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Activity Coefficients at Infinite Dilution Measurements for Organic Solutes and Water in the Ionic Liquid 1-Butyl-3-methyl-pyridinium Trifluoromethanesulfonate

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The activity coefficients at infinite dilution, γ_{13}^{∞}, for 37 solutes: alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, thiophene, ethers, ketones, and water in the ionic liquid 1-butyl-3-methyl-pyridinium trifluoromethanesulfonate [1,3bmPY][CF_3SO_3] were determined by gas−liquid chromatography at the temperatures from (308.15 to 358.15) K. The partial molar excess enthalpies at infinite dilution values $\Delta H_1^{E,\infty}$ were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. The selectivities for the aliphatic/aromatic hydrocarbon separation problem were calculated from γ_{13}^{∞} and compared to the literature values for other ionic liquids, *N*-methylpyrrolidone and sulfolane.

Introduction

Ionic liquids (ILs) have negligible vapor pressure. This property makes them a good replacement for conventional volatile, often flammable, and toxic organic solvents in chemical industry, especially as entrainers in separation processes. Additionally, ILs have other important properties required for entrainers, namely, a wide liquid range and stability at high temperatures. In the selection of solvents for extraction and extractive distillation processes knowledge of the activity coefficients at infinite dilution (γ_{13}^{∞}) is very important and useful. It was shown that a large number of ILs have better selectivity and capacity in the extraction of aromatics from aromatic/aliphatic mixtures than typical solvents such as sulfolane and *N*-methylpyrrolidone (NMP).[1] In separation processes both properties of extractant are important, namely, selectivity *S* and capacity *k*, which can be directly calculated from activity coefficients at infinite dilution for different separation problems.[1] This work concerns measurements of activity coefficients at infinite dilution for 1-butyl-3-methyl-pyridinium trifluoromethanesulfonate [1,3bmPY][CF_3SO_3] IL. To illustrate the influence of cation structure on γ_{13}^{∞}, obtained data were compared to other ILs based on the trifluoromethanesulfonate anion, 1-butyl-3-methyl-imidazolium trifluoromethanesulfonate [bmim][CF_3SO_3][2] and 1-butyl-1-methyl-pyrrolidinium trifluoromethanesulfonate [bmPYR][CF_3SO_3].[3]

Materials and Methods

The IL [1,3bmPY][CF_3SO_3] had a purity of > 0.99 mass fraction and was supplied by IoLiTec. The IL was further purified by subjecting the liquid to a very low pressure of about $5 \cdot 10^{-3}$ Pa at a temperature about 90 °C for approximately 5 h. This procedure removed any volatile chemicals and water from the IL. The water content was analyzed by the Karl Fischer titration technique (method TitroLine KF). The sample of the IL was dissolved in methanol and titrated with steps of 2.5 μL. The results obtained have shown the water content to be less than 100 ppm. The solutes, purchased from Aldrich and Fluka, had purities above 0.99 mass fraction and were used without further purification because the GLC technique separated any impurities on the column.

The experiments were performed using a PerkinElmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using TotalChrom Workstation software. The column preparation and the packing method used in this work have been described previously.[4] Glass columns of length (1 and 4) mm internal diameter were used. Chromosorb W HP 80/100 mesh was used as the solid support and was supplied by Supelco. Coating the solid support material with the IL was performed by dispersing a certain portion of Chromosorb in a solution of the IL in methanol followed by evaporation of the solvent using a rotating evaporator. The masses of the stationary phase and of the solid support were weighed with a precision of ± 0.0001 g. The solvent column packing varied from mass fraction $100\ w = 45.0$ to 52.1 of the IL, large enough to prevent any residual adsorption of solute onto the column packing. Care was taken to ensure that the methanol had completely evaporated from the IL-coated solid before making up the column. Before the experiment each column was conditioned by blowing carrier gas at a high flow rate (about 2.0 $cm^3 \cdot s^{-1}$) at the high temperature (about 373 K) through about 8 h. The second column was used to check the reproducibility of the results at different packing. On the second column measurements were performed at three temperatures, (308.15, 328.15, and 348.15) K. Results from these two different columns were repeatable with errors less than 0.3 %.

