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Solubilities of the Gaseous and Liquid Solutes and Their Thermodynamics of Solubilization in the Novel Room-Temperature Ionic Liquids at Infinite Dilution by Gas Chromatography

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The solubilities of C_2H_4 and CO_2 and the interactions of polar and nonpolar solutes with the novel ionic liquids (ILs) 1-butyronitrile-3-methylimidazolium bis(trifluoromethylsulfonyl) imidate (CpMIm[NTf_2]), 1-butyronitrile-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl) imidate (CpMMIm[NTf_2]), 1-butyronitrile-3-methylimidazolium dicyanamide (CpMIm[$N(CN)_2$]), 1-butyronitrile-2,3-dimethylimidazolium dicyanamide (CpMMIm[$N(CN)_2$]), 1-butyl-3-methylimidazolium palmitate (BMIm[n-$C_{16}H_{33}COO$]), and 1-butyl-3-methylimidazolium stearate (BMIm[n-$C_{18}H_{35}COO$]) were studied by gas chromatography at infinite dilution at T = (303.15, 313.15, 323.15, and 333.15) K. Henry's law constant k_H of C_2H_4 and CO_2 gas, infinite dilution activity coefficient γ^∞, molar enthalpies of solution $\Delta_{sol}H^\infty$, and partial molar excess enthalpies of solution $\Delta H^{E\infty}$ and of Gibbs energies $\Delta G^{E\infty}$ were determined for polar and nonpolar solutes in these novel ILs. Compared with the 1,3-dialkylimidazolium ILs, cyano functional group substitution on the alkyl chain results in a remarkable decrease of the interactions of hydrocarbons. BMIm[n-$C_{16}H_{31}OO$] and BMIm[n-$C_{18}H_{35}OO$] demonstrate strong solubilization for both polar and nonpolar solutes. Straight lines of ln V_g versus $1/T$ and ln γ^∞ versus $1/T$ were obtained for the majority of solutes in the temperature range. BMIm[NTf_2] and 1-octyl-3-methylimidazolium tetrafluoroborate (OMIm[BF_4]) show much better solubility for thiophene and are better solvents for the separations of thiophene from hydrocarbons.

Introduction

Room-temperature ionic liquids (RTILs) have been utilized extensively as clean solvents and catalysts for green chemistry.[1−6] Interest in this class of solvent stems from the properties exhibited by the liquids. These materials have negligible vapor pressure, which allows for easy separation of organic compounds by direct distillation without loss of IL. Many of these materials are based on an imidazolium cation, 1-alkyl-3-methylimidazolium. Simply by changing the anion or the alkyl chain on the cation, a wide range of tuneable properties can be obtained, such as, for example, hydrophobicity, viscosity, density, and solvation. Unlike water and other hydroxylic solvents, they will dissolve a wide range of organic molecules to an appreciable extent, the solubility being controlled by the nature of the counteranion and the substituent on the side chain. The relations between physicochemical properties and the structure of the ILs have become an important issue, and the selective solubility of various solutes in the ILs is particularly important among them and has been less studied.

One of the most important potential applications of ILs is for the separations of gas mixtures. The nonvolatility of ILs would not cause contamination in a gas stream, and thus this feature gives ILs a big advantage over conventional solvents used for absorbing gases. To select an efficient IL as a gas separation medium, it is necessary to know the solubility of the gases in the IL phase which have been studied according to the static equilibrium method or molecular dynamics simulations.[7−9] Gas chromatography has been considered to be a particularly convenient technique for the determination of the solubility of gases in nonvolatile liquids based on Henry's law constants for a certain range of temperatures.[10]

Infinite dilution activity coefficients γ^∞ are very useful for the research and comparison of the interactions between different solutes and solvents, especially for the process of synthesis and design. For example, γ^∞ can be directly used for the selection of solvents for azeotropic/extractive distillation, liquid extraction, solvent-aided crystallization, and even chemical reaction. Also, γ^∞ data provide valuable information for testing predictive models or computer simulation methods because values of γ^∞ give a direct measure of interactions between unlike molecules in the absence of solute−solute interactions. Therefore, the solubilization ability of the IL stationary phases for different kinds of solutes could be characterized through the determined γ^∞. Due to its simpleness and accuracy compared with other methods, gas chromatography has been used to determine the thermodynamic properties of different solutes in various stationary solvents.[10] Simultaneously, the interactions of organic solutes with ILs have been studied based on a large amount of γ^∞ data in the literature.[11−15] However, most of them are limited in conventional ILs with 1,3-dialkyl-substituted imidazolium or pyridium salts.

