Ion Pair Formation of Alkylimidazolium Ionic Liquids in Dichloromethane

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The 1:1 ion pair formation constants ($K_{IP}{}^0$) of 1-alkyl-3-methylimidazolium ($[RMeIm]^+$; R = butyl, hexyl, and octyl) and 1-butyl-2,3-dimethylimidazolium ($[BuMe_2Im]^+$) ions with tetrafluoroborate ($[BF_4]^-$), hexafluorophosphate ($[PF_6]^-$), bis(trifluoromethanesulfonyl)amide ($[NTf_2]^-$), and 2,4,6-trinitrophenolate (picrate, $[Pic]^-$) ions have been determined conductometrically in dichloromethane at 25 °C. The $K_{IP}{}^0$ determinations have also been made for symmetric tetraalkylammonium ions ($[R_4N]^+$; R = methyl, ethyl, propyl, and butyl) for comparison. For a given anion, the $K_{IP}{}^0$ value of the $[RMeIm]^+$ salt is almost independent of the length of the alkyl chain (R), whereas that of the $[R_4N]^+$ salt decreases with increasing alkyl chain length. Such a difference in the alkyl chain length dependence of the ion pair formation ability can be explained on the basis of the structures of the ion pairs calculated by density functional theory. The $K_{IP}{}^0$ values of $[BuMeIm]^+$, $[BuMe_2Im]^+$, and $[Et_4N]^+$, which are similar in the van der Waals volume, are in the order of $[BuMeIm]^+ \gg [BuMe_2Im]^+ \approx [Et_4N]^+$, showing that the C2−H atom on the imidazolium ring makes an important contribution to the strong ion pair formation ability of $[RMeIm]^+$. For a given cation, the $K_{IP}{}^0$ value is generally smaller for the larger anion, i.e., $[BF_4]^- \geq [PF_6]^- \geq [NTf_2]^- > [Pic]^-$ for $[Et_4N]^+$ and $[BuMe_2Im]^+$, and $[BF_4]^- > [PF_6]^- \geq [Pic]^- \geq [NTf_2]^-$ for $[RMeIm]^+$.

Introduction

Ionic liquids are ambient-temperature liquids composed of only cations and anions, and therefore the interactions between the component ions are one of the most fundamental subjects in the research of ionic liquids. It has been pointed out that the properties of ionic liquids such as viscosity, ionic conductivity, and thermal properties are closely related to the interionic interactions.[1–5] The interionic interaction energy for a gaseous ion pair, which is difficult to determine experimentally, has been theoretically estimated.[4,6–10] For example, Turner et al. reported that the interaction energy of 1-alkyl-3-methylimidazolium halides increases in magnitude with decreasing alkyl chain length based on ab initio calculations at the Hartree−Fock level.[7] Tsuzuki et al. investigated several types of ionic liquids with ab initio calculations at the MP2 level. They reported that the interaction energy depends on the kind of the anion but is insensitive to the cation species.[8]

Although the ion pair formation constants of salts in normal solvents can be determined experimentally and should provide quantitative information on the interionic interactions, there are only limited data available for ionic liquid salts.[11,12] In this study, we have determined the 1:1 ion pair formation constants at 25 °C of the ionic liquid salts of 1-alkyl-3-methylimidazolium ($[RMeIm]^+$; R = butyl, hexyl, and octyl) and 1-butyl-2,3-dimethylimidazolium ($[BuMe_2Im]^+$) cations in dichloromethane by conductometry. The measurements have also been made for the salts of symmetric tetraalkylammonium ions ($[R_4N]^+$; R = methyl, ethyl, propyl, and butyl) for comparison. Anions used are tetrafluoroborate ($[BF_4]^-$), hexafluorophosphate ($[PF_6]^-$), bis(trifluoromethanesulfonyl)amide ($[NTf_2]^-$), and 2,4,6-trinitrophenolate (picrate, $[Pic]^-$). The $[Pic]^-$ salts were used for comparison with tetraalkylammonium picrates that we previously investigated.[13] The main purpose of this study is to obtain experimental and quantitative information for the interactions between these cations and anions. The ion pair formation constants in dichloromethane are expected to reflect strongly the direct interactions between the ions because the solvent has low polarity and low solvation power for the ions. Another reason for using dichloromethane as a solvent is that the polarity of dichloromethane is not too low to make precise determinations of the ion pair formation constants. The features in the ion pair formation of the alkylimidazolium salts are discussed based on the structures of their ion pairs calculated by density functional theory (DFT).

