Physicochemical Properties and Activity Coefficients at Infinite Dilution for Organic Solutes and Water in the Ionic Liquid 1-Decyl-3-methylimidazolium Tetracyanoborate

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The activity coefficients at infinite dilution γ_{13}^{∞} and gas−liquid partition coefficients K_L for 43 solutes—alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols, carboxylic acids, thiophene, ethers, ketones, and water—in the ionic liquid 1-decyl-3-methylimidazolium tetracyanoborate ([dmim][TCB]) were determined by gas−liquid chromatography at temperatures from 318.15 to 378.15 K. The partial molar excess Gibbs energies $\Delta G_1^{E,\infty}$, enthalpies $\Delta H_1^{E,\infty}$, and entropies $\Delta S_1^{E,\infty}$ at infinite dilution were calculated from the experimental γ_{13}^{∞} values obtained over the temperature range. Additionally, the densities for investigated ionic liquid over the temperature range were determined. The selectivities for the aliphatic/aromatic hydrocarbon separation problem were calculated from γ_{13}^{∞} and compared to the literature values for *N*-methyl-2-pyrrolidinone (NMP) and sulfolane. It was found that the investigated [dmim][TCB] ionic liquid shows much higher capacity than NMP and sulfolane and selectivity on the same level as NMP and lower than that for sulfolane for the separation of aliphatic hydrocarbons from aromatic hydrocarbons.

Introduction

Separation of aromatics from aromatic/aliphatic mixtures plays a key role in chemical industry and is used, inter alia, to produce kerosene with a better smoke point, diesel oil with a higher cetane number, or a mineral oil with a better viscosity index. In industrial processes, different types of entrainers are used, namely, di-, tri-, and tetra-ethyleneglycols (abbreviations: DEG, TEG, and TETRA, respectively), *N*-methyl-2-pyrrolidinone (NMP), *N*-formylmorpholine (NFM), dimethylsulfoxide (DMSO), and tetramethylenesulfone (sulfolane).[1] Although the processes based on these solvents are well-known, there is still a need to find better environmentally friendly solvents with better selectivity and capacity (solvent power). From activity coefficients at infinite dilution measurements, it was shown that a large number of ionic liquids (ILs) have better selectivity and capacity in extraction of aromatics from aromatic/aliphatic mixtures than typical solvents such as sulfolane and NMP.[2] Additionally, ionic liquids have other important properties required for entrainers, namely, negligible vapor pressure, a wide liquid range, and stability at high temperatures. Ionic liquids are a relatively new class of salts with a melting temperature below 373.15 K.[3] In general, ILs are composed of organic cations with either inorganic or organic anions.

From previous measurements and literature data analysis,[2] it is clear that ionic liquids containing cyano groups, −C≡N, reveal a high selectivity for aromatic/aliphatic separation. For the *n*-heptane/benzene separation problem, the values of selectivity are as follows at *T* = 323.15 K: 109 for 1-ethyl-3-methyl-imidazolium thiocyanate, [emim][SCN];[4] 90.7 for 1-butyl-3-methyl-imidazolium thiocyanate, [bmim][SCN];[5] 35.0 for 1-hexyl-3-methyl-imidazolium thiocyanate, [hmim][SCN];[6] 70.9 for 1-ethyl-3-methyl-imidazolium dicyanamide, [emim][DCA].[7] Unfortunately, the capacities for the above-mentioned ionic liquids are low and take the following values, respectively: 0.29,[4]

0.46,[5] 0.50,[6] and 0.39.[7] Increasing the alkyl chain on the imidazolium ring gives higher values of capacity but unfortunately decreases the selectivity. For these reasons, the proposed for this measurements ionic liquid, 1-decyl-3-methylimidazolium tetracyanoborate [dmim][TCB] with long alkyl chain on the imidazolium ring suppose to increase capacity and four −C≡N groups in anion suppose to increase selectivity.