The novel ILs of BMIm[n-$C_{16}H_{33}COO$], BMIm[n-$C_{18}H_{37}COO$], and CpMIm[X] and CpMMIm[X] (X = NTf_2, $N(CN)_2$) have been successfully synthesized in our group. On the basis of our elementary research of their physicochemical properties,[16] their selective interactions with various solutes were further studied by the gas chromatography technique in this work. By comparisons of the novel ILs with 1,3-dialkyl imidazolium ILs, the effect of the characteristics of the ILs such as the chain length on the imidazolium cation moiety, the presence of the 2C-methyl group, the property of the anion, and especially the

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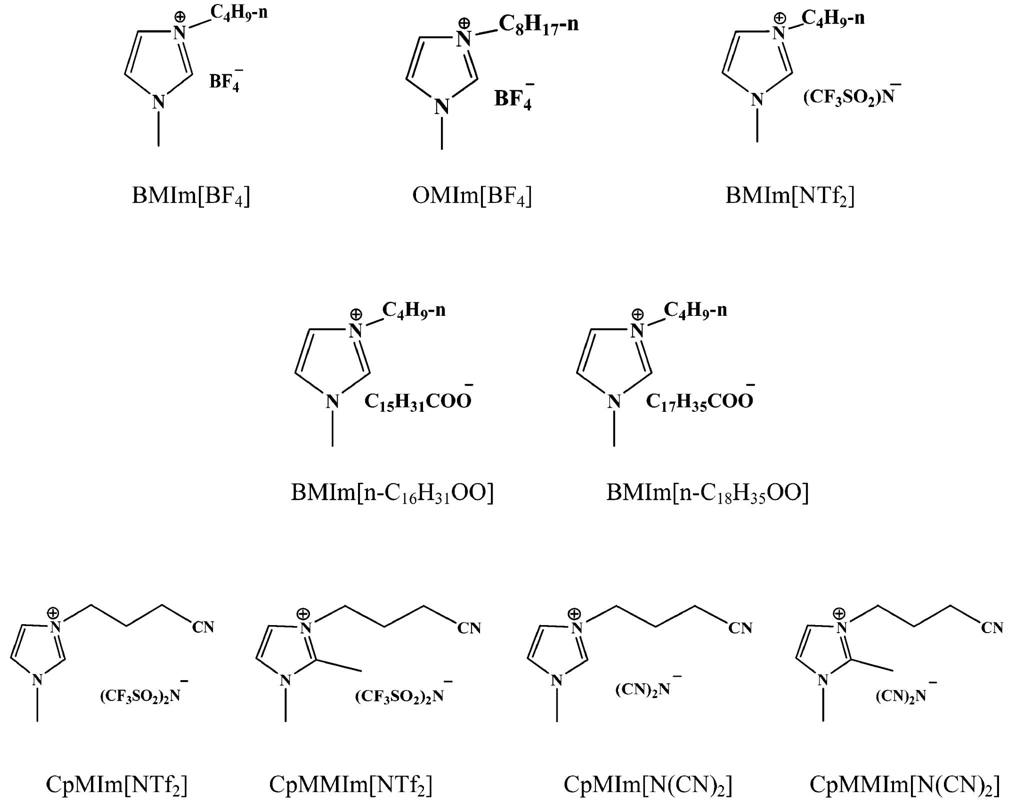

Figure 1. 1,3-Dialkylimidazolium and 1-butyronitrile-3-methylimidazolium ILs used as gas chromatography stationary phases.

effect of functional groups in the side chain on the thermodynamics of different solutes in ILs was studied in this work.

Experimental

Preparation of RTILs. The RTILs shown in Figure 1 were synthesized in our group according to the following procedure.[16] A mixture of 1-methylimidazole (0.25 mol) and 4-chlorobutyronitrile (0.3 mol) was stirred at 353 K for 48 h. The resulting solid (**1a**) was washed with ethyl acetate (3 × 30 mL) and then dried in a vacuum for 24 h. A mixture of **1a** (0.05 mol) and lithium trifluoromethanesulfonimide (0.06 mol) in distilled water (50 mL) was stirred at room temperature for 10 h and then extracted with dichloromethane (200 mL), washed with distilled water, and dried under a vacuum, and CpMIm[NTf_2] was obtained. A mixture of **1a** (0.05 mol) and sodium dicyanamide (0.06 mol) in ethanol (150 mL) was stirred at room temperature for 48 h. After filtration and removal of the solvents, the resulting viscous liquid was washed with diethyl ether under vigorous stirring three times and then dried in a vacuum for 24 h, and CpMIm[$N(CN)_2$] was obtained. CpMMIm[NTf_2] and CpMMIm[$N(CN)_2$] were prepared in the same procedure as above using 1,2-dimethylimidazole as starting material. BMIm[n-$C_{16}H_{31}OO$] and BMIm[n-$C_{18}H_{35}OO$] were synthesized according to the following procedure: 1-butyl-3-methylimidazolium hydroxide (BMIm[OH]) was obtained by exchange of the anion of 1-butyl-3-methylimidazolium chloride on ion-exchange resin which was treated by sodium hydroxide before use, and then the acid−base reaction of BMIm[OH] with palmitic acid and stearic acid proceeded, respectively. BMIm[BF_4], OMIm[BF_4], and BMIm[NTf_2] employed here for comparison were synthesized and purified according to the literature.[3] The RTILs were further purified by subjecting them to 2.13 kPa at 373 K for 2 h to eliminate the absorbed moisture and volatile components before each column packing.

Gaseous and Chemical Solutes. The organic liquid solutes (hexane, heptane, octane, cyclohexane, methyl cyclohexane, 1-hexene, 1-octene, benzene, toluene, methanol, ethanol, ethyl acetate, tetrahydrofuran, and thiophene) used were of analytical purity and used without further purification. The carrier gas of argon and gaseous solutes of CO_2 and C_2H_4 were 99.999 % purity.

