Stability of Ion Pairs of Bis(trifluoromethanesulfonyl)amide-Based Ionic Liquids in Dichloromethane

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The ion pair formation constants at infinite dilution (K_{IP}^0) of bis(trifluoromethanesulfonyl)amide ($[NTf_2]^-$) salts in dichloromethane were determined conductometrically at 298.2 K. The cations used were nine monovalent organic ions having similar molecular size, i.e., 1-butyl-3-methylimidazolium ($[BuMeIm]^+$), 1-butyl-2,3-dimethylimidazolium ($[BuMe_2Im]^+$), 1-butylpyridinium ($[BuPy]^+$), 1-propyl-2,3,5-trimethylpyrazolium ($[Me_3PrPyra]^+$), 1-butyl-1-methylpyrrolidinium ($[BuMePyrr]^+$), 1-methyl-1-propylpiperidinium ($[MePrPip]^+$), methyltripropylammonium ($[MePr_3N]^+$), propyltrimethylammonium ($[Me_3PrN]^+$), and tetraethylammonium ($[Et_4N]^+$), where the results for $[BuMeIm]^+$, $[BuMe_2Im]^+$, and $[Et_4N]^+$ were cited from our previous study. It was found from the K_{IP}^0 values that the ion pair stability varies with the cation in the order $[BuMeIm]^+ > [Me_3PrN]^+ > [BuPy]^+ \geq [BuMePyrr]^+ \geq [MePrPip]^+ > [MePr_3N]^+ \geq [Et_4N]^+ \approx [BuMe_2Im]^+ \geq [Me_3PrPyra]^+$, which was explained on the basis of the structures of the cations. For the salts used, the fundamental properties as ionic liquids, such as density, viscosity, and electric conductivity, were also measured. The activation energies for viscous flow were determined from the temperature dependence of the viscosity, and their relation with the K_{IP}^0 values was discussed.

Introduction

Up to now, a number of room-temperature ionic liquids have been synthesized, and their physicochemical properties and application to various fields of chemistry have been extensively investigated.[1,2] On the other hand, much less work has been focused on the properties of the component ions. For example, there is not sufficient information on the interaction between a cation and an anion of the ionic liquid salt except for the estimations from theoretical calculations.[3−8] We previously reported the ion pair formation constants in dichloromethane experimentally determined for the salts of 1-alkyl-3-methylimidazolium ($[RMeIm]^+$; R = butyl (Bu), hexyl, and octyl), 1-butyl-2,3-dimethylimidazolium ($[BuMe_2Im]^+$), and tetraethylammonium ($[Et_4N]^+$) with several anions.[9] The ion pair formation constant in dichloromethane is expected to be a relative measure expressing the strength of the cation−anion interaction because the solvent is low polar and has a low solvation power for the ions. In the present study, we have further determined the ion pair formation constants of various salts of bis(trifluoromethanesulfonyl)amide ($[NTf_2]^-$) in dichloromethane at 298.2 K. The cations used were 1-butylpyridinium ($[BuPy]^+$), 1-propyl-2,3,5-trimethylpyrazolium ($[Me_3PrPyra]^+$), 1-butyl-1-methylpyrrolidinium ($[BuMePyrr]^+$), 1-methyl-1-propylpiperidinium ($[MePrPip]^+$), methyltripropylammonium ($[MePr_3N]^+$), and propyltrimethylammonium ($[Me_3PrN]^+$). The structures of the cations are shown in Figure 1. All the cations, including $[BuMeIm]^+$, $[BuMe_2Im]^+$, and $[Et_4N]^+$, are similar in the molecular size (for details, refer to Table 1). On the basis of the ion pair formation constants, the effects of the cation structures on the ion pair stability are discussed. In addition, the fundamental properties of the salts as ionic liquids, such as density, viscosity, and electric conductivity, have also been measured. The activation energies for viscous flow have been determined from the temperature dependence of the viscosity,