The outlet pressure P_o was kept at atmospheric pressure. The pressure drop ($P_i - P_o$) was varied between (20 and 70) kPa depending on the flow rate of the carrier gas. The pressure drop was measured by a gas chromatograph with an uncertainty of ± 0.1 kPa. The atmospheric pressure was measured using a digital barometer with an uncertainty of ± 0.1 hPa.

The carrier gas was helium. The flow rate of the carrier gas was determined using a calibrated soap bubble flowmeter which was placed at the outlet after the detector. The flow rate was set for a series of runs and was allowed to stabilize for at least

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Table 1. Experimental Activity Coefficients at Infinite Dilution γ_{13}^{∞} for the Solutes in IL [1,3bmPY][CF$_3$SO$_3$] at Different Temperatures and Excess Molar Enthalpies at Infinite Dilution $\Delta H_1^{E,\infty}$ and Correlation Coefficients *a* and *b* of Equation 3 for the Investigated IL

	T/K						$\Delta H_1^{E,\infty}$		*b*
solute	308.15	318.15	328.15	338.15	348.15	358.15	kJ·mol^{-1}	*a*	K
pentane	18.5	17.3	16.4	15.5	14.8	14.1	4.9	1.01	587.92
hexane	24.7	23.2	22.1	20.9	20.0	19.1	4.6	1.39	558.49
heptane	35.1	32.7	30.8	29.0	27.5	26.1	5.4	1.45	650.25
octane	49.6	46.3	43.4	40.7	38.5	36.2	5.8	1.66	692.23
nonane	71.7	65.9	61.1	56.8	53.2	49.9	6.6	1.68	798.83
decane	104.3	94.9	87.6	80.2	74.6	69.5	7.5	1.74	896.27
cyclopentane	9.40	8.89	8.51	8.15	7.80	7.54	4.1	0.657	487.23
cyclohexane	13.2	12.4	11.7	11.1	10.6	10.1	4.8	0.713	574.37
cycloheptane	16.4	15.4	14.6	13.8	13.2	12.5	4.9	0.867	594.78
cyclooctane		19.8	18.6	17.5	16.5	15.7	5.5	0.890	666.60
pent-1-ene	8.67	8.44	8.23	8.03	7.88	7.73	2.1	1.33	253.93
hex-1-ene	11.9	11.5	11.2	10.9	10.6	10.3	2.6	1.46	312.79
hept-1-ene	17.1	16.4	15.9	15.4	15.0	14.5	3.0	1.68	355.82
oct-1-ene	24.3	23.2	22.3	21.5	20.8	20.0	3.5	1.81	423.94
hex-1-yne	2.86	2.94	3.03	3.11	3.19	3.27	−2.5	2.01	−297.41
hept-1-yne	4.09	4.18	4.28	4.37	4.46	4.53	−1.9	2.16	−230.84
oct-1-yne		5.88	5.97	6.05	6.14	6.23	−1.4	2.29	−164.46
benzene	1.20	1.23	1.25	1.27	1.29	1.31	−1.5	0.778	−182.08
toluene		1.76	1.79	1.82	1.85	1.88	−1.6	1.17	−194.02
ethylbenzene		2.76	2.78	2.80	2.81	2.83	−0.62	1.25	−74.326
o-xylene		2.16	2.20	2.25	2.29	2.33	−1.9	1.48	−226.23
m-xylene		2.57	2.62	2.67	2.71	2.76	−1.6	1.57	−198.31
p-xylene		2.46	2.52	2.57	2.62	2.68	−2.0	1.64	−234.82
methanol		0.642	0.617	0.592	0.570	0.551	3.7	−1.82	439.82
ethanol		0.907	0.867	0.827	0.790	0.759	4.3	−1.71	512.76
propan-1-ol		1.11	1.06	1.00	0.958	0.919	4.5	−1.61	546.31
butan-1-ol		1.42	1.34	1.26	1.20	1.15	5.0	−1.54	599.77
water		0.890	0.857	0.820	0.789	0.765	3.7	−1.50	440.23
thiophene		0.898	0.919	0.937	0.955	0.972	−1.9	0.600	−224.93
THF[a]	1.19	1.20	1.21	1.23	1.24	1.25	−0.89	0.522	−107.46
MTBE[b]	4.21	4.22	4.23	4.23	4.24	4.24	−0.14	1.49	−16.866
diethyl ether	4.29	4.24	4.18	4.14	4.10	4.07	0.99	1.07	118.72
di-*n*-propyl ether	10.4	10.1	9.86	9.60	9.35	9.14	2.4	1.40	289.98
di-*n*-butyl ether	21.1	20.2	19.4	18.5	17.8	17.1	3.9	1.54	464.88
acetone	0.743	0.752	0.762	0.770	0.776	0.783	−0.95	0.074	−113.98
pentan-2-one		1.35	1.36	1.38	1.39	1.41	−1.00	0.676	−120.03
pentan-3-one		1.39	1.42	1.44	1.46	1.48	−1.4	0.872	−172.19