Preparation of Supported ILs and Packed Columns. The solvent dichloromethane or methanol was used to coat ILs onto the solid support 101 AW (80/100 mesh) (the inert and white diatomite provided by Shanghai Reagent Corporation) by a rotary evaporator to ensure the homogeneous spread of the ILs onto the surface of support. After evaporation of the solvent under vacuum, the supported material was equilibrated at 393 K for 6 h for the preparation of packed columns. The IL loading onto the support varied from (30 to 40) % by mass, which is large enough to prevent any residual adsorption onto the column packing.

Stainless steel columns with a length of 2.0 m and an inner diameter of 0.20 mm were carefully filled with the IL-coated support material. The mass of the packing material was calculated from the mass of the packed and empty columns and was checked during the experiments. Every packed column was conditioned at 423 K for 10 h until the baseline was flat before the measurement of retention values; meanwhile, the water and volatile components were removed.

Experimental Procedure and Apparatus. Sp 6890 gas chromatography was supplied by Shandong Lunanruihong Chemical Engineering Instrument Corporation in China. A thermal conductivity detector was used, and the carrier gas was dry argon. The temperature of the oven was controlled within 0.1 K. The carrier gas flow rate was determined by a Field-Cal 570 flow calibrator placed at the outlet of the detector. The flow rate was set for a series of runs for stabilization for at least 15 min before any k_H and γ^∞ determinations. The flow rates were corrected for water vapor pressure and ranged from (15 to 40) $mL\cdot min^{-1}$. Sample injections {liquid, (0.6 to 1) μL; gases, 100 μL} were considered small enough to ensure the conditions of

Table 1. Henry's Law Constants k_H of CO_2 and C_2H_4 Gases in Different ILs

	k_H/bar					
	CO_2			C_2H_4		
T/K	303	313	323	303	313	323
BMIm[BF_4]	66.0	81.6	91.6 (88.9)[9]	206.5	217.1	255.2
OMIm[BF_4]	53.9	65.7	75.6	134.6	141.9	151.2
BMIm[n-$C_{16}H_{31}OO$]		82.0[a]	75.5		81.4[a]	72.2
BMIm[n-$C_{18}H_{35}OO$]		62.1[a]	59.2		62.3[a]	59.3
BMIm[NTf_2]	33.4	41.2	47.7 (48.7)[9]	87.3	93.7	108.4 (97)[20]
CpMIm[NTf_2]	42.1	52.1	58.9	195.3	208.2	214.5
CpMMIm[NTf_2]	46.2	55.7	59.6	182.1	196.3	203.1
CpMIm[$N(CN)_2$]	110.6	127.2	154.2	546.3	561.3	636.6
CpMMIm[$N(CN)_2$]	136.3	151.9	162.9	266.6	348.8	475.9

[a] k_H determined at 318 K.

Table 2. Infinite Dilution Activity Coefficients γ^∞ of Various Solutes in Tetrafluoroborate with Different Alkyl Chain Lengths on the Imidazolium Cation

	γ^∞			
	BMIm[BF_4]		OMIm[BF_4]	
T/K	298	323	298	323
hexane	65.9	50.6 (76.5)	8.6	6.7 (12.8)
heptane	83.5	70.3 (115.3)	11.0	8.4 (16.3)
octane	116.8	95.5	16.1	11.0
cyclohexane	30.7	24.7 (38.4)	5.3	3.9 (8.0)
methyl cyclohexane	43.7	35.5	6.7	5.3
1-hexene	25.8	21.8	4.9	3.9
1-octene	59.1	48.3	7.8	6.6
benzene	1.5	1.5 (2.4)	0.7	0.6 (1.3)
toluene	2.5	2.4 (4.1)	1.0	0.9 (1.8)
methanol	0.8	0.7 (1.2)	0.3	0.3 (0.9)
ethanol	1.1	1.0	0.5	0.4
ethyl acetate	1.8	1.7	0.9	0.8
THF	1.4	1.4	0.7	0.6
thiophene	1.7	1.5	0.9	0.8

infinite dilution. The "air peak" method was used for the determination of gas holdup. The GLC technique was tested for the system hexane in hexadecane at 298 K, and the results were within 1.2 % of the literature values.[10] The calculation of the thermodynamic data was based on the average of the measurement of two columns with different IL loadings in the range of (25 to 30) % by mass. The estimated uncertainty in the determined k_H and γ^∞ values is (2 to 3) % as a result of the measured errors on determining the carrier gas flow rate (0.1 mL·min^{-1}), the solute retention time (0.008 min), and the amount of the solvent on the column (0.2 mg).

Theories

Calculation of Henry's Law Constant k_H. Prausnitz and coworkers have shown how it is possible to determine k_H in a wide temperature range using gas chromatography.[17] k_H, for a gaseous solute in a solvent, is given by

$$k_H = \lim_{x \to 0} (p_1/x) \tag{1}$$

where p_1 is the partial pressure of the solute and x is its mole fraction. Neglecting gas-phase imperfections, Henry's law constant is related to the corrected net retention volume V_N by

$$k_H = RTm_L/M_LV_N \tag{2}$$

where m_L and M_L are the mass and molecular weight of the solvent, respectively.