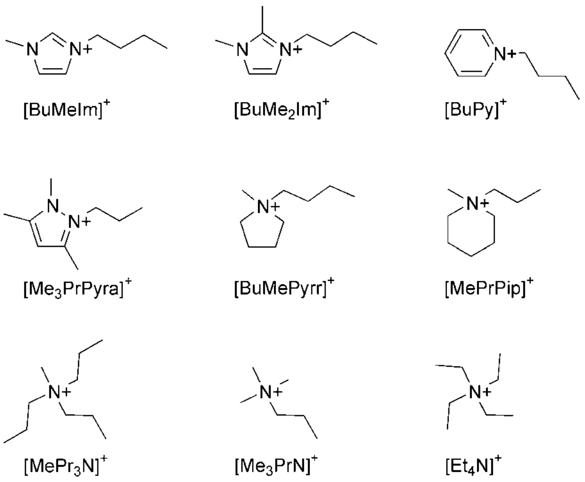

Figure 1. Structural formulas of the cations studied and their abbreviations.

Table 1. van der Waals Volumes and Radii of Ions

ion	V_{vdw} / $cm^3 \cdot mol^{-1}$	r_{vdw} / 10^{-10} m
$[BuMeIm]^+$	91.1[a]	3.31[a]
$[BuMe_2Im]^+$	101.1[a]	3.42[a]
$[BuPy]^+$	89.6	3.29
$[Me_3PrPyra]^+$	100.9	3.42
$[BuMePyrr]^+$	101.0	3.42
$[MePrPip]^+$	100.4	3.41
$[MePr_3N]^+$	117.3	3.60
$[Me_3PrN]^+$	76.9	3.12
$[Et_4N]^+$	96.9[b]	3.37[b]
$[NTf_2]^-$	146.1[c]	3.30[c]

[a] Ref 9. [b] Ref 14. [c] Ref 15.

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and the relationship with the ion pair formation constants in dichloromethane is discussed.

Experimental Section

Chemicals. [BuPy][NTf$_2$] was prepared by extracting it twice with dichloromethane (300 cm^3) from an aqueous solution (600 cm^3) of 0.04 mol·dm^{-3} Li[NTf$_2$] (Wako Pure Chemicals, >98 % purity) and 0.01 mol·dm^{-3} [BuPy]Cl (Tokyo Chemical Industries, >98 % purity). After the dichloromethane solution was washed three times with deionized water at 3:1 ratio in volume, the solvent was evaporated, and the residue was dried in vacuo at 333 K for 24 h (80 % yield). The purity was checked by Karl Fischer titrations for water, ion-selective electrode potentiometry for Cl$^-$, and atomic absorption spectrophotometry for Li$^+$ (water, $w = 3 \cdot 10^{-4}$; Li, $w < 1 \cdot 10^{-5}$; Cl, $w < 1 \cdot 10^{-4}$). [MePr$_3$N][NTf$_2$] was prepared in a similar manner from an aqueous solution containing 0.1 mol·dm^{-3} HNTf$_2$ (Kanto Chemicals, >99 % purity) and 0.1 mol·dm^{-3} [MePr$_3$N][OH] (Fluka, 20 % aqueous solution), and its water mass fraction was $1 \cdot 10^{-3}$. [BuMePyrr][NTf$_2$] (Wako Pure Chemicals, "for synthesis" grade), [MePrPip][NTf$_2$] (Kanto Chemicals, "for advanced material research" grade), and [Me$_3$PrPyra][NTf$_2$] (Kanto Chemicals, "for advanced material research" grade) were washed three times with deionized water at 1:5 or 1:4 ratio in mass and dried in vacuo at 333 K for 24 h. For these three salts, the results of purity check were as follows: water, $w = 2 \cdot 10^{-4}$; Li, $w < 1 \cdot 10^{-6}$; Cl, $w < 1 \cdot 10^{-5}$. [Me$_3$PrN][NTf$_2$] of special grade (water, $w = 1 \cdot 10^{-5}$; Li, $w = 7 \cdot 10^{-7}$; Cl, $w = 3 \cdot 10^{-5}$) was supplied from Kanto Chemicals. Other ionic liquids used were the same as reported earlier.[9] 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}.