Experimental Method

Materials. The ionic liquid [dmim][TCB] had a purity of >0.9996 mass fraction and was supplied by Merck. The water content was analyzed by the Karl Fischer titration technique (method TitroLine KF). The sample of 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. Due to the high purity, the ionic liquid was used without further purification. The solutes, purchased from Aldrich and Fluka, had a purity above 0.99 mass fraction and were used without further purification because the GLC technique separated any impurities on the column. The structure of the investigated IL is presented below:
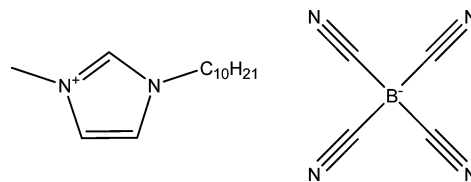
Apparatus and Experimental Procedure. The experiments were performed using a PerkinElmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The data were collected and processed using TotalChrom Workstation software. The column preparation and the packing method used in this work have been described previously.[8] Glass columns of 1 m length and 4 mm internal diameter were used.

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TABLE 1: Experimental Activity Coefficients at Infinite Dilution γ_{13}^{∞} for the Solutes in Ionic Liquid [dmim][TCB] at Different Temperatures

solute	*T*/K						
	318.15	328.15	338.15	348.15	358.15	368.15	378.15
n-pentane	4.97	4.77	4.61	4.45	4.30	4.18	
n-hexane	6.11	5.84	5.63	5.43	5.25	5.06	
n-heptane	7.70	7.32	7.02	6.72	6.45	6.21	
n-octane	9.68	9.16	8.72	8.36	8.03	7.68	
2,2,4-trimethylpentane	8.83	8.41	8.04	7.71	7.44	7.17	
n-nonane		11.5	10.9	10.4	9.93	9.50	
n-decane		14.5	13.7	13.1	12.4	11.8	
cyclopentane	2.85	2.73	2.64	2.55	2.47	2.39	
cyclohexane	3.69	3.50	3.36	3.22	3.09	2.97	
methylcyclohexane	4.57	4.35	4.19	4.04	3.88	3.73	
cycloheptane	4.18	3.98	3.80	3.66	3.52	3.38	
cyclooctane		4.67	4.45	4.28	4.10	3.94	
pent-1-ene	2.89	2.84	2.79	2.75	2.71	2.68	
hex-1-ene	3.61	3.50	3.41	3.33	3.25	3.19	
cyclohexene	2.19	2.14	2.10	2.05	2.02	1.98	
hept-1-ene	4.50	4.38	4.28	4.19	4.09	4.03	
oct-1-ene		5.57	5.40	5.25	5.12	4.99	
hex-1-yne	1.52	1.53	1.54	1.55	1.56	1.57	
hept-1-yne		1.89	1.91	1.92	1.93	1.94	
oct-1-yne		2.38	2.38	2.39	2.40	2.40	
benzene		0.581	0.591	0.602	0.610	0.619	
toluene		0.736	0.753	0.767	0.782	0.796	
ethylbenzene		0.987	1.000	1.020	1.030	1.050	
o-xylene		0.870	0.886	0.905	0.922	0.935	
m-xylene		0.968	0.990	1.01	1.03	1.05	
p-xylene		0.954	0.978	1.00	1.02	1.04	
methanol	0.826	0.771	0.724	0.687	0.647	0.619	0.593
ethanol	0.965	0.896	0.834	0.785	0.738	0.700	0.665
propan-1-ol		0.938	0.879	0.833	0.790	0.750	0.719
butan-1-ol		1.04	0.976	0.925	0.879	0.831	0.796
water		2.12	1.92	1.72	1.58	1.47	1.35
acetic acid		0.274	0.288	0.303	0.316	0.328	0.343
butyric acid		0.622	0.623	0.623	0.623	0.623	0.623
thiophene		0.527	0.536	0.543	0.552	0.561	
tetrahydrofuran		0.362	0.376	0.389	0.400	0.413	
methyl *tert*-butyl ether	1.13	1.16	1.18	1.22	1.25	1.28	
methyl *tert*-pentyl ether	1.42	1.45	1.48	1.51	1.54	1.57	
diethyl ether	1.13	1.15	1.17	1.19	1.20	1.22	
di-*n*-propyl ether	2.29	2.29	2.28	2.28	2.27	2.27	
di-*n*-butyl ether		3.62	3.59	3.56	3.53	3.51	
acetone		0.301	0.310	0.318	0.326	0.334	
pentan-2-one		0.389	0.403	0.416	0.428	0.442	
pentan-3-one		0.374	0.390	0.405	0.420	0.436	

Chromosorb W/AW-DCMS 120/140 mesh was used as the solid support and was supplied by Sigma-Aldrich. 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 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 ±0.0001 g giving in result uncertainty of the IL amount in the column on the level 2×10^{-4} mmol. The solvent column packing varied from 46.1 to 50.5 mass percent of the ionic liquid, 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 experiment, each column was conditioned by blowing carrier gas at a high flow rate (about $2.0 \text{ cm}^3 \cdot \text{s}^{-1}$) at the high temperature (373.15 K) through about 8 h. The second column was used to check reproducibility of results at different packing. In the second column, measurements were performed at two temperatures (338.15 and 358.15 K). Results from these two different columns were repeatable with error less than 0.2%.