Calculation of Infinite Dilution Activity Coefficient γ^∞ and Thermodynamic Data. Everett and Cruikshank et al. have developed the following equation for obtaining the activity coefficient at infinite dilution for a volatile solute in a nonvolatile solvent[18,19]

$$\ln \gamma^\infty = \ln(n_3RT/V_N\, p_1^*) - (B_{11} - V_1^*)p_1^*/RT + (2B_{12} - V_1^\infty)\cdot J_2^{\,3}p_o/RT \tag{3}$$

where V_N denotes net solute retention volume; p_o is the outlet pressure and is equal to atmospheric pressure; $J_2^{\,3}p_o$ is the mean column pressure; n_3 is the amount of IL solvent on the column; p_1^* is the vapor pressure of the solute determined according to the Antoine equation;[19] V_1^* is the molar volume of the solute; V_1^∞ the partial molar volume of the solute at infinite dilution in the solvent of IL (here equated to V_1^*); B_{11} is the second virial coefficient of the pure solute; and B_{12} is the mixed second virial coefficient of the solute (1) and the carrier gas (2), determined with the McGlashan and Potter equation and the combining rules adopted by Hudson and McCoubrey.[10] The net solute retention volume V_N and specific retention volume V_g are given by

$$V_N = (J_2^{\,3})^{-1}F_0((p_0 - p_w)/p_0)(T/T_f)t_R' \tag{4}$$

$$V_g = (J_2^{\,3})^{-1}F_0((p_0 - p_w)/p_0)(273.15/T_f)t_R'/w \tag{5}$$

$$J_2^{\,3} = 2((p_i/p_0)^3 - 1)/3((p_i/p_0)^2 - 1) \tag{6}$$

where F_0 is the volumetric flow rate (m^3·min^{-1}) of the carrier gas, at the column outlet, measured with a Field-Cal 570 flow calibrator; T_f is the temperature of the flow meter; p_w is the vapor pressure of water at T_f; and p_i is the column inlet pressure measured with a precise manometer.

The values of B_{11} and B_{12} were calculated using the McGlashan and Potter equation[10]

$$B/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n - 1)(T_c/T)^{4.5} \tag{7}$$

in which n refers to the number of carbon atoms. Critical data used to calculate B_{11} and B_{12} used in the calculation of T_c are based on the literature.[12−14]

The molar solvation enthalpy at infinite dilution, $\Delta_{sol}H^\infty$, is obtained from a plot of ln(V_g) versus 1/T

$$\Delta_{sol}H^\infty = \partial \ln V_g/\partial(1/T) \tag{8}$$

The partial molar excess enthalpy of solution at infinite dilution is usually evaluated from the slope of plots of ln(γ^∞) versus 1/T

$$\Delta H^{E\infty} = \partial \ln \gamma^\infty/\partial(1/T) \tag{9}$$

$$\Delta G^{E\infty} = RT \ln \gamma^\infty \tag{10}$$

Results and Discussion

Table 1 shows Henry's law constants k_H of CO_2 and C_2H_4 gases in different ILs at T = {303, 313 (318), and 323} K. The values in the brackets are the k_H values reported in the literature which were measured through the static equilibrium method by a gravimetric microbalance.[8,9] Maybe the difference in the method is the major reason for the differences between the measured k_H in this work and k_H in the literature.[8] But the general agreement on the determined k_H by the two methods

Table 3. Infinite Dilution Activity Coefficients γ^∞ of Various Solutes in 1-Butyl-3-methylimidazolium RTILs with Different Anions

	$\gamma\infty$				
	BMIm[NTf_2]	BMIm[BF_4]	BMIm[n-$C_{16}H_{31}OO$]	BMIm[n-$C_{18}H_{35}OO$]	
T/K	323	323	333	323	333
hexane	12.8	50.6	1.3	1.7	1.4
heptane	15.5	70.3	1.4	1.8	1.5
octane	23.4	95.5	1.6	2.1	1.6
cyclohexane	6.7	24.7	0.9	1.1	1.2
methyl cyclohexane	9.1	35.5	1.0	1.3	1.3
1-hexene	6.0	21.8	1.1	1.4	1.2
1-octene	12.3	48.3	1.4	1.7	1.4
benzene	0.8	1.45	0.7	0.7	0.7
toluene	1.2	2.44	0.8	0.8	0.8
methanol	0.8	0.7	0.3	0.3	0.3
ethanol	1.2	1.0	0.4	0.5	0.4
ethyl acetate	0.7	1.7	1.0	1.1	1.1
THF	0.4	1.4	0.6	0.7	0.6
thiophene	0.7	1.5	0.9	0.8	0.8
H_2O	2.6	–	–	–	–

Table 4. Infinite Dilution Activity Coefficients γ^∞ of Various Solutes in 1-Butyronitrile-3-methylimidazolium RTILs