Conductivity Measurements of Dichloromethane Solutions of Salts. The conductivity measurements were performed with a linear-bridge conductometer system (Husou Electrochemical System, HECS 360 series) at 298.2 K. Reproducibility and uncertainty of the temperature are within 0.005 and 0.1 K, respectively. Custom-made two-electrode cells (inner volume 300 cm^3, Pt-black electrodes) with cell constants of (0.03483 ± 0.00003) cm^{-1} and (0.03233 ± 0.00006) cm^{-1} were used. The experimental procedure to obtain the ion pair formation constants was almost the same as that described in a previous paper.[9] The concentration range of the salts was ($2 \cdot 10^{-5}$ to $4 \cdot 10^{-4}$) mol·dm^{-3}. The estimated uncertainties are within 0.02 % for the molar concentration and within 0.2 % for the molar conductivity. The water mass fraction of the salt solution after each run was in the range $7 \cdot 10^{-5}$ to $2 \cdot 10^{-4}$.

Table 3. Limiting Molar Conductivities and Ion Pair Formation Constants at Infinite Dilution of [NTf$_2$]$^-$ Salts in Dichloromethane at 298.2 K

cation	Λ_s^0 S·cm^2·mol^{-1}	K_{IP}^0 10^4 mol^{-1}·dm^3	log (K_{IP}^0/mol^{-1}·dm^3)	a^a 10^{-10} m
[BuMeIm]$^+$	129.6^b	11.55^b	5.063^b	4.9
[BuMe$_2$Im]$^+$	125.9^b	3.13^b	4.496^b	5.7
[BuPy]$^+$	124.6 ± 2.2	6.15 ± 0.25	4.79 ± 0.02	5.2
[Me$_3$PrPyra]$^+$	130.3 ± 0.4	2.87 ± 0.03	4.458 ± 0.005	5.7
[BuMePyrr]$^+$	130.6 ± 1.0	5.41 ± 0.11	4.733 ± 0.009	5.3
[MePrPip]$^+$	127.4 ± 0.5	4.36 ± 0.04	4.639 ± 0.004	5.4
[MePr$_3$N]$^+$	119.6 ± 0.4	3.40 ± 0.04	4.531 ± 0.005	5.6
[Me$_3$PrN]$^+$	135.9 ± 0.4	8.20 ± 0.11	4.914 ± 0.006	5.1
[Et$_4$N]$^+$	135.7^b	3.15^b	4.50^b	5.7

[a] The center-to-center distance of the ions in an ion pair evaluated from the K_{IP}^0 value by using Fuoss's theory. The uncertainty is within ($1 \cdot 10^{-11}$) m. [b] Ref 9.

Measurements of Properties of Pure Salts. Melting points were measured by the rising melting point method using a thermocontrolled water bath (Thermo NESLAB, RTE-7) and a primary standard thermometer (Nihon Keiryoki Kogyo, No. 1, uncertainty: ± 0.03 K). The reproducibility of the melting point measurements is within 1 K. Densities were measured at (292.2 to 315.1) K with an oscillating U-tube density meter (Anton Paar, DMA35n) calibrated with pure water. The uncertainties are estimated to be within $1 \cdot 10^{-3}$ g·cm^{-3} for the density and within 0.2 K for the temperature. Kinematic viscosities were measured at (292.5 to 308.7) K using an Ubbelohde-type viscometer (KUSANO, No. 2, viscometer constant: 0.09655 mm^2·s^{-2}) in a thermocontrolled water bath in which the reproducibility and uncertainty of the temperature are 0.05 and 0.1 K, respectively. The reproducibility of the kinematic viscosity measurements is within 0.05 mm^2·s^{-1}. The electric conductivities were measured with a digital conductometer