The pressure drop ($P_i - P_o$) was varied between 60 and 80 kPa depending on the flow rate of the carrier gas. The inlet pressure P_i was measured by a pressure gauge installed on the gas chromatograph with an uncertainty of ±0.1 kPa. The outlet pressure P_o was measured using an Agilent Precision Gas Flow Meter with an uncertainty of ±0.07 kPa.

The carrier gas was helium. The flow rate of the carrier gas was determined using an Agilent Precision Gas Flow Meter which was placed at the outlet after the detector with an uncertainty of ±0.1 mL·min^{-1}. The flow rate was set for a series of runs and was allowed to stabilize for at least 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 318.15 and 378.15 K. The temperature of the column was maintained constant to within ±0.02 K. At a given temperature, each experiment was repeated two to three times to check the reproducibility. Retention times were generally reproducible within 0.001−0.01 min depending on

TABLE 2: Experimental Gas−Liquid Partition Coefficients K_L for the Solutes in Ionic Liquid [dmim][TCB] at Different Temperatures

solute				T/K			
	318.15	328.15	338.15	348.15	358.15	368.15	378.15
n-pentane	11.6	9.24	7.45	6.13	5.13	4.34	
n-hexane	27.7	20.9	16.1	12.7	10.2	8.32	
n-heptane	64.1	46.0	33.7	25.4	19.5	15.3	
n-octane	146	99.7	70.0	50.3	37.0	28.1	
2,2,4-trimethylpentane	53.4	38.9	28.9	22.1	17.1	13.5	
n-nonane		213	143	97.9	69.6	50.7	
n-decane		454	290	191	130	91.5	
cyclopentane	30.6	23.8	18.7	15.1	12.3	10.2	
cyclohexane	68.4	51.1	38.8	30.2	23.9	19.3	
methylcyclohexane	109	78.7	58	43.8	33.9	26.8	
cycloheptane	233	164	118	86.3	65.0	50.1	
cyclooctane		447	306	214	154	114	
pent-1-ene	16.5	13.0	10.3	8.41	6.95	5.82	
hex-1-ene	39.7	29.6	22.5	17.5	13.9	11.2	
cyclohexene	124	89.7	66.5	50.4	38.9	30.7	
hept-1-ene	90.8	64.3	46.7	34.8	26.6	20.6	
oct-1-ene		138	95.9	68.4	50.1	37.5	
hex-1-yne	124	87.8	63.7	47.3	36	27.8	
hept-1-yne		191	132	94.0	68.6	51.1	
oct-1-yne		405	268	183	128	92.4	
benzene		307	218	158	118	89.6	
toluene		692	467	325	232	169	
ethylbenzene		1309	852	571	393	279	
o-xylene		2034	1300	855	580	405	
m-xylene		1503	967	640	438	306	
p-xylene		1468	945	627	430	301	
methanol	207	148	108	80.0	61.4	47.3	37.3
ethanol	338	231	164	118	87.5	66.0	50.8
propan-1-ol		522	350	241	171	125	92.8
butan-1-ol		1206	770	506	343	242	174
water		229	163	121	90.1	67.5	52.6
acetic acid		2924	1833	1184	790	542	378
butyric acid		12273	7050	4210	2604	1663	1094
thiophene		390	274	199	147	111	
tetrahydrofuran		307	217	158	118	89.2	
methyl tert-butyl ether	95.5	68.4	50.3	37.7	28.9	22.7	
methyl tert-pentyl ether	221	152	107	76.8	56.8	42.9	
diethyl ether	47.9	35.7	27.2	21.2	16.8	13.5	
di-n-propyl ether	161	111	79.0	57.6	43.0	32.8	
di-n-butyl ether		490	317	212	145	103	
acetone		273	196	145	109	83.9	
pentan-2-one		1039	691	474	335	241	
pentan-3-one		1062	706	482	338	242	

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, and the results compared very favorably with the literature values.[9]

The densities were measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria), with a precision of 10^{-5} g·cm^{-3}.