Experimental Section

Chemicals. $[BuMeIm][BF_4]$, $[BuMeIm][PF_6]$, $[HxMeIm][NTf_2]$, and $[OcMeIm][NTf_2]$ were purchased from Merck as "High Purity" grade reagents (water, $w < 1 \cdot 10^{-4}$; halide, $w < 1 \cdot 10^{-4}$). $[BuMeIm][NTf_2]$ of special grade (water, $w = 8 \cdot 10^{-6}$; halide, $w = 2.3 \cdot 10^{-6}$) was supplied from Kanto Chemicals. These ionic liquids were used as obtained. The ionic liquids of "For Synthesis grade" from Merck, $[HxMeIm][BF_4]$, $[HxMeIm][PF_6]$, $[OcMeIm][BF_4]$, and $[OcMeIm][PF_6]$, were washed five times with deionized water at a 1:1 ratio in mass and dried in vacuo at 70 °C for 24 h. The water mass fraction as determined by Karl Fischer titrations was less than $1 \cdot 10^{-4}$. $[Et_4N][BF_4]$ and $[Et_4N][PF_6]$ (Aldrich, 99 % purity) were dried at 80 °C in vacuo. The picrate salts of the $[RMeIm]^+$ ions were prepared by extracting them with dichloromethane from aqueous solutions of 0.04 mol·dm^{-3} [RMeIm]Cl (Tokyo Chemical Industry or Acros Organics, > 98 % purity), 0.1 mol·dm^{-3} sodium picrate monohydrate (Kanto Chemicals, > 95 % purity),

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Table 1. Molar Conductivities of Dialkylimidazolium Salts in Dichloromethane at 25 °C