Table 2. Conductivity Data for Dichloromethane Solutions of [NTf$_2$]$^-$ Salts at 298.2 K^a

c_s / 10^{-4} mol·dm^{-3}	Λ_s / S·cm^2·mol^{-1}	c_s / 10^{-4} mol·dm^{-3}	Λ_s / S·cm^2·mol^{-1}	c_s / 10^{-4} mol·dm^{-3}	Λ_s / S·cm^2·mol^{-1}
Cation = [BuPy]$^+$		Cation = [Me$_3$PrPyra]$^+$		Cation = [BuMePyrr]$^+$	
0.2445	69.897	0.2936	85.462	0.1668	84.250
0.5334	54.605	0.4859	75.234	0.3446	69.194
0.8083	47.160	0.5725	72.001	0.5653	59.339
1.1580	41.359	0.9417	62.070	0.7591	53.682
1.5422	37.071	1.3156	55.820	1.0600	47.840
2.4940	30.863	1.8797	49.596	1.3078	44.472
3.0695	28.343	2.7854	43.282	1.7959	39.416
3.5861	26.563			2.2051	36.613
4.2320	24.687			3.0105	32.450
				3.6667	30.234
Cation = [MePrPip]$^+$		Cation = [MePr$_3$N]$^+$		Cation = [Me$_3$PrN]$^+$	
0.2329	79.769	0.2106	81.107	0.3969	59.719
0.3991	69.037	0.3171	73.486	0.5674	52.684
0.6916	58.192	0.4417	67.113	0.7046	48.697
0.9486	52.471	0.5071	64.465	0.8410	45.645
1.4797	44.939	0.7119	58.172	1.6104	35.523
2.0896	39.689	1.1480	49.757	3.2766	26.638
2.8832	35.245	1.6495	43.893	3.9835	24.579
3.8364	31.667	3.4168	33.402		

[a] c_s and Λ_s denote, respectively, the molar concentration and the observed molar conductivity for the salts in dichloromethane solutions.

Table 4. Densities of Pure $[\mathrm{NTf_2}]^-$ Salts at Different Temperatures

T	ρ	T	ρ	T	ρ
K	$\mathrm{g\cdot cm^{-3}}$	K	$\mathrm{g\cdot cm^{-3}}$	K	$\mathrm{g\cdot cm^{-3}}$
Cation = $[\mathrm{BuMeIm}]^+$		Cation = $[\mathrm{BuMe_2Im}]^+$		Cation = $[\mathrm{Me_3PrPyra}]^+$	
293.2	1.4426	292.2	1.4211	296.5	1.4302
294.2	1.4411	293.2	1.4200	297.2	1.4294
295.2	1.4407	294.2	1.4189	298.2	1.4283
297.1	1.4395	295.2	1.4180	301.2	1.4258
298.2	1.4373	296.2	1.4174	303.3	1.4238
299.2	1.4366	297.2	1.4167	305.2	1.4218
300.2	1.4358	298.2	1.4159	305.9	1.4212
301.1	1.4352	299.2	1.4152	307.9	1.4191
302.2	1.4343	300.2	1.4144	311.2	1.4152
303.2	1.4335	301.2	1.4136	313.1	1.4126
304.1	1.4327	302.2	1.4128		
305.1	1.4317	303.2	1.4119		
307.0	1.4298	304.2	1.4112		
308.4	1.4283	305.2	1.4103		
		306.1	1.4096		
		307.1	1.4087		
		308.2	1.4078		
		310.5	1.4056		
Cation = $[\mathrm{BuMePyrr}]^+$		Cation = $[\mathrm{MePrPip}]^+$		Cation = $[\mathrm{Me_3PrN}]^+$	
292.2	1.4010	293.2	1.4193	298.2	1.4296
293.2	1.3999	294.2	1.4185	299.2	1.4290
294.2	1.3988	295.2	1.4168	301.2	1.4277
295.2	1.3981	296.2	1.4155	303.2	1.4256
296.2	1.3977	297.2	1.4147	305.2	1.4237
297.2	1.3974	298.2	1.4137	307.2	1.4218
298.2	1.3970	299.2	1.4129	309.0	1.4202
299.2	1.3962	300.2	1.4121	311.1	1.4182
300.2	1.3953	301.2	1.4113	313.0	1.4163
301.1	1.3954	302.2	1.4105	315.1	1.4142
302.2	1.3936	303.2	1.4096		
303.2	1.3926	304.2	1.4087		
304.1	1.3918	305.3	1.4077		
305.1	1.3909	306.1	1.4069		
306.2	1.3898	307.1	1.4059		
307.1	1.3889	308.0	1.4051		
308.2	1.3878	309.1	1.4040		
308.6	1.3873	310.1	1.4030		
309.7	1.3862	312.1	1.4009		
		313.1	1.3998		
		314.9	1.3976		