	$\gamma\infty$							
	CpMIm[NTf_2]		CpMIm[$N(CN)_2$]		CpMMIm[NTf_2]		CpMMIm[$N(CN)_2$]	
T/K	303	323	303	323	303	323	303	323
hexane	126.0	112.8	212.9	144.7	66.3	54.3	163.0	136.7
heptane	134.1	126.5	231.3	196.7	88.5	67.0	173.9	123.0
octane	190.9	158.7	264.1	203.6	101.6	88.6	182.2	132.1
cyclohexane	55.4	45.9	81.7	58.9	36.7	28.3	97.5	61.3
methyl cyclohexane	75.1	66.2	118.0	84.9	48.5	39.6	113.5	80.2
1-hexene	54.2	47.1	71.7	60.4	32.0	25.3	103.6	64.0
1-octene	118.8	105.7	142.1	135.5	60.8	55.1	129.5	102.5
benzene	1.8	1.7	2.3	2.2	1.9	1.71	3.0	2.8
toluene	3.3	3.1	4.3	4.0	3.3	3.1	5.3	4.6
methanol	1.1	1.0	0.3	0.3	1.9	1.5	0.4	0.4
ethanol	1.7	1.4	0.5	0.4	2.6	2.2	0.8	0.7
H_2O	–	1.8	–	–	–	2.3	–	–
ethyl acetate	2.1	2.1	2.8	2.7	1.6	1.5	4.2	3.9
THF	1.3	1.2	1.6	1.5	1.4	1.4	2.3	2.2
thiophene	1.5	1.4	1.7	1.6	1.5	1.4	2.3	2.3

Table 5. Molar Enthalpies of Solution $\Delta_{sol}H^\infty$/(kJ·mol^{-1}) and Partial Molar Excess Enthalpies of Solution $\Delta H^{E\infty}$/(kJ·mol^{-1}) of Various Solutes in Seven RTILs at Infinite Dilution

		BMIm[BF_4]	OMIm[BF_4]	BMIm[NTf_2]	CpMIm[NTf_2]	CpMIm[$N(CN)_2$]	CpMMIm[NTf_2]	CpMMIm[$N(CN)_2$]
hexane	$-\Delta_{sol}H^\infty$	18.8	24.5	27.3	32.0	33.0	21.6	21.1
	$\Delta H^{E\infty}$	8.8	6.9	4.0	9.4	22.0	9.4	10.3
heptane	$-\Delta_{sol}H^\infty$	27.4	28.2	30.8	40.1	35.0	26.2	25.2
	$\Delta H^{E\infty}$	9.5	7.9	5.1	12.9	18.5	8.9	12.5
octane	$-\Delta_{sol}H^\infty$	29.0	30.0	35.4	42.5	35.1	36.1	28.8
	$\Delta H^{E\infty}$	11.7	10.9	5.3	14.9	15.9	6.4	12.1
cyclohexane	$-\Delta_{sol}H^\infty$	23.3	24.4	28.9	22.4	22.1	21.5	14.7
	$\Delta H^{E\infty}$	9.3	8.3	3.7	10.5	11.7	11.3	18.0
methyl cyclohexane	$-\Delta_{sol}H^\infty$	25.6	27.4	30.7	24.0	22.9	25.3	16.4
	$\Delta H^{E\infty}$	9.2	7.5	4.1	11.1	11.1	9.3	18.5
1-hexene	$-\Delta_{sol}H^\infty$	23.0	24.4	29.2	22.2	22.7	20.5	13.3
	$\Delta H^{E\infty}$	7.5	6.2	1.4	8.9	8.0	10.8	17.3
1-octene	$-\Delta_{sol}H^\infty$	31.6	36.2	36.7	32.4	34.0	33.8	28.5
	$\Delta H^{E\infty}$	8.0	2.7	2.9	7.6	7.6	6.6	11.2
benzene	$-\Delta_{sol}H^\infty$	30.6	32.1	35.4	30.4	30.9	30.3	30.0
	$\Delta H^{E\infty}$	2.2	0.8	-2.1	3.4	2.6	3.2	3.4
toluene	$-\Delta_{sol}H^\infty$	33.8	66.8		36.5	35.8	34.2	33.1
	$\Delta H^{E\infty}$	3.0	1.2		2.9	1.8	1.2	4.2
THF	$-\Delta_{sol}H^\infty$	29.3	22.8	35.6	30.0	30.6		36.6
	$\Delta H^{E\infty}$	2.4	0.8	−4.2	2.7	1.8		1.2
ethyl acetate	$-\Delta_{sol}H^\infty$	32.8	28.1	38.7	32.4	33.2	33.3	38.1
	$\Delta H^{E\infty}$	2.2	0.3	−4.1	5.9	2.6	8.6	2.0
ethanol	$-\Delta_{sol}H^\infty$	31.6	30.1	33.1	47.8		33.3	33.0
	$\Delta H^{E\infty}$	9.8	2.6	4.6	6.7		8.6	1.7
methanol	$-\Delta_{sol}H^\infty$	34.7			43.1		28.8	30.6
	$\Delta H^{E\infty}$	3.1			6.5		8.9	3.7

suggests the reliability of the gas chromatographic method for solubility determination of CO_2 and C_2H_4 gases in ILs. Equation 1 implies that a smaller k_H indicates larger gas solubility in the stationary solvent. Therefore, as can be seen in Table 1, CO_2 has higher solubility in the ILs with NTf_2 as the anion. This suggests that CO_2 could be associated with NTf_2 more strongly