$\frac{c}{10^{-4}\ \mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{10^{-4}\ \mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{10^{-4}\ \mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{10^{-4}\ \mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$
[BuMeIm][BF_4]		[BuMeIm][PF_6]		[BuMeIm][NTf_2]		[BuMeIm][Pic]	
0.4455	37.008	0.6999	38.069	0.3993	50.313	0.4170	35.231
1.3041	23.530	1.3293	29.484	0.7416	39.997	0.8709	26.534
2.0718	19.267	1.7431	26.366	1.0938	34.398	1.2266	23.134
2.8051	16.892	2.1329	24.249	1.4393	30.851	1.6401	20.499
3.5916	15.197	2.5432	22.591	1.8193	28.067	2.0311	18.761
4.2625	14.120	3.1233	20.733	2.0957	26.512	2.4317	17.386
5.1827	12.988	3.6651	19.409	2.3775	25.192	2.9128	16.122
6.2499	12.000	4.3789	18.037	2.6859	23.942	3.5452	14.807
7.2682	11.267	5.4474	16.470	2.9800	22.963	4.0737	13.962
8.4577	10.584	6.3927	15.412	3.2728	22.113		
[HxMeIm][BF_4]		[HxMeIm][PF_6]		[HxMeIm][NTf_2]		[HxMeIm][Pic]	
0.5560	31.764	0.2071	57.488	0.3872	48.263	0.4125	30.802
1.6800	19.931	0.5447	40.579	0.7796	37.269	0.8131	23.749
3.0100	15.507	0.8254	34.479	1.1336	32.242	1.2123	20.183
4.4161	13.150	1.1440	30.249	1.4710	29.067	1.5753	18.091
5.2883	12.177	1.5503	26.726	1.8115	26.741	1.9103	16.685
6.6266	11.069	2.0893	23.626	2.1203	25.096	2.2895	15.458
7.5659	10.476	2.6266	21.482	2.4540	23.655	2.6426	14.546
9.1892	9.669	3.1226	19.960	2.7457	22.606	3.1633	13.473
1.0935	9.009	3.9028	18.214	3.0458	21.687	3.6675	12.653
1.2434	8.560	4.5508	17.096	3.3130	20.971	4.1092	12.055
[OcMeIm][BF_4]		[OcMeIm][PF_6]		[OcMeIm][NTf_2]		[OcMeIm][Pic]	
0.7212	27.808	0.2186	53.491	0.1807	59.189	0.3786	32.891
1.2989	21.709	0.5202	39.252	0.4306	44.258	0.8574	24.069
2.1903	17.353	0.8128	32.979	0.7895	35.358	1.3044	20.247
2.9570	15.238	1.3119	27.173	1.1555	30.476	1.7225	18.028
3.8270	13.636	1.7405	24.197	1.5160	27.377	2.1318	16.466
4.6652	12.528	2.2796	21.638	1.9339	24.823	2.6849	14.927
5.7195	11.487	2.8467	19.728	2.3608	22.912	3.2049	13.839
6.9006	10.611	3.5001	18.103	2.7578	21.529	3.6926	13.027
8.2228	9.860	4.1116	16.931	3.2203	20.217	4.1906	12.298
9.5843	9.257	4.6799	16.051	3.6896	19.130	4.7270	11.686
[$BuMe_2Im$][BF_4]		[$BuMe_2Im$][PF_6]		[$BuMe_2Im$][NTf_2]		[$BuMe_2Im$][Pic]	
0.4614	60.487	0.4824	68.154	0.1989	88.337	0.3305	75.484
0.9614	47.002	0.9247	55.296	0.6027	66.836	0.7029	64.840
1.5517	39.417	1.6939	44.681	0.9148	58.850	1.0588	57.991
2.1855	34.586	2.3510	39.658	1.2396	53.357	1.4275	53.220
2.7631	31.607	3.1472	35.568	1.5639	49.349	1.8053	49.512
3.4720	28.911	3.9844	32.544	1.8882	46.276	2.1577	46.782
4.1961	26.841	4.8256	30.282	2.3657	42.780	2.6213	43.887
5.0210	25.025	5.8638	28.095	2.8594	40.010	3.1487	41.290
5.9847	23.364	7.0387	26.233	3.2990	38.017	3.6269	39.363
6.8272	22.201	8.0919	24.813	3.7420	36.342	4.1282	37.663

and 0.01 mol·dm^{-3} NaOH (Merck, GR grade). The dichloromethane solutions of the picrate salts were washed three times with deionized water at 1:1 ratio in volume, and after evaporation of the solvent, the products were dried in vacuo at 70 °C for 24 h (80 % yield). The purities of the [RMeIm][Pic] salts were determined to be more than 99 % from Karl Fischer titrations of water and spectrophotometric determination of the picrate ion ($\varepsilon = 1.45 \cdot 10^4$ cm^{-1}·mol^{-1}·dm^3 at 356 nm in aqueous solution). [$BuMe_2Im$]Cl was synthesized according to the literature method.[14] [$BuMe_2Im$][NTf_2] was extracted with dichloromethane from an aqueous solution of 0.02 mol·dm^{-3} [$BuMe_2Im$]Cl and 0.04 mol·dm^{-3} Li[NTf_2] (Wako Pure Chemicals, > 98 % purity). After the dichloromethane solution was washed three times with deionized water, the product was dried in vacuo at 60 °C for 24 h (75 % yield). The purity was checked by Karl Fischer titrations for water, ion-selective electrode determination for Cl^-, and atomic absorption spectrophotometry for Li^+ (water, $w = 7.8 \cdot 10^{-4}$; Cl^-, $w < 3 \cdot 10^{-4}$; Li^+, $w < 3 \cdot 10^{-7}$). [Et_4N][NTf_2] was prepared in a similar manner from [Et_4N][OH] (Kanto Chemical Co., Inc.) and Li[NTf_2]. Dichloromethane (Kanto Chemicals, GR grade) was dried over molecular sieves 4A and distilled twice just before use. The water mass fraction of dichloromethane was $5 \cdot 10^{-5}$, and the specific conductance was about $4 \cdot 10^{-9}$ S·cm^{-1}. Water was distilled and further deionized with a Milli-Q Labo system (Millipore). Potassium chloride (Merck, Suprapur grade) was dried at 250 °C under vacuum.