Density Measurements. The density of the IL was measured using an Anton Paar GmbH 4500 vibrating-tube densimeter (Graz, Austria), thermostatted at different temperatures. Two integrated Pt 100 platinum thermometers provided good precision of the internal control of temperature ($T \pm 0.01$ K). The densimeter includes an automatic correction for the viscosity of the sample. The apparatus is precise to within 1×10^{-5} g·cm^{-3}, and the uncertainty of the measurements was estimated

to be better than $\pm 5 \times 10^{-5}$ g·cm^{-3}. The densimeter's calibration was performed at atmospheric pressure using doubly distilled and degassed water, specially purified benzene (CHEMIPAN, Poland 0.999), and dried air.

Theoretical Basis. The equation developed by Everett[10] and Cruickshank et al.[11] was used in this work to calculate the γ_{13}^∞ values of solutes in the ionic liquid.

$$\ln \gamma_{13}^\infty = \ln\left(\frac{n_3 RT}{V_N P_1^*}\right) - \frac{P_1^*(B_{11} - V_1^*)}{RT} + \frac{P_o J_2^3 (2B_{12} - V_1^\infty)}{RT}$$

(1)

V_N denotes the net retention volume of the solute, P_o the outlet pressure, $P_o J_2^3$ the mean column pressure, n_3 the number of moles of solvent on the column packing, T the column temperature, P_1^* the saturated vapor pressure of the solute at temperature T, B_{11} the second virial coefficient of pure solute, V_1^* the molar volume of the solute, V_1^∞ the partial molar volume of the solute at infinite dilution in the solvent, and B_{12} (where

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2 refers to the carrier gas, helium) the mixed second virial coefficient of the solute and the carrier gas. The thermophysical properties required in calculations were calculated using equations and constants taken from the literature.[12] The values of B_{12} were calculated using the Tsonopolous[13] equation.

The pressure correction term J_2^3 is given by

$$J_2^3 = \frac{2}{3}\frac{(P_i/P_o)^3 - 1}{(P_i/P_o)^2 - 1} \tag{2}$$

The net retention volume of the solute V_N is given by

$$V_N = J_2^3 U_o(t_R - t_G) \tag{3}$$

where t_R and t_G are the retention times for the solute and an unretained gas, respectively, and U_o is the column outlet flow rate corrected for the vapor pressure of water given by

$$U_o = U\left(1 - \frac{P_w}{P_o}\right)\frac{T}{T_f} \tag{4}$$

where T_f is the temperature at the column outlet, P_w is the vapor pressure of water at T_f, and U is the flow rate measured with the flow meter.

The gas−liquid partition coefficients $K_L = (c_1^L/c_1^G)$ for a solute partitioning between a carrier gas and the ionic liquid are calculated from the solute retention according to the following equation:

$$\ln(K_L) = \ln\left(\frac{V_N \rho_3}{m_3}\right) - \frac{P_o J_2^3(2B_{12} - V_1^\infty)}{RT} \tag{5}$$

where ρ_3 is the density of the solvent.

While the activity coefficients at infinite dilution are determined as a function of temperature, $\ln \gamma_{13}^\infty$ can be split into its respective enthalpy and entropy components

$$\ln \gamma_{13}^\infty = \frac{\Delta H_1^{E,\infty}}{RT} - \frac{\Delta S_1^{E,\infty}}{R} \tag{6}$$

Assuming that the temperature dependence follows a linear van't Hoff plot

$$\ln \gamma_{13}^\infty = a/T + b \tag{7}$$

the partial molar excess enthalpy $\Delta H_1^{E,\infty} = Ra$ at infinite dilution can be obtained from the slope.

Results and Discussion

Tables 1 and 2 list the activity coefficients at infinite dilution and the gas−liquid partition coefficient values, respectively, for the investigated ionic liquid in the temperature range from 318.15 to 378.15 K.