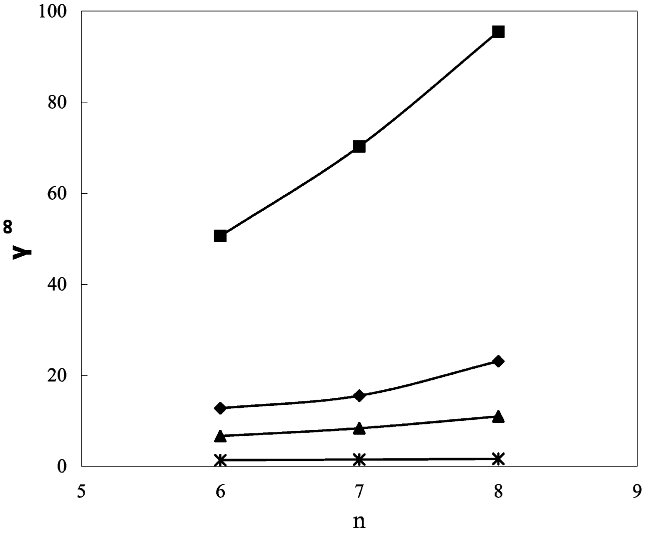

Figure 2. Dependence of infinite dilution activity coefficients γ^{∞} on the number of carbon atoms (n) of n-alkanes over: ■, BMIm[BF_4]; ●, BMIm[NTf_2]; ▲, OMIm[BF_4]; *, BMIm[n-$C_{18}H_{35}OO$].

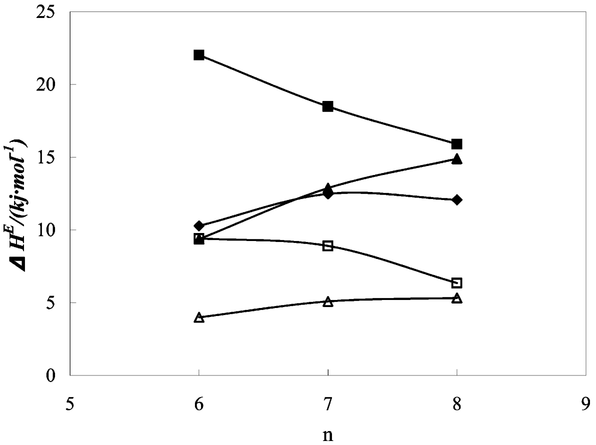

Figure 3. Dependence of partial molar excess enthalpies of solution ΔH^E on the number of carbon atoms of n-alkanes (n) over: △, BMIm[NTf_2]; □, CpMIm[NTf_2]; ▲, CpMMIm[NTf_2]; ■, CpMIm[$N(CN)_2$]; ●, CpMMIm[$N(CN)_2$].

than with BF_4 and $N(CN)_2$.[8] For BMIm[BF_4] and OMIm[BF_4], increasing the alkyl chain length on the imidazolium cation results in an increase of solubility of CO_2 greatly. With the substitution of n-butyl with the polar butyronitrile group on the imidazolium cation, the solubility of CO_2 decreases slightly. From the comparison of k_H for the two pairs, CpMIm[NTf_2]/CpMMIm[NTf_2] and CpMIm[$N(CN)_2$]/CpMMIm[$N(CN)_2$], it can be concluded that the presence of the 2C-methyl group slightly decreases the solubility of CO_2 in the ILs. As for C_2H_4, the increase of the alkyl side chain length results in an increase of its solubility in ILs. C_2H_4 has the highest solubility in BMIm[n-$C_{18}H_{35}OO$]. With the butyronitrile substitution as the side chain, C_2H_4's solubility in the ILs is decreased more greatly than CO_2; e.g., at 303 K, k_H for C_2H_4 is 87.3 in BMIm[NTf_2] and markedly increases to 195.3 in CpMIm[NTf_2]. This indicates that the length and polarity of the side chain on the imidazolium cation could affect C_2H_4's solubility more remarkably. Contrary to the case of CO_2, the presence of the 2C-methyl group on the cation increases the solubility of C_2H_4 in ILs. Unexpectedly, in BMIm[n-$C_{16}H_{31}OO$] (and BMIm[n-$C_{18}H_{35}OO$]), C_2H_4 has comparable solubility with CO_2 due to the strong molecular interactions between C_2H_4 and the anion of palmitate and stearate, and the increase of the temperature has little effect on k_H of both C_2H_4 and CO_2.

In the tetrafluoroborate ILs, the values in Table 2 show the following hierarchy of γ^{∞}: alkanes > alkenes > aromatics. Thus, the solubility of the solutes in tetrafluoroborate ILs follows: alkanes < alkenes < aromatics. The larger magnitude of γ^{∞} can be explained by the much weaker interactions of nonpolar hydrocarbons with polar ILs than that of polarizable aromatics with π-delocalized electrons and hydrogen bond acids and bases like alcohols, tetrahydrofuran, and ethyl acetate with ILs. The imidazolium cation moiety is more likely to interact with aromatics and alkenes than alkanes. The more intensified hydrogen bond interactions could be formed between alcohols and the BF_4 anion, so the smallest magnitudes of γ^{∞} for ethanol and methanol were obtained. As for 1-alkyl-3-methylimidazole tetrafluoborate, as indicated in Table 2, the smaller γ^{∞} for hydrocarbons in OMIm[BF_4] than in BMIm[BF_4] suggests the stronger interactions of hydrocarbons with OMIm[BF_4] with a longer alkyl chain. With different composed anions, the ILs show visible distinction in the solubilization ability for organic solutes (Table 3). BMIm[NTf_2] shows much stronger interactions with hydrocarbons than BMIm[BF_4], but it shows weaker interactions with alcohols and water than BMIm[BF_4]. BMIm[NTf_2] exhibits stronger solubilization ability for ethyl acetate and tetrahydrofuran than alcohols, and BMIm[BF_4] shows stronger solubilization ability for alcohols. With the introduction of the amphoteric anion, BMIm[n-$C_{18}H_{35}OO$] could better solubilize both aliphatic and aromatic hydrocarbons. At 323 K, the discrepancy of γ^{∞} of different hydrocarbons in BMIm[n-$C_{16}H_{31}OO$] is not so remarkable as in the case of other ILs. BMIm[n-$C_{16}H_{31}OO$] behaves similarly to BMIm[n-$C_{18}H_{35}OO$].