Conductivity Measurements. All solutions were prepared by mass. The concentration of solutions on a molar scale was calculated by using the density of dichloromethane, 1.3161 g·cm^{-3}.[15] Conductivities were measured using a linear-bridge conductometer system (Fuso 360 series) at 1 kHz. A custom-made two-electrode cell (inner volume 300 cm^3, Pt-black electrodes) was used in a thermocontrolled water bath. The cell constant, (0.03334 ± 0.00007) cm^{-1}, was determined with standard aqueous solutions of potassium chloride using the constants of Chiu and Fuoss.[16] The cell was equipped with a thermistor for monitoring small variations of temperature of the solution. For each measurement, the conductivity of the solution was recorded as a function of the temperature, (24.9 to 25.1) °C, with an XY plotter for precise determination of the conductivity at 25.0 °C with a reproducibility of ± 0.005 °C; the temperature uncertainty is within ± 0.1 °C. Initially, ca. 200 cm^3 of dichloromethane was accurately weighed into the cell, and a conductivity measurement was made. Then, a known amount of a dichloromethane solution of the salt was added stepwise to the cell to give an appropriate concentration, ($2 \cdot 10^{-5}$ to $1 \cdot 10^{-3}$) mol·dm^{-3}, and the conductivity was measured after each addition. The molar conductivities (Λ) at different concentrations (c) are listed in Table 1 and Table 2. The uncertainties are estimated to be within 0.02 % for concentration and within 0.2 % for conductivity.

Molecular Calculations. The equilibrium geometries of the cations, the anions, and the picrate ion pairs in the gas phase

Table 2. Molar Conductivities of Tetraalkylammonium Salts in Dichloromethane at 25 °C

$\frac{c}{10^{-4}\ \mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{10^{-4}\ \mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$	$\frac{c}{10^{-4}\ \mathrm{mol \cdot dm^{-3}}}$	$\frac{\Lambda}{\mathrm{S \cdot cm^2 \cdot mol^{-1}}}$
$[Et_4N][BF_4]$		$[Et_4N][PF_6]$		$[Et_4N][NTf_2]$	
0.5650	60.936	0.2991	86.811	0.2423	91.048
1.2503	46.455	0.7038	67.796	0.5571	74.267
2.0546	38.877	1.2886	55.422	0.9604	63.109
2.8191	34.591	1.8123	49.107	1.4846	54.309
3.7659	31.009	2.3840	44.476	1.8893	50.430
4.7133	28.473	2.9935	40.898	2.4188	46.288
5.7362	26.426	3.6688	37.942	2.8766	43.389
6.9912	24.502	4.2305	35.995	4.0282	38.822
7.9808	23.301	5.0803	33.653	4.6318	37.156
8.9752	22.271	6.0567	31.530		
$[Me_4N][NTf_2]$		$[Pr_4N][NTf_2]$		$[Bu_4N][NTf_2]$	
0.1807	69.036	0.2208	85.421	0.3138	78.923
0.4669	50.190	0.4726	74.771	0.6110	69.030
0.8293	40.433	0.8420	64.755	1.3735	56.028
1.2252	34.647	1.1828	58.623	1.7247	52.500
1.6693	30.574	1.5510	54.147	2.1610	48.902
2.0899	27.915	2.0270	49.804	2.6319	46.034
2.6765	25.214	2.4095	47.131	3.1611	43.421
3.3294	23.053	2.9360	44.138	3.6719	41.333
4.0617	21.233	3.5241	41.436	4.1413	39.878
4.9623	19.571	4.0385	39.706		