Figures 1−5 show the natural logarithm of the activity coefficients in the ionic liquid as a function of the inverse absolute temperature for all investigated solutes for [dmim][TCB] ionic liquid.
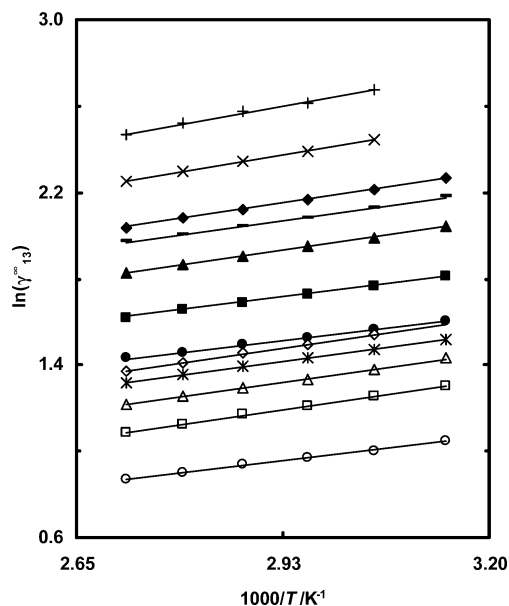

Figure 1. Plot of $\ln(\gamma_{13}^\infty)$ for ionic liquid [dmim][TCB] versus $1/T$ for the solutes: (●) *n*-pentane; (■) *n*-hexane; (▲) *n*-heptane; (◆) *n*-octane; (−) 2,2,4-trimethylpentane; (×) *n*-nonane; (+) *n*-decane; (○) cyclopentane; (□) cyclohexane; (∗) methylcyclohexane; (△) cycloheptane; (◇) cyclooctane.
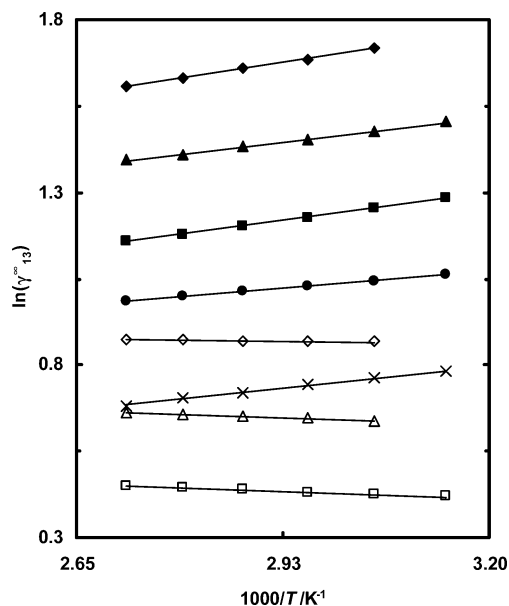

Figure 2. Plot of $\ln(\gamma_{13}^\infty)$ for ionic liquid [dmim][TCB] versus $1/T$ for the solutes: (●) pent-1-ene; (■) hex-1-ene; (▲) hept-1-ene; (◆) oct-1-ene; (×) cyclohexene; (□) hex-1-yne; (△) hept-1-yne; (◇) oct-1-yne.