Figure 2 shows the increase of γ^{∞} in the 1,3-dialkylimidazolium ILs with increasing carbon number of n-alkanes. The distinctions in the solubility among the homologous compounds of alkanes are the most remarkable in BMIm[BF_4] but the least in BMIm[n-$C_{18}H_{35}OO$] due to the stronger interactions between alkanes and BMIm[n-$C_{18}H_{35}OO$].

According to the lists in Table 4, in CpMIm[NTf_2], the introduction of the polar functional group of butyronitrile in the side chain leads to a great increase of γ^{∞} for the measured solutes compared with BMIm[NTf_2]. The higher polarity of the side chain on the imidazolium ring results in much lower solubility of aliphatic hydrocarbons but still a high solubility of polar solutes; therefore, the cyano-functionalized CpMIm[NTf_2] possesses superior selective solubility for polar solutes. The same hierarchy, γ^{∞}(alkanes) > γ^{∞}(alkenes) > γ^{∞}(aromatics), as BMIm[NTf_2] could also be obtained in CpMIm[NTf_2]. γ^{∞} values for alkanes and alkenes decrease notably in CpMMIm[NTf_2] compared to CpMIm[NTf_2] suggesting that the existence of the 2C-methyl substituent could enhance the interactions of aliphatic hydrocarbons with IL. 2C-H substitution with the methyl group leads to the disappearance of hydrogen bond interactions of alcohols with IL; therefore, γ^{∞} values for ethanol and methanol in CpMMIm[NTf_2] are somewhat larger than in CpMIm[NTf_2]. CpMIm[$N(CN)_2$] shows a much inferior solubilization ability for hydrocarbons than other ILs. In all the studied ILs in this work, methanol bears the largest γ^{∞}.

Foco et. al have measured γ^{∞} of both polar and nonpolar solutes in 1-alkyl-3-methylimidazole tetrafluoroborate by gas chromatography.[20] The results (shown in the brackets in Table 2) reported by these authors are all in excess of γ^{∞} in this work. The discrepancies may largely result from the residual adsorption effect even if the phase loadings of RTILs are large enough to avoid this impact.

Good linearity of the $\ln(V_g)-1/T$ straight line for all the solutes in the measured ILs within the determined temperature

Table 6. Partial Molar Excess Gibbs Energies $\Delta G^{E\infty}$/(kJ·mol^{-1}) and Entropies $\Delta TS^{E\infty}$/(kJ·mol^{-1}) of Solution of Various Solutes in RTILs at 323 K at Infinite Dilution

	BMIm[BF$_4$]		OMIm[BF$_4$]		BMIm[NTf$_2$]		CpMIm[NTf$_2$]	
	$\Delta G^{E\infty}$	$\Delta TS^{E\infty}$	$\Delta G^{E\infty}$	$TS^{E\infty}$	$\Delta G^{E\infty}$	$\Delta TS^{E\infty}$	$\Delta G^{E\infty}$	$\Delta TS^{E\infty}$
hexane	10. 5	−1.7	5.1	1.8	6.5	−2.5	12.7	−3.2
heptane	11.4	−1.8	5.7	2.2	7.4	−2.3	13.0	−0.1
octane	12.3	−0.6	6.4	4.5	8.4	−3.1	13.6	1.3
cyclohexane	8.6	0.7	3.7	4.6	5.1	−1.4	10.3	0.2
methyl cyclohexane	9.6	−0.4	4.5	3.1	5.9	−1.8	11.3	−0.2
1-hexene	8.3	−0.8	3.7	2.6	4.8	−3.5	10.4	−1.6
1-octene	10.4	−1.5	5.1	−2.3	6.8	−3.9	12.5	−4.9
benzene	1.0	1.2	−1.2	2.0	−0.6	−1.6	1.4	1.9
toluene	2.4	0.6	−0.2	1.5	0.4		3.0	−0.1
THF	0.8	1.6	−1.4	2.1	−1.6	−2.6	0.5	2.2
ethyl acetate	1.5	0.7	−0.5	0.8	−1.1	−3.0	2.0	3.9
ethanol	0.1	9.7	−2.4	4.9	0.4	4.2	−0.1	6.7
methanol	−0.9	3.9	−3.2		−0.1		0.9	5.6

Table 7. Partial Molar Excess Gibbs Energies $\Delta G^{E\infty}$/(kJ·mol^{-1}) and Entropies $\Delta TS^{E\infty}$/(kJ·mol^{-1}) of Solution of Various Solutes in CpMMIm[NTf$_2$] and CpMMIm[N(CN)$_2$] at Infinite Dilution at 323 K