Table 3. van der Waals Volumes and Radii of Ions

ion	$V_{\mathrm{vdw}}/\mathrm{cm^3 \cdot mol^{-1}}$	$r_{\mathrm{vdw}}/10^{-10}\ \mathrm{m}$
$[BuMeIm]^+$	91.1	3.31
$[HxMeIm]^+$	111.4	3.53
$[OcMeIm]^+$	131.7	3.74
$[BuMe_2Im]^+$	101.1	3.42
$[Me_4N]^+$	56.6[a]	2.82[a]
$[Et_4N]^+$	96.9[a]	3.37[a]
$[Pr_4N]^+$	137.4[a]	3.79[a]
$[Bu_4N]^+$	178.0[a]	4.13[a]
$[BF_4]^-$	29.5	2.27
$[PF_6]^-$	42.4	2.56
$[NTf_2]^-$	90.8	3.30
$[Pic]^-$	95.1[a]	3.35[a]

[a] Ref 13.

were calculated using a hybrid DFT method, B3LYP,[17,18] at the 6-31G* basis set level with the Gaussian 03 program package.[19] The molar van der Waals volumes (V_{vdw}) of the ions were calculated from the optimized geometries using the Winmostar program.[20] The van der Waals radii (r_{vdw}) were calculated assuming spherical shapes. The values of V_{vdw} and r_{vdw} are summarized in Table 3.

Results and Discussion

The ion pair formation constant K_{IP}^0, which is defined as K_{IP}^0 = [ion pair]/[cation][anion], and molar conductivities Λ^0 for the salts at infinite dilution were obtained from analysis of the conductivity data by the Fuoss−Onsager−Skinner equation[21]

$$\Lambda = \Lambda^0 - Sc^{1/2}\gamma^{1/2} + E'c\gamma\ln(6E_1'c\gamma) + Jc\gamma - K_{\mathrm{IP}}^0 c\gamma f^2\Lambda \tag{1}$$

where γ and f denote the degree of dissociation of the salt and the mean activity coefficient of the ions, respectively and S, E', E_1', and J are functions of the viscosity η and relative permittivity ε_r of the solvent. The values of η and ε_r of dichloromethane used in this analysis were 0.4160 mPa·s[15] and 8.93,[22] respectively. Furthermore, the mean distance (a) of closest approach between the centers of charge of the cation and anion in an ion pair was evaluated from each K_{IP}^0 value on the basis of Bjerrum's theory[23] of electrostatic ion association.

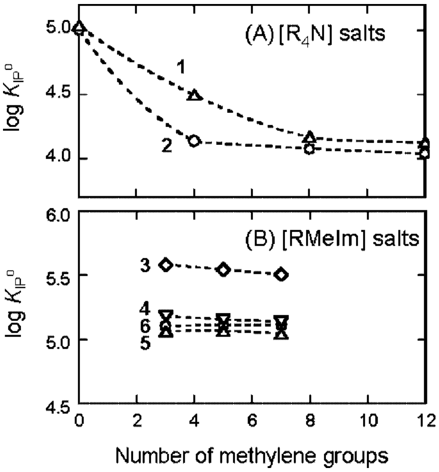

Figure 1. Dependence of the logarithmic ion pair formation constants in dichloromethane on the number of methylene groups in the cation for (1) $[R_4N][NTf_2]$, (2) $[R_4N][Pic]$, (3) $[RMeIm][BF_4]$, (4) $[RMeIm][PF_6]$, (5) $[RMeIm][NTf_2]$, and (6) $[RMeIm][Pic]$.

The results obtained are summarized in Table 4, together with the literature values for the $[R_4N][Pic]$ salts.[13] The water mass fraction of the salt solution after each run was in the range $5 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$. It is expected from previous work[13] that such a level of water content has only little influence on the ion pair formation constant.

The Λ^0 value is generally greater for the bulkier ion as expected from the Stokes−Einstein relation. However, the Λ^0 values determined in this study may have considerable errors because the degree of ionization is very low as seen from the large K_{IP}^0 values. Hence, further discussion on the ion mobility is not made here.