It is obvious that the more aliphatic a compound, the higher the value of γ_{13}^∞; therefore, the highest values of activity coefficients at infinite dilution are for alkanes, cycloalkanes, and alkenes. 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. Cycloalkanes compared with linear alkanes show lower values of γ_{13}^∞. It stands that aliphatic hydrocarbons with a cyclic structure, analogous to the imidazolium structure (in ionic liquid cation), reveal higher interactions than linear alkanes. Moreover, the molar volume of cycloalkanes (1.089×10^{-4} m^3·mol^{-1} for cyclohexane)[12] is smaller than that for linear alkanes (1.314×10^{-4} m^3·mol^{-1} for *n*-hexane);[12] therefore, the packing effect
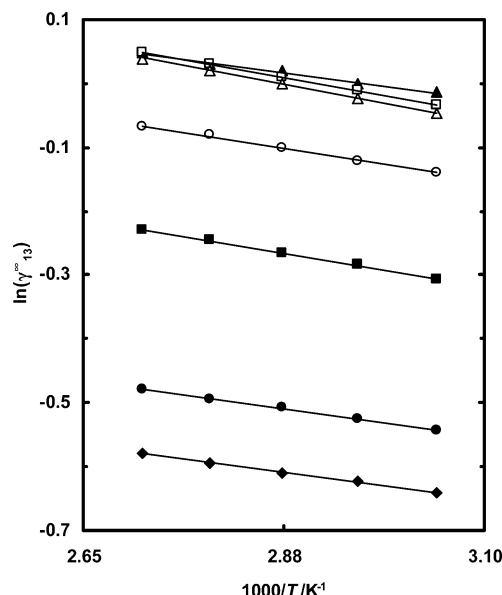
Figure 3. Plot of $\ln(\gamma_{13}^{\infty})$ for ionic liquid [dmim][TCB] versus $1/T$ for the solutes: (●) benzene; (■) toluene; (▲) ethylbenzene; (○) o-xylene; (□) m-xylene; (△) p-xylene; (◆) thiophene.
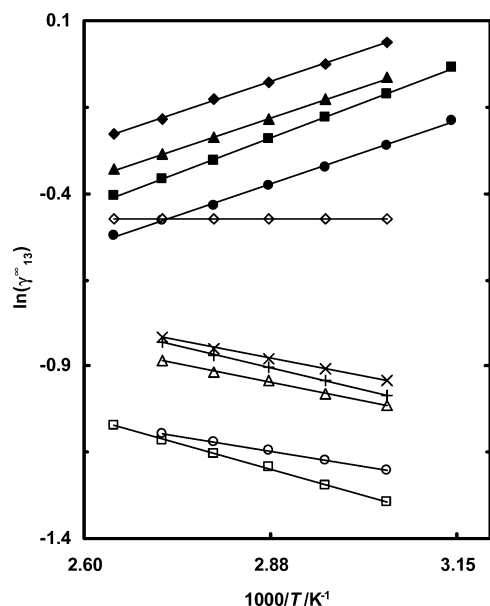

Figure 4. Plot of $\ln(\gamma_{13}^{\infty})$ for ionic liquid [dmim][TCB] versus $1/T$ for the solutes: (●) methanol; (■) ethanol; (▲) propan-1-ol; (◆) butan-1-ol; (○) acetone; (×) pentan-2-one; (+) pentan-3-one; (□) acetic acid; (◇) butyric acid; (△) THF.
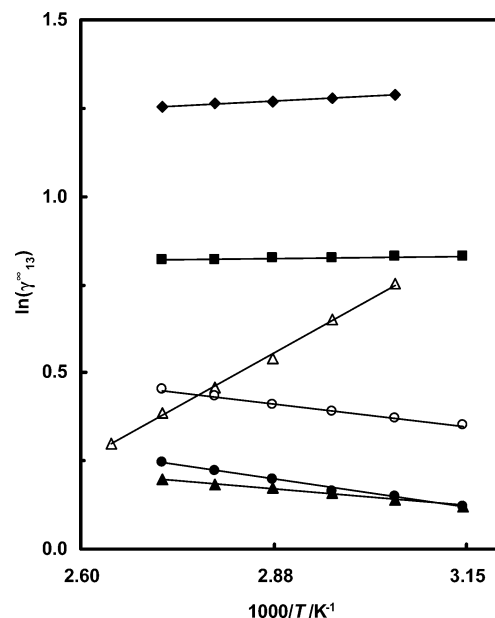

Figure 5. Plot of $\ln(\gamma_{13}^{\infty})$ for ionic liquid [dmim][TCB] versus $1/T$ for the solutes: (●) MTBE; (○) TAME; (▲) diethyl ether; (■) di-n-propyl ether; (◆) di-n-butyl ether; (△) water.

additionally increases interactions. The packing effect is also observed for *n*-alkanes. *n*-Octane has higher values of γ_{13}^{∞} than isooctane (2,2,4-trimethylpentane). The interaction of the double bond in alkenes with polar ionic liquid causes lower values of γ_{13}^{∞} for alkenes than alkanes with the same carbon number. The hydrogen atom of the triple bond in alkynes, which shows slightly acidic properties and π electrons of triple bond cause interactions of alkynes with polar ionic liquid, consequently alkynes have lower values of γ_{13}^{∞} than corresponding alkanes, alkenes, and cycloalkanes. Aromatic hydrocarbons have the smallest values of γ_{13}^{∞} as compared with the rest of the investigated hydrocarbons. Strong interactions between six π-delocalized electrons in benzene structure with the polar ionic liquid are responsible for reduction of γ_{13}^{∞}. The lowest values of γ_{13}^{∞} are for carboxylic acids, tetrahydrofuran (THF), ketones,