(TOA Electrics, CM-40S) in a water bath thermostatted at 298.2 K whose reproducibility and uncertainty are 0.05 and 0.1 K, respectively. A two-electrode cell (Pt-black electrodes) of a cell constant (0.9791 ± 0.0007) $\mathrm{cm^{-1}}$ was used. The reproducibility of the conductivity measurements is within 0.01 $\mathrm{mS\cdot cm^{-1}}$.

Molecular Calculations. The equilibrium geometries of the cations in the gas phase were calculated using a hybrid DFT method, B3LYP,[10,11] at the 6-31G* basis set level with the Gaussian 03 program package.[12] The molar van der Waals volumes (V_{vdw}) of the ions were calculated from the optimized geometries using the Winmostar program.[13] The van der Waals radii (r_{vdw}) were calculated assuming spherical shapes. The V_{vdw} and r_{vdw} values are listed in Table 1, together with the data previously reported.[9,14,15] The atomic charge distributions were calculated by the electrostatic potential fitting analysis using the Merz−Kollman−Singh method.[16,17]

Results and Discussion

Ion Pair Formation in Dichloromethane. The molar conductivities of the salts (Λ_s) in dichloromethane were measured at 298.2 K as a function of the salt concentration (c_s) and are shown in Table 2. The ion pair formation constants at infinite dilution (K_{IP}^0) and the limiting molar conductivities of the salts (Λ_s^0) were obtained from analysis of the conductivity data by the Fuoss−Onsager−Skinner equation[18]

$$\Lambda_s = \Lambda_s^0 - S c_s^{1/2}\gamma_s^{1/2} + E' c_s\gamma_s \ln(6E_1' c_s\gamma_s) + L c_s\gamma_s - K_{\mathrm{IP}}^0 c_s\gamma_s f^2\Lambda_s \qquad (1)$$

where γ_s and f denote the degree of dissociation of the salt and the mean activity coefficient of the ions (calculated by the limiting Debye−Hückel equation), respectively; S, E', E_1', and L are functions of 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 $\mathrm{mPa\cdot s}$[19] and 8.93,[20] respectively. Furthermore, the center-to-center distance of the ions in an ion pair (a) was evaluated from each K_{IP}^0 value on the basis of Fuoss's theories of ion association[21]

$$K_{\mathrm{IP}}^0 = \frac{4\pi N_A a^3}{3000}\exp\left(\frac{e^2}{a\varepsilon_r kT}\right) \qquad (2)$$

where N_A, e, and k are Avogadro's number, elementary electric charge, and Boltzmann's constant, respectively. The results obtained are summarized in Table 3, together with the literature values for $[\mathrm{BuMeIm}][\mathrm{NTf_2}]$, $[\mathrm{BuMe_2Im}][\mathrm{NTf_2}]$, and $[\mathrm{Et_4N}][\mathrm{NTf_2}]$.[9]

It is found from the Λ_s^0 values that these salts, which are similar in size, are also similar in mobility in dichloromethane. At this stage, it is difficult to discuss the small differences in the Λ_s^0 values because considerable errors are expected for the Λ_s^0 values owing to the high stability of the ion pairs in dichloromethane.

The K_{IP}^0 value obviously depends on the cation species and decreases in the order $[\mathrm{BuMeIm}]^+ > [\mathrm{Me_3PrN}]^+ > [\mathrm{BuPy}]^+ \geq [\mathrm{BuMePyrr}]^+ \geq [\mathrm{MePrPip}]^+ > [\mathrm{MePr_3N}]^+ \geq [\mathrm{Et_4N}]^+ \approx [\mathrm{BuMe_2Im}]^+ \geq [\mathrm{Me_3PrPyra}]^+$. The largest K_{IP}^0 value for the $[\mathrm{BuMeIm}]^+$ salt is about 4 times the smallest one for the $[\mathrm{Me_3PrPyra}]^+$ salt. The ion pair's interionic distance, a, calculated from each K_{IP}^0 value is somewhat smaller (67 % to 77 %) than the sum of the r_{vdw} values of the cation and the anion (Table 1), indicating the formation of contact ion pairs. However, the differences in the a values for the different cations are considerably larger than those in the r_{vdw} values, and there is