For each ion pair, the mean distance a of closest approach of the ions is somewhat smaller (61 % to 86 %) than the sum of the ionic r_{vdw} values. This result supports the formation of contact ion pairs. The K_{IP}^0 values of the $[RMeIm]^+$ salts are in the range $(1.1\ \text{to}\ 3.8) \cdot 10^5\ \mathrm{mol^{-1} \cdot dm^3}$ which are a bit greater than those of $[Me_4N]^+$ salts and considerably greater (4 to 12 times) than those of the other $[R_4N]^+$ salts. The r_{vdw} values of $[BuMeIm]^+$ and $[OcMeIm]^+$ are, respectively, close to those

Table 4. Limiting Molar Conductivities and Ion Pair Formation Constants at Infinite Dilution of Salts in Dichloromethane at 25 °C

cation	anion	$\frac{\Lambda^0}{\mathrm{S\cdot cm^2\cdot mol^{-1}}}$	$\frac{K_{IP}^0}{10^4\ \mathrm{mol^{-1}\cdot dm^3}}$	$\log\left(\frac{K_{IP}^0}{\mathrm{mol^{-1}\cdot dm^3}}\right)$	$\frac{a^a}{10^{-10}\ \mathrm{m}}$
$[BuMeIm]^+$	$[BF_4]^-$	162.5 ± 2.9	38.43 ± 0.90	5.58 ± 0.01	3.9
	$[PF_6]^-$	135.0 ± 2.1	15.22 ± 0.35	5.18 ± 0.01	4.3
	$[NTf_2]^-$	129.6 ± 0.9	11.55 ± 0.15	5.063 ± 0.006	4.4
	$[Pic]^-$	96.3 ± 0.9	12.66 ± 0.20	5.102 ± 0.007	4.3
$[HxMeIm]^+$	$[BF_4]^-$	148.9 ± 4.2	35.10 ± 1.30	5.55 ± 0.02	3.9
	$[PF_6]^-$	127.6 ± 1.0	14.32 ± 0.20	5.156 ± 0.006	4.3
	$[NTf_2]^-$	123.2 ± 1.0	11.63 ± 0.18	5.066 ± 0.007	4.4
	$[Pic]^-$	86.1 ± 0.7	12.99 ± 0.18	5.114 ± 0.006	4.3
$[OcMeIm]^+$	$[BF_4]^-$	138.4 ± 3.8	32.27 ± 1.16	5.51 ± 0.02	4.0
	$[PF_6]^-$	119.6 ± 1.3	13.82 ± 0.27	5.141 ± 0.008	4.3
	$[NTf_2]^-$	115.2 ± 0.5	11.20 ± 0.09	5.049 ± 0.003	4.4
	$[Pic]^-$	87.8 ± 1.6	12.93 ± 0.39	5.11 ± 0.01	4.3
$[BuMe_2Im]^+$	$[BF_4]^-$	131.7 ± 0.5	6.33 ± 0.05	4.801 ± 0.003	4.7
	$[PF_6]^-$	133.9 ± 0.7	4.44 ± 0.05	4.647 ± 0.005	4.9
	$[NTf_2]^-$	125.9 ± 0.2	3.13 ± 0.02	4.496 ± 0.003	5.1
	$[Pic]^-$	102.1 ± 1.0	1.31 ± 0.06	4.12 ± 0.02	5.8
$[Me_4N]^+$	$[NTf_2]^-$	134.5 ± 1.1	11.06 ± 0.18	5.044 ± 0.007	4.4
	$[Pic]^-$	111.4 ± 2.0[b]	10.16 ± 0.31[b]	5.01 ± 0.01[b]	4.4
$[Et_4N]^+$	$[BF_4]^-$	129.5 ± 1.0	4.87 ± 0.07	4.688 ± 0.006	4.8
	$[PF_6]^-$	144.9 ± 0.8	4.05 ± 0.06	4.607 ± 0.006	4.9
	$[NTf_2]^-$	135.7 ± 2.6	3.15 ± 0.18	4.50 ± 0.02	5.1
	$[Pic]^-$	123.1 ± 2.3[b]	1.37 ± 0.10[b]	4.14 ± 0.03[b]	5.8
$[Pr_4N]^+$	$[NTf_2]^-$	109.9 ± 1.1	1.49 ± 0.07	4.17 ± 0.02	5.7
	$[Pic]^-$	115.6 ± 1.0[b]	1.20 ± 0.05[b]	4.08 ± 0.02[b]	5.9
$[Bu_4N]^+$	$[NTf_2]^-$	105.7 ± 0.6	1.36 ± 0.04	4.13 ± 0.01	5.8
	$[Pic]^-$	109.2 ± 1.0[b]	1.09 ± 0.05[b]	4.04 ± 0.02[b]	6.0

[a] Mean distance of closest approach of ions evaluated from the K_{IP}^0 value by using Bjerrum's theory. Uncertainty is less than $(1\cdot10^{-11})$ m. [b] Ref 13.