	CpMMIm[NTf$_2$]		CpMMIm[N(CN)$_2$]	
	$\Delta G^{E\infty}$	$\Delta TS^{E\infty}$	$\Delta G^{E\infty}$	$\Delta TS^{E\infty}$
hexane	10.7	−1.3	13.1	−2.8
heptane	11.4	−2.5	12.9	−0.5
octane	12.4	−6.1	13.1	−0.04
cyclohexane	9.2	2.2	11.1	6.9
methyl cyclohexane	9.9	−0.5	11.8	7.7
1-hexene	8.7	2.1	11.2	6.1
1-octene	10.8	−4.2	12.4	−1.3
benzene	1.4	1.7	2.7	0.6
toluene			4.2	0.01
THF			2.1	−0.9
ethyl acetate	1.1	7.4	3.7	−1.7
ethanol	2.1	6.5	−0.8	2.6
methanol	1.0	7.9	−2.7	6.4

range could be obtained with a linearity correlation coefficient square (R^2) higher than 0.995, while only good linearity of ln(γ^∞) versus $1/T$ for hydrocarbons, ethyl acetate, and tetrahydrofuran with higher R^2 (0.980 to 0.998) is obtained. According to Table 5, $-\Delta_{sol}H^\infty$ of the alkanes increases with an increase of the carbon atom number of the *n*-alkane series. $-\Delta_{sol}H^\infty$ increases, whereas $\Delta H^{E\infty}$ decreases with an increase of the alkyl chain length on the cation of 1-alkyl-3-methylimidazolium tetrafluoroborate. $-\Delta_{sol}H^\infty$ of the measured solutes in BMIm[BF$_4$] is smaller than that in BMIm[NTf$_2$], whereas $\Delta H^{E\infty}$ of the solutes in BMIm[BF$_4$] is larger than that in BMIm[NTf$_2$]. The substitution of the cyano functional group on the cation results in an obvious increase of $-\Delta_{sol}H^\infty$ of alkanes, and the majority of solutes have larger $\Delta H^{E\infty}$ values in CpMIm[NTf$_2$] than those in BMIm[NTf$_2$]. As shown in Figure 3, $\Delta H^{E\infty}$ of alkanes in CpMIm[NTf$_2$] and CpMIm[N(CN)$_2$] decreases with an increase of the carbon atom number of hydrocarbons. But it is the opposite case in CpMMIm[NTf$_2$] and CpMMIm[N(CN)$_2$]. The presence of the 2C-methyl group in the cyano-functionalized ILs leads to a decrease of $-\Delta_{sol}H^\infty$ of alkanes, but it has a slight effect on $-\Delta_{sol}H^\infty$ and $\Delta H^{E\infty}$ of the polar and polarizable solutes. All the solutes have positive $\Delta H^{E\infty}$ values in the eight ILs, except benzene, tetrahydrofuran, and ethyl acetate which have negative $\Delta H^{E\infty}$ values in BMIm[NTf$_2$].

$\Delta G^{E\infty}$ for *n*-alkanes and hexenes in BMIm[BF$_4$] and OMIm[BF$_4$] at 323 K (Table 6) increases with an increase of the carbon atom number of the alkanes. Moreover, the increase of the alkyl chain length on the imidazolium cation results in a remarkable decrease of $\Delta G^{E\infty}$ for the measured solutes. $\Delta G^{E\infty}$ (Table 6 and Table 7) of all the solutes except ethanol is increased in CpMIm[NTf$_2$] compared with that in BMIm[NTf$_2$]. All the alkanes and alkenes in the ILs show positive discrimination to the ideal solution at infinite dilution.

Conclusions

On the basis of the novel ILs synthesized in our group, in this work, the solubilities of C_2H_4 and CO_2 in the cyano-functionalized imidazolium ILs as well as in the 1-butyl-3-methylimidazole stearic ILs at different temperatures were studied by the gas chromatography method and compared with conventional ILs. It shows that the ILs with NTf$_2$ as the anion moiety have relatively superior solubility for C_2H_4 and CO_2, and butyronitrile substitution on the imidazolium cation results in a decrease of their solubility in the ILs. The stearic ILs demonstrate the peculiar solubility for C_2H_4 and CO_2 and that temperature has little effect on their Henry's law constants, and C_2H_4 and CO_2 have comparable solubility in these ILs.

The interactions of various organic solutes in the novel ILs have also been measured in this work by gas chromatography. The property of the anion moiety has a distinct effect on the solubility of organic solutes in the ILs, including the difference in hydrophilicity and hydrophobicity as well as the composition of the anions. For example, BMIm[NTf$_2$] possesses stronger solubilization for hydrocarbons than BMIm[BF$_4$], while BMIm[*n*-$C_{16}H_{31}OO$] and BMIm[*n*-$C_{18}H_{35}OO$] with amphoteric anions have better solubilities for both polar and nonpolar solutes. The substitution of the cyano group on the alkyl chain results in a greater decrease of the solubility of hydrocarbons, ethyl acetate, and tetrahydrofuran. Methanol has the strongest interactions with all the measured ILs. Additionally, the existence of the 2C-methyl group could have a smaller effect on the thermodynamics of solutes in ILs. BMIm[NTf$_2$] and OMIm[BF$_4$] manifest larger solubility for thiophene and can be used for the separations of the thiophene component from gasoline.

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