Table 5. Kinematic and Dynamic Viscosities of Pure $[\mathrm{NTf_2}]^-$ Salts at Different Temperatures

T	ν	η	T	ν	η	T	ν	η
K	$\mathrm{mm^2\cdot s^{-1}}$	$\mathrm{mPa\cdot s}$	K	$\mathrm{mm^2\cdot s^{-1}}$	$\mathrm{mPa\cdot s}$	K	$\mathrm{mm^2\cdot s^{-1}}$	$\mathrm{mPa\cdot s}$
Cation = $[\mathrm{BuMeIm}]^+$			Cation = $[\mathrm{BuMe_2Im}]^+$			Cation = $[\mathrm{Me_3PrPyra}]^+$		
293.0	43.55 ± 0.06	62.83	292.6	89.53 ± 0.00	127.18	292.6	74.15 ± 0.08	106.3
298.2	34.74 ± 0.00	49.95	298.3	65.92 ± 0.01	93.33	297.9	55.64 ± 0.04	79.50
303.2	28.35 ± 0.05	40.64	303.5	48.61 ± 0.05	68.62	302.7	44.05 ± 0.03	62.73
308.2	23.34 ± 0.04	33.35	308.3	40.89 ± 0.04	57.56	308.6	33.90 ± 0.04	48.09
Cation = $[\mathrm{BuMePyrr}]^+$			Cation = $[\mathrm{MePrPip}]^+$			Cation = $[\mathrm{Me_3PrN}]^+$		
292.9	71.20 ± 0.04	99.73	293.1	140.31 ± 0.03	199.11	292.5	71.71 ± 0.06	102.92
298.0	55.78 ± 0.03	77.89	298.3	102.55 ± 0.06	145.02	297.3	56.45 ± 0.02	80.77
302.8	45.10 ± 0.03	62.81	303.3	74.25 ± 0.02	104.64	303.2	43.44 ± 0.02	61.93
308.7	35.46 ± 0.00	49.22	308.7	59.55 ± 0.03	83.61	308.2	35.40 ± 0.00	50.29

Table 6. Density−Temperature Equation Parameters for Pure $[NTf_2]^-$ Salts ($\rho = -aT + b$)

cation	a $10^{-4}\cdot g\cdot cm^{-3}\cdot K^{-1}$	b $g\cdot cm^{-3}$	correlation coefficient
$[BuMeIm]^+$	9.0 ± 0.2	1.706 ± 0.005	0.9982
	9.40[a]	1.72[a]	
$[BuMe_2Im]^+$	8.12 ± 0.08	1.658 ± 0.002	0.9992
$[Me_3PrPyra]^+$	10.3 ± 0.3	1.74 ± 0.008	0.9976
$[BuMePyrr]^+$	8.1 ± 0.2	1.639 ± 0.007	0.9937
	9.09[a]	1.67[a]	
$[MePrPip]^+$	9.5 ± 0.1	1.698 ± 0.004	0.9985
$[Me_3PrN]^+$	9.2 ± 0.1	1.706 ± 0.004	0.9990

[a] Ref 22.

Table 7. Viscosity−Temperature Equation Parameters for Pure $[NTf_2]^-$ Salts ($\eta = A \exp(E_{vis}/RT)$)

cation	A $10^{-5}\cdot mPa\cdot s$	E_{vis} $kJ\cdot mol^{-1}$	correlation coefficient
$[BuMeIm]^+$	17 ± 1	31.3 ± 0.2	1.0000
$[BuMe_2Im]^+$	2 ± 1	39 ± 2	0.9971
$[BuPy]^+$	6 ± 1[a]	34.2 ± 0.5[a]	0.9998[a]
$[Me_3PrPyra]^+$	2.4 ± 0.8	37.2 ± 0.8	0.9995
$[BuMePyrr]^+$	10 ± 2	33.6 ± 0.5	0.9998
$[MePrPip]^+$	0.5 ± 0.6	42 ± 2	0.9968
$[Me_3PrN]^+$	8 ± 2	34.1 ± 0.6	0.9997

[a] Calculated from the literature data of η at (293.2 to 308.2) K (ref 22).

no correlation between the values of a and r_{vdw}. Therefore, the cation size is not responsible for the cation dependence of the K_{IP}^0 value.