and thiophene. These polar compounds show the highest interaction with [dmim][TCB] ionic liquid. Due to the acidic character, the carboxylic acids interact strongly with the anion of the ionic liquid. Sulfur in thiophene and oxygen in THF and ketones have no surrounding blocking group; therefore, these polar parts of compounds can strongly interact with polar ionic liquid. Ethers, even though they contain oxygen in their structure, do not interact as strongly, as mentioned above for polar compounds with [dmim][TCB]. It is caused by steric effects—alkyl groups mask the oxygen from two sides. The hydroxyl group in alcohols and water do not interact with ionic liquid as strongly as the carboxylic group in carboxylic acids, resulting in higher values of γ_{13}^{∞}.

The gas—liquid partition coefficients $K_L = (c_i^L/c_i^G)$ for a solute (see Table 2) decrease with an increase of temperature and increase with an increase of the alkane chain of the solute. The highest values are observed for acetic acid and butyric acid.

$\Delta H_1^{E,\infty}$ is a basic thermodynamic function, calculated from the experimental data, which informs us about the fundamental interaction between solute and solvent. In general, within each of the series alkane, cycloalkane, and alkene, the $\Delta H_1^{E,\infty}$ values increase with increasing carbon number of the solute. Such an effect is always observed for specific ILs with the longer alkane chain in the cation or anion. The calculated values of $\Delta H_1^{E,\infty}$ are small and positive besides for alkynes, aromatic hydrocarbons, acids, ethers, and ketones, for which they are all negative (see Table 3). Much larger negative values were observed previously for most of these solutes in different ILs.[4,5] The values of $\Delta H_1^{E,\infty}$ for benzene, toluene, *p*-xylene, acetic acid, and THF in this work are −1.6, −2.0, −2.2, −4.6, and −3.2 kJ·mol⁻¹, respectively. This indicates that the intermolecular interactions are slightly higher than those for other solutes. The error for the calculations of $\Delta H_1^{E,\infty}$ is the same as that for the linear regression of the natural logarithm of the activity coefficients as a function of the inverse absolute temperature. The entropy, $T_{ref}\Delta S_1^{E,\infty}$, is small and negative for alkanes, cycloalkanes, and alkenes.

Figure 6 presents the selectivity ($S_{ij}^{\infty} = \gamma_i^{\infty}/\gamma_j^{\infty}$) and capacity ($k_j^{\infty} = 1/\gamma_j^{\infty}$) for aliphatic/aromatic hydrocarbon separation as a

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TABLE 3: Limiting Partial Molar Excess Gibbs Energies $\Delta G_1^{E,\infty}$, Enthalpies $\Delta H_1^{E,\infty}$, and Entropies $T_{ref}\Delta S_1^{E,\infty}$ for the Solutes in Ionic Liquid [dmim][TCB] at the Reference Temperature $T_{ref} = 328.15$ K

solute	$\Delta G_1^{E,\infty}/$ kJ·mol^{-1}	$\Delta H_1^{E,\infty}/$ kJ·mol^{-1}	$T_{ref}\Delta S_1^{E,\infty}/$ kJ·mol^{-1}
n-pentane	4.0	3.4	−0.62
n-hexane	4.5	3.6	−1.1
n-heptane	5.1	4.2	−1.7
n-octane	5.7	4.4	−2.3
2,2,4-trimethylpentane	5.5	4.0	−2.1
n-nonane	6.3	4.8	−2.9
n-decane	6.9	5.1	−3.5
cyclopentane	2.6	3.4	0.81
cyclohexane	3.2	4.2	0.18
methylcyclohexane	3.8	3.9	−0.38
cycloheptane	3.5	4.1	−0.15
cyclooctane	3.9	4.3	−0.56
pent-1-ene	2.7	1.5	0.7
hex-1-ene	3.2	2.5	0.18
cyclohexene	1.9	2.0	1.4
hept-1-ene	3.8	2.2	−0.40
oct-1-ene	4.4	2.7	−1.0
hex-1-yne	1.1	−0.71	2.3
hept-1-yne	1.6	−0.65	1.8
oct-1-yne	2.2	−0.23	1.2
benzene	−1.4	−1.6	4.8
toluene	−0.79	−2.0	4.2
ethylbenzene	−0.03	−1.5	3.4
o-xylene	−0.36	−1.9	3.7
m-xylene	−0.08	−2.1	3.5
p-xylene	−0.12	−2.2	3.5
methanol	−0.67	5.5	4.1
ethanol	−0.28	6.2	3.7
propan-1-ol	−0.16	5.5	3.6
butan-1-ol	0.10	5.6	3.3
water	1.9	9.2	1.5
acetic acid	−3.3	−4.6	6.7
butyric acid	−1.2	−0.01	4.6
thiophene	−1.6	−1.5	5.0
tetrahydrofuran	−2.6	−3.2	6.0
methyl *tert*-butyl ether	0.38	−2.5	3.0
methyl *tert*-pentyl ether	1.0	−1.9	2.4
diethyl ether	0.36	−1.5	3.0
di-*n*-propyl ether	2.1	0.21	1.3
di-*n*-butyl ether	3.3	0.81	0.09
acetone	−3.1	−2.6	6.5
pentan-2-one	−2.4	−3.2	5.8
pentan-3-one	−2.5	−3.8	5.9