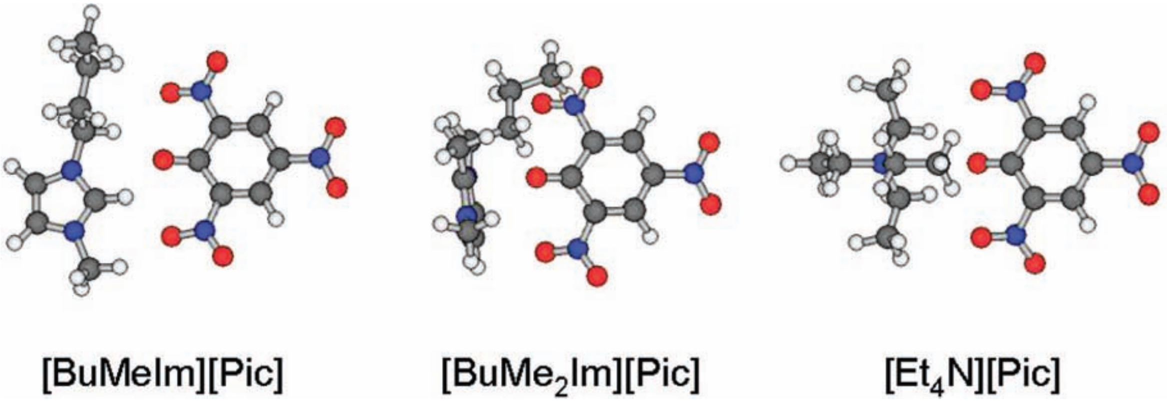

Figure 2. Equilibrium geometries of [BuMeIm][Pic], $[BuMe_2Im][Pic]$, and $[Et_4N][Pic]$ in the gas phase.

of $[Et_4N]^+$ and $[Pr_4N]^+$ (Table 3). Therefore, it can be said that the $[RMeIm]^+$ ion has a greater ability to form an ion pair with an anion than the $[R_4N]^+$ ion of comparable size. For a given anion, the K_{IP}^0 value of the $[BuMe_2Im]^+$ ion is significantly smaller than the $[BuMeIm]^+$ ion and very close to the $[Et_4N]^+$ ion. This shows that the C2−H atom of the $[RMeIm]^+$ ion makes a large contribution to its strong ion pair formation ability. In Figure 1, the log K_{IP}^0 values are shown as a function of the number of methylene groups in the alkyl chains of the cation. It can be seen from Figure 1 that the length of the alkyl chain (R) of the $[RMeIm]^+$ ion has little effect on the stability of the ion pairs. This tendency is different from that for the $[R_4N]^+$ ion whose ion pair stability decreases with increasing alkyl chain length of the cation.

According to the results from ab initio or DFT calculations for the ion pairs of various $[RMeIm]^+$ salts,[4,6–10,24] the anion is located near the C2−H atom of the cation at the most stable geometry in the gas phase. On the other hand, the structure of 1-ethyl-2,3-dimethylimidazolium tetrafluoroborate shows that the anion is above the plain of the imidazolium ring and has close contact with the C2 atom.[8] We have also obtained similar results for the $[Pic]^-$ salts from B3LYP/6-31G* level DFT calculations. The optimized structures of [BuMeIm][Pic] and $[BuMe_2Im][Pic]$ are shown in Figure 2. The centers of charges of these cations, calculated from the Mulliken charge or electrostatic potential charge of each atom, are placed near the C2 atoms. In the case of $[BuMe_2Im][Pic]$, the anion approaches the cation by orienting the phenolic oxygen atom to the C2 atom of the cation above the imidazolium ring. The major interionic interaction is regarded as a normal electrostatic interaction. On the other hand, a remarkably different geometry is found for [BuMeIm][Pic]. The phenolic oxygen atom of the anion is close to the C2−H atom of the cation, and the aromatic rings of the cation and anion are nearly in the same plain. This is probably due to the hydrogen bonding of the C2−H atom with the phenolic O atom of the anion. These results from theoretical calculations support the significant role of the C2−H atom of the $[RMeIm]^+$