The K_{IP}^0 value order for the aromatic cations is $[BuMeIm]^+ > [BuPy]^+ > [BuMe_2Im]^+ \geq [Me_3PrPyra]^+$. From the atomic charges calculated by the electrostatic potential fitting analysis, the position of the center of positive charge was evaluated for each cation. It was found that the center of charge locates between the C2 and N1 atoms for $[BuMeIm]^+$ and $[BuMe_2Im]^+$, on the N1 atom for $[BuPy]^+$, and between the N1 and N2 atoms for $[Me_3PrPyra]^+$. According to the results from ab initio calculations for the ion pairs of 1-ethyl-2,3-dimethylimidazolium ($[EtMe_2Im]^+$) and $[BuPy]^+$ with $[BF_4]^-$,[6] the anion is located near the charge center of the cation at the most stable geometry in the gas phase. The number of alkyl chains near the center of charge is one for $[BuMeIm]^+$ and $[BuPy]^+$ (1-Bu) and two for $[BuMe_2Im]^+$ (1-Bu and 2-Me) and $[Me_3PrPyra]^+$ (1-Pr and 2-Me). These alkyl groups sterically hinder the approach of the anion to the positive-charge center of the cation. The K_{IP}^0 value decreases with an increase in the number of the alkyl groups near the positive-charge center except for the value of $[BuMeIm][NTf_2]$. Thus it appears that the steric hindrance of the alkyl groups is an important factor determining the ion pairing ability of the aromatic cations. In the case of the $[BuMeIm]^+$ salt, it is known that the anion prefers to interact with the C2−H atom of the cation because the C2−H atom has a relatively high charge density.[5,6,9] From comparison of the results for $[BuMeIm]^+$ and $[BuMe_2Im]^+$, the remarkable ion-pairing ability of $[BuMeIm]^+$ is attributable to the contribution of the C2−H atom.

The K_{IP}^0 value for the aliphatic cations decreases in the order $[Me_3PrN]^+ > [BuMePyrr]^+ \geq [MePrPip]^+ > [MePr_3N]^+ \geq [Et_4N]^+$. For these cations, the theoretical calculations showed that the center of positive charge locates on the quaternary nitrogen atom. There is a tendency that the K_{IP}^0 value is greater for the cation in which the number of methyl groups bound to the nitrogen atom is larger. This result indicates that the approach of the anion to the charge center of the aliphatic cation is much less hindered by the methyl group than by the longer alkyl chains. The three aliphatic cations having one methyl group on the nitrogen atom ($[BuMePyrr]^+$, $[MePrPip]^+$, and $[MePr_3N]^+$) are similar in the K_{IP}^0 value; the small differences in the K_{IP}^0 values indicate that the ion-pairing ability of the ammonium cation is enhanced by cyclic structures, particularly, the pyrrolidinium ring.

Bulk Properties. For the $[NTf_2]^-$ salts of $[BuMeIm]^+$, $[BuMe_2Im]^+$, $[Me_3PrPyra]^+$, $[BuMePyrr]^+$, $[MePrPip]^+$, and $[Me_3PrN]^+$, which are liquid at room temperature, the densities (ρ) and kinematic viscosities (ν) in the pure liquid state were measured at different temperatures (T) and are listed in Tables 4 and 5, respectively. The density always increases linearly with decreasing temperature, and the parameters for the density−temperature equation, $\rho = -aT + b$, are summarized in Table 6, together with literature values.[22] The dynamic viscosities ($\eta = \nu\rho$) of the salts at different T are calculated using the ρ values from the density−temperature equation and shown in Table 5. In the temperature range studied, linear relationships were observed between η and $1/T$. The temperature dependence of η was analyzed based on Andrade's equation