TABLE 4: Densities for Ionic Liquid [dmim][TCB] as a Function of Temperature

T/K	ρ/g·cm^{-3}	T/K	ρ/g·cm^{-3}
298.15	0.96227	328.15	0.94208
308.15	0.95553	338.15	0.93543
318.15	0.94876	348.15	0.92883

function of temperature for the investigated ionic liquid in comparison with NMP[14] and sulfolane.[15] The selectivity at a given temperature of 328.15 K is about 1.5 times lower than that for sulfolane and comparable to NMP. The capacity is almost 4 times higher than that for sulfolane and almost 2 times higher than that for NMP.

Conclusions

Activity coefficients at infinite dilution and the gas−liquid partition coefficients for various solutes in the ionic liquid 1-decyl-3-methylimidazolium tetracyanoborate were measured by gas−liquid chromatography at temperatures from 318.15 to 378.15 K.
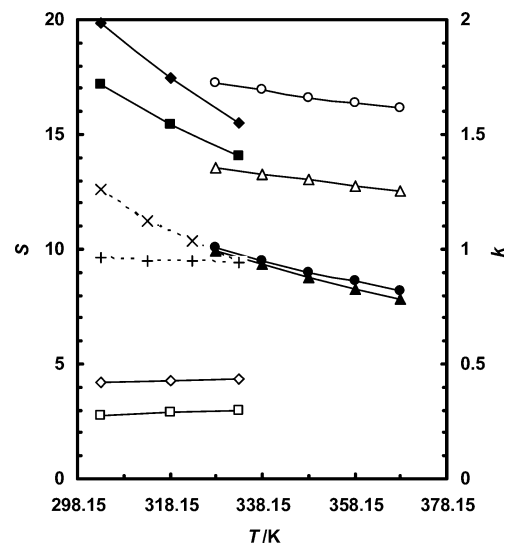

Figure 6. Selectivity S and capacity k for aliphatic/aromatic hydrocarbon separation for ionic liquid [dmim][TCB], NMP, and sulfolane as a function of temperature: (●) $S_{n\text{-hexane/benzene}}^{\infty}$ [dmim][TCB]; (○) $k_{\text{benzene}}^{\infty}$ [dmim][TCB]; (▲) $S_{n\text{-heptane/toluene}}^{\infty}$ [dmim][TCB]; (△) $k_{\text{toluene}}^{\infty}$ [dmim][TCB]; (×) $S_{n\text{-hexane/benzene}}^{\infty}$ NMP;[14] (+) $k_{\text{benzene}}^{\infty}$ NMP;[14] (◆) $S_{n\text{-hexane/benzene}}^{\infty}$ sulfolane;[15] (◇) $k_{\text{benzene}}^{\infty}$ sulfolane;[15] (■) $S_{n\text{-heptane/toluene}}^{\infty}$ sulfolane;[15] (□) $k_{\text{toluene}}^{\infty}$ sulfolane.[15]

It was found that the investigated [dmim][TCB] ionic liquid shows much higher capacity than NMP and sulfolane and selectivity on the same level as NMP and lower than that for sulfolane for the separation of aliphatic hydrocarbons from aromatic hydrocarbons. To increase selectivity, the ionic liquid with a shorter alkyl chain on the imidazolium ring should be proposed.

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