ion in the ion pair formation. The anion of [Et$_4$N][Pic],[13] as also shown in Figure 2, approaches the cation from the spaces between the alkyl chains to the nitrogen atom of the cation where the center of charge of the cation is located. The cation−anion interaction for [Et$_4$N][Pic] is expected as a normal electrostatic interaction, similarly to the case of [BuMe$_2$Im][Pic].

Effect of the alkyl chain length on the ion pair formation constant can also been explained on the basis of the ion pair structures. In the case of [R$_4$N][Pic], the distance between the phenolic oxygen of the anion and the nitrogen atom of the cation increases with the alkyl chain length in the order $[\mathrm{Me_4N}]^+$ (0.322 nm) > $[\mathrm{Et_4N}]^+$ (0.355 nm) ≥ $[\mathrm{Pr_4N}]^+$ (0.357 nm) ≥ $[\mathrm{Bu_4N}]^+$ (0.358 nm). In the case of [RMeIm][Pic], the distance between the phenolic oxygen atom of the anion and the C2 atom of the cation is always 0.283 nm for different alkyl chains at the C1-position. Namely, the difference in the length of these alkyl chains has no structural influence on the approach of the anion to the cation because the anion is located near the C2−H atom. The variation of the cation−anion distance corresponds well with that of the ion pair formation constant.

The K_{IP}^0 values for $[\mathrm{BuMe_2Im}]^+$ and $[\mathrm{Et_4N}]^+$ are generally smaller for the larger anion, i.e., $[\mathrm{BF_4}]^- \geq [\mathrm{PF_6}]^- \geq [\mathrm{NTf_2}]^- > [\mathrm{Pic}]^-$, whereas the $[\mathrm{RMeIm}]^+$ ions show a slightly different sequence, $[\mathrm{BF_4}]^- > [\mathrm{PF_6}]^- \geq [\mathrm{Pic}]^- \geq [\mathrm{NTf_2}]^-$. The difference in log K_{IP}^0 between the $[\mathrm{BuMeIm}]^+$ salt and the corresponding $[\mathrm{BuMe_2Im}]^+$ or $[\mathrm{Et_4N}]^+$ salt is particularly large when the anion is $[\mathrm{Pic}]^-$. This suggests that the $[\mathrm{Pic}]^-$ ion has a specific affinity for the $[\mathrm{RMeIm}]^+$ ion. The sequence of K_{IP}^0 for $[\mathrm{BF_4}]^-$, $[\mathrm{PF_6}]^-$, and $[\mathrm{NTf_2}]^-$ is slightly different from that of the interaction energy from ab initio calculations ($[\mathrm{BF_4}]^- > [\mathrm{NTf_2}]^- \approx [\mathrm{PF_6}]^-$).[8]

In conclusion, it was found in this study that the important features of $[\mathrm{RMeIm}]^+$ ions in ion pair formation with an anion are the remarkable ability to form ion pairs and the low sensitivity to the alkyl chain length at the C1 position. The features of the $[\mathrm{RMeIm}]^+$ ions can be accounted for by the structures of ion pairs from theoretical calculations and largely attributed to the contribution of the C2−H atom. However, the cation and anion dependences of the K_{IP}^0 values show some differences from those of the interaction energies theoretically calculated.[7,8] This may be due to the fact that the theoretical results are based on the most stable structure of the ion pair, whereas the actual ion pair exists in some different structures of different energy. The K_{IP}^0 value sequence of the ions is expected to be little affected by the solvent because the ion pair formation constant is simply in inverse proportion to the dielectric constant if the medium is an inert low-polar solvent.[25] A further experimental study is being conducted for a better understanding of the interionic interactions of ionic liquids.

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