[a] Tetrahydrofuran. [b] Methyl-*tert*-butyl ether.

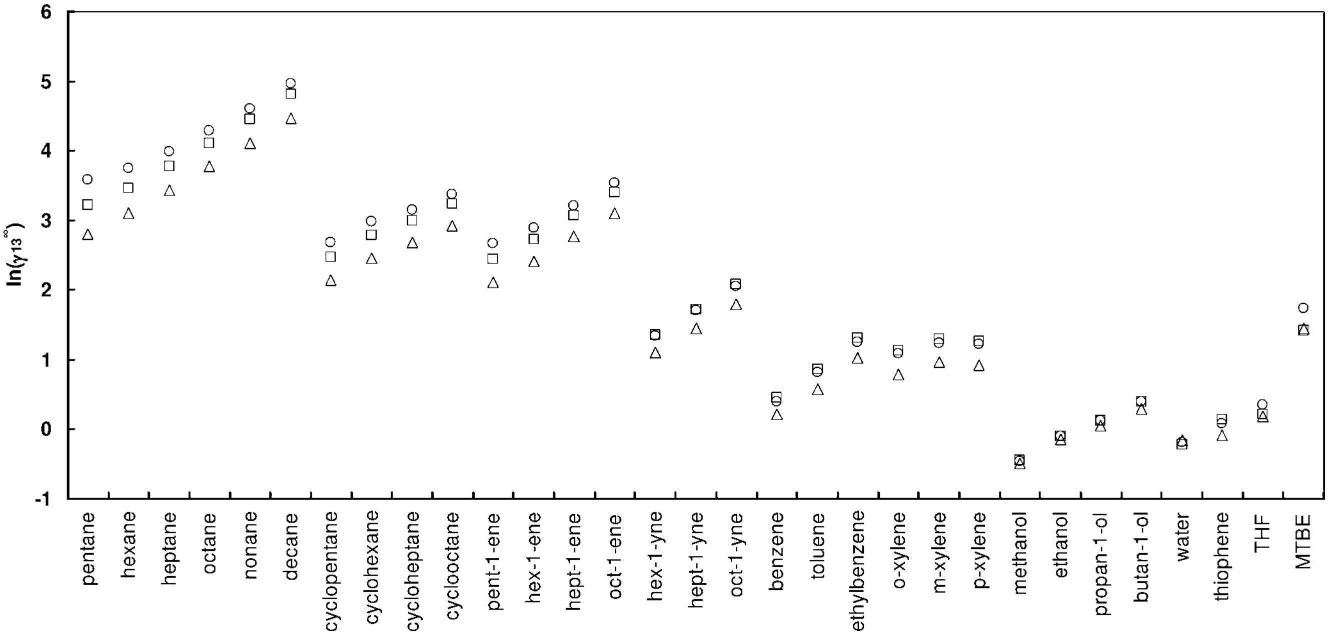

Figure 1. Comparison of γ_{13}^{∞} for an IL based on the [CF$_3$SO$_3$]$^-$ anion at T = 328.15 K; ○, [bmPYR]$^+$;[3] □, [bmim]$^+$;[2] △, [1,3bmPY]$^+$.

15 min before any γ_{13}^{∞} determinations were made. The flow rates were corrected for water vapor pressure. Solute injections ranged from (0.01 to 0.3) μL and were considered to be at infinite dilution on the column.