Table 8. Fundamental Properties of Pure $[NTf_2]^-$ Salts at 298.2 K

		measured					calculated		
cation	M_r	mp °C	ρ $g\cdot cm^{-3}$	η $mPa\cdot s$	κ $mS\cdot cm^{-1}$	ref	V_m[a] $cm^3\ mol^{-1}$	c[a] $mol\cdot dm^{-3}$	Λ[a] $S\cdot cm^2\cdot mol^{-1}$
$[BuMeIm]^+$	419.37	−3	1.438	50.1	4.08	this work	291.6	3.429	1.19
		−3	1.44	50	3.9	22			
$[BuMe_2Im]^+$	433.39	<−14	1.416	93.6	2.14	this work	306.1	3.267	0.655
		−13	1.42	93	1.6	26			
$[BuPy]^+$	416.36	26	1.45	59	3.2	22	287	3.48	0.92
$[Me_3PrPyra]^+$	433.39	17	1.429	79.0	2.66	this work	303.3	3.297	0.807
		19	1.43 (293 K)	43	2.6	30			
$[BuMePyrr]^+$	422.41		1.396	77.6	2.76	this work	302.6	3.305	0.835
		−15	1.40	75	2.8	22			
		−18	1.41	85	2.2	31			
$[MePrPip]^+$	422.41	12	1.414	145.8	1.58	this work	298.7	3.347	0.472
		9		117	1.5	32			
$[MePr_3N]^+$	438.45	46				this work			
$[Me_3PrN]^+$	382.35	19	1.430	78.1	3.03	this work	267.4	3.740	0.810
		17	1.44	72	3.3	33			
$[Et_4N]^+$	410.40	101				this work			

[a] V_m, c, and Λ denote, respectively, the molar volume, the molar concentration, and the molar conductivity for the salts in the pure liquid state.

$$\eta = A \exp(E_{\text{vis}}/RT) \qquad (3)$$

where A is the pre-exponential factor and E_{vis} is the activation energy for viscous flow. The A and E_{vis} values are summarized in Table 7, together with the values for the $[\text{BuPy}]^+$ salt calculated from literature data of η.[22] The E_{vis} value decreases in the following cation order: $[\text{MePrPip}]^+ > [\text{BuMe}_2\text{Im}]^+ \approx [\text{Me}_3\text{PrPyra}]^+ > [\text{BuPy}]^+ \approx [\text{Me}_3\text{PrN}]^+ \approx [\text{BuMePyrr}]^+ > [\text{BuMeIm}]^+$. For various liquids including molten salts, the E_{vis} value has been known to be approximately proportional to the energy of vaporization.[23−25] Therefore, this cation order is expected to reflect the order of the cohesive energy (or vaporization energy) for the $[\text{NTf}_2]^-$ salts, although the cohesive energy has not yet been determined except for $[\text{BuMeIm}][\text{NTf}_2]$.[26,27]

In Figure 2, the E_{vis} value is plotted against the log $K_{\text{IP}}{}^0$ value in dichloromethane. Except for the data of $[\text{MePrPip}][\text{NTf}_2]$, there is a rough correlation between increasing log $K_{\text{IP}}{}^0$ and decreasing E_{vis}. If the $K_{\text{IP}}{}^0$ value reflects the degree of association in the ionic liquids, the relation in Figure 2 suggests that the cohesive energy is generally smaller for the ionic liquid in which the fraction of dissociated ions is smaller. Tokuda and Watanabe et al.[22,28] evaluated the ionic nature of ionic liquids by the ratio of molar conductivity obtained from the impedance measurements (Λ_{imp}) to that calculated based on the pulse-field-gradient spin−echo NMR diffusivity (Λ_{NMR}). The $\Lambda_{\text{imp}}/\Lambda_{\text{NMR}}$ values showed that the ionicity of some $[\text{NTf}_2]^-$ salts varies with the cation in the order $[\text{BuMePyrr}]^+ > [\text{Me}_3\text{BuN}]^+ > [\text{BuPy}]^+ > [\text{BuMeIm}]^+$. This ionicity order almