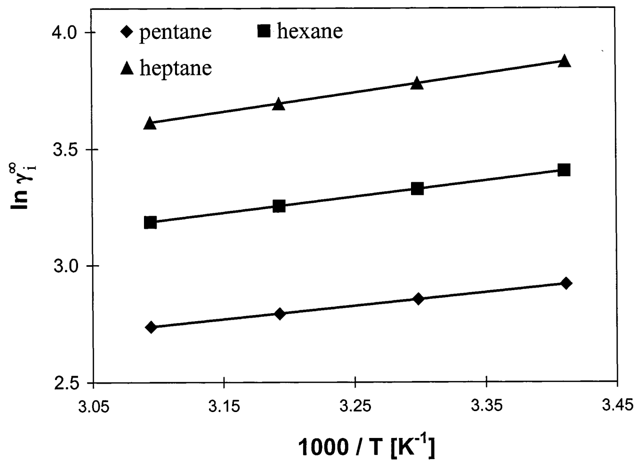

Figure 5. Experimental activity coefficients at infinite dilution $\ln(\gamma_i^\infty)$ for three alkanes in the solvent $[EMIM]^+[(CF_3SO_2)_2N]^-$ as a function of inverse temperature: (◆) *n*-pentane; (■) *n*-hexane; (◆) *n*-heptane; (—) linear regression.

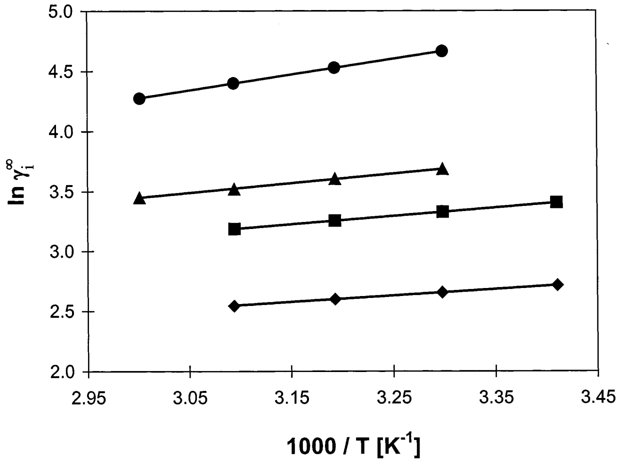

Figure 6. Experimental activity coefficients at infinite dilution $\ln(\gamma_i^\infty)$ for *n*-hexane in different ionic liquids as a function of inverse temperature: (◆) $[BMIM]^+[(CF_3SO_2)_2N]^-$; (■) $[EMIM]^+[(CF_3SO_2)_2N]^-$; (▲) $[MMIM]^+[(CF_3SO_2)_2N]^-$; (●) $[EMIM]^+[C_2H_5OSO_3]^-$; (—) linear regression.

molar excess enthalpy at infinite dilution ($H_i^{E,\infty}$) can be obtained directly from the slope of a straight line derived from[11]

$$\left(\frac{\partial \ln \gamma_i^\infty}{\partial (1/T)}\right)_{P,x} = \frac{H_i^{E,\infty}}{R} \tag{2}$$

In Table 9 the values for $H_i^{E,\infty}$ observed by linear regression from the experimental γ_i^∞ data and the values for $H_i^{E,\infty}$ derived from experimental H^E data [14] (measured by isothermal flow calorimetry[15]), using polynomials (Redlich−Kister, SSF),[16] are given. A comparison of the obtained partial molar excess enthalpies indicates a good agreement. This confirms the observed temperature dependence of the γ_i^∞ values. Small deviations of the partial molar excess enthalpies can be explained by the larger relative errors of H^E data in the diluted range.

Conclusion

Activity coefficients at infinite dilution for 20 solutes in the ionic liquids $[MMIM]^+[(CF_3SO_2)_2N]^-$, $[EMIM]^+[(CF_3SO_2)_2N]^-$, $[BMIM]^+[(CF_3SO_2)_2N]^-$, and $[EMIM]^+[C_2H_5OSO_3]^-$ have been measured at different temperatures using the dilutor technique.

Table 9. Calculated Partial Molar Excess Enthalpies at Infinite Dilution $H_i^{E,\infty}$ for the Different Systems

solvent (1)	solute (2)	$H_2^{E,\infty\ a}$ J·mol^{-1}	ϑ °C	$H_2^{E,\infty\ b}$ J·mol^{-1}	ϑ °C
$[EMIM]^+[(CF_3SO_2)_2N]^-$	1-hexene	2800	20−50	2860	50
	benzene	−480	20−50	−670	50
	cyclohexane	6000	20−50	6200	50
	cyclohexene	3900	20−50	3700	50
	ethanol	7200	20−50	7500	50
	1-propanol	6900	20−50	7300	50

[a] Calculated by linear regression from experimental γ_i^∞ data using eq 2. [b] From experimental H^E data calculated using polynomials (Redlich−Kister, SSF)[16] (investigated with an isothermal flow calorimeter[15]).

The results demonstrate a significant influence of the cation and anion on the γ_i^∞ values.

Surprisingly, it was found that the investigated ionic liquids show distinctly higher selectivities at infinite dilution than the entrainers actually used for the separation of aliphatic from aromatic hydrocarbons by extractive distillation or extraction.

To check the quality of the measured data, a comparison with measured H^E data was performed.

Additionally, γ_i^∞ measurements using gas−liquid chromatography (GLC) and VLE measurements were carried out for these ionic liquids. The results will be published soon together with the experimental excess enthalpy data.

Acknowledgment

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