Experiments were carried out at different temperatures (in steps of 10 K) between (308.15 and 358.15) K. The temperature of the column was maintained constant to within ± 0.02 K. At a given temperature, each experiment was repeated two to four times to check the reproducibility. Retention times were generally reproducible within (0.001 to 0.01) min depending on the temperature and the individual solute. At each temperature values of the dead time t_G identical to the retention time of a nonretainable component were measured. While our GC was equipped with a TCD detector, air was used as a nonretainable component. The estimated overall error in γ_{13}^{∞} was less than 3 %, taking into account the possible errors in determining the column loading, the retention times, and solute vapor pressure. The GLC technique was tested for the system hexane in hexadecane at 298.15 K with the result of $\gamma_{13}^{\infty} = 0.903$ and compared to the literature value of 0.90.[5]

Theoretical Basis

The equation developed by Everett[6] and Cruickshank et al.[7] was used in this work to calculate the γ_{13}^{∞} of solutes in the IL. (See electronic Supporting Information for a detailed description.)

$$\ln \gamma_{13}^{\infty} = \ln\left(\frac{n_3RT}{V_NP_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_oJ_2^{\,3}(2B_{12} - V_1^{\infty})}{RT} \qquad (1)$$

Results and Discussion

Table 1 lists the activity coefficients at infinite dilution values for the investigated IL in the temperature range from (308.15 to 358.15) K and partial molar excess enthalpies at infinite dilution $\Delta H_1^{E,\infty}$ determined from the Gibbs−Helmholtz equation:

$$\frac{\partial \ln \gamma_i^{\infty}}{\partial(1/T)} = \frac{\Delta H_1^{E,\infty}}{R} \qquad (2)$$

The values of γ_{13}^{∞} have been correlated by the linear regression:

$$\ln \gamma_i^{\infty} = a + \frac{b}{T} \qquad (3)$$

The coefficients *a* and *b* are given in Table 1.

Figures 1S to 5S of the Supporting Information show the natural logarithm of the activity coefficients in the IL as a function of the inverse absolute temperature for all investigated solutes for the [1,3bmPY][CF$_3$SO$_3$] IL.

The highest values of γ_{13}^{∞} are for alkanes, alkenes, cycloalkanes, and ethers, especially for di-*n*-propyl ether and di-*n*-butyl ether. High values of γ_{13}^{∞} indicate very small interactions between solute and solvent. The values of γ_{13}^{∞} for a series of solutes increase with an increase of the solute alkyl chain. It means the more aliphatic character of the solute the higher value of γ_{13}^{∞}. This behavior is typical for other ILs. Alkenes show lower values of γ_{13}^{∞} than alkanes with the same carbon number. The interaction of the double bond in alkenes with a polar IL causes these differences. The cyclic structure of cycloalkanes reduces the value of γ_{13}^{∞} in comparison to the corresponding linear alkane. Alkynes have lower values of γ_{13}^{∞} than corresponding alkanes, alkenes, and cycloalkanes. Alkynes can interact with polar solvent through π electrons of the triple bond and the hydrogen atom of triple bond which shows slightly acidic properties. From investigated hydrocarbons the aromatic ones have the smallest values of γ_{13}^{∞}. This is the result of interaction between six π-delocalized electrons in benzene structure with the polar IL. The lowest values of γ_{13}^{∞} have alcohols, water, thiophene, ketones, and tetrahydrofuran (THF). These types of polar compounds show the highest interaction with the [1,3bmPY][CF$_3$SO$_3$] IL. Ethers (except of THF) even though they contain oxygen in structure do not interact as strongly as other polar compounds with solvent. It is caused by steric effects: alkyl groups mask oxygen from two sides. THF structure is different from aliphatic ethers. This compound is cyclic; therefore, reduction of γ_{13}^{∞} is observed similarly to linear and cyclic alkanes.

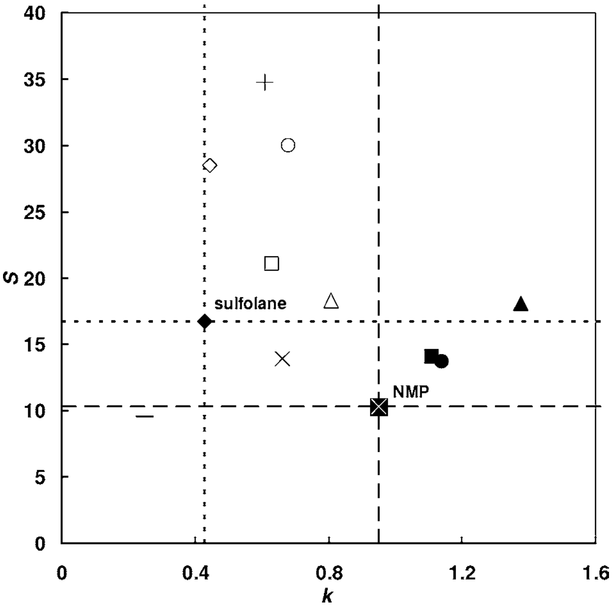

Figure 2. Separation *S* versus capacity *k* for hexane/benzene separation for selected ILs at *T* = 323.15 K; △, [1,3bmPY][CF$_3$SO$_3$]; □, [bmim][CF$_3$SO$_3$];[2] ○, [bmPYR][CF$_3$SO$_3$];[3] ◇, [emim][CF$_3$SO$_3$];[14] black ×, [hmim][CF$_3$SO$_3$];[10] ▲, [1,4bmPY][NTf$_2$];[11] +, [1,4bmPY][BF$_4$];[15] −, [1,4bmPY][TOS];[16] ●, [bmPYR][NTf$_2$];[12] ■, [bmim][NTf$_2$];[13] ◆, sulfolane;[9] white ×, NMP;[8] dotted line indicates the value of selectivity and capacity for sulfolane; dashed line indicates the value of selectivity and capacity for NMP.

Figure 1 compares the activity coefficients at infinite dilution for IL based on the [CF$_3$SO$_3$]$^-$ anion with methyl and *n*-butyl groups at *T* = 328.15 K. For all hydrocarbons values of γ_{13}^{∞} are the lowest for the 1-butyl-3-methylpyridinium cation, and the order is as follows: [bmPYR]$^+$ > [bmim]$^+$ > [1,3bmPY]$^+$. For aromatic hydrocarbons and thiophene, values of γ_{13}^{∞} for an IL with the [1,3bmPY]$^+$ cation are lower than for ILs with [bmPYR]$^+$ and [bmim]$^+$ cations. This is caused by the aromatic structure of the pyridinium cation. For alcohols, water, and THF, the differences in values of γ_{13}^{∞} for these three cations are small.

A very important factor in designing extraction processes is knowledge about selectivity S_{12}^{∞} and capacity k_2^{∞} of entrainers which can be calculated directly from the experimental γ_{13}^{∞} values:[1]

$$S_{ij}^{\infty} = \gamma_i^{\infty}/\gamma_j^{\infty} \qquad (4)$$

$$k_j^{\infty} = 1/\gamma_j^{\infty} \qquad (5)$$

Figure 2 shows the influence of the structure of ILs based on the [CF$_3$SO$_3$]$^-$ anion on S_{12}^{∞} and k_2^{∞} for the hexane/benzene separation problem at *T* = 323.15 K in contrast to NMP,[8] sulfolane,[9] and other selected ILs.[2,3,10–16] For ILs based on the [bmPY]$^+$ cation selectivity takes following order: [TOS]$^-$ < NMP < sulfolane < [NTf$_2$]$^-$ ≈ [CF$_3$SO$_3$]$^-$ < [BF4]$^-$, while the capacity order is as follows: [NTf$_2$]$^-$ < NMP < [CF$_3$SO$_3$]$^-$ < [BF4]$^-$ < sulfolane < [TOS]$^-$.

Conclusions

Activity coefficients at infinite dilution for various solutes in the IL 1-butyl-3-methyl-pyridinium trifluoromethanesulfonate were measured by GLC at the temperatures from (308.15 to 358.15) K.

It was found that the investigated [1,3bmPY][CF_3SO_3] IL shows higher selectivity at infinite dilution than the general used organic solvents such as NMP[8] or sulfolane[9] for the separation aliphatics from aromatic hydrocarbon processes. The capacity is higher than for sulfolane and comparable to NMP.

Supporting Information Available:

Theoretical basis and equations. Table 1S, critical data of solutes. Table 2S, the saturated vapor pressures of the solutes, P_1^*, and the molar volumes of the solutes, V_1^*, at different temperatures. Figures 1S to 5S, plot of $\ln(\gamma_{13}^\infty)$ for the IL [1,3bmPY][CF_3SO_3] versus $1/T$ for the solutes. This material is available free of charge via the Internet at http://pubs.acs.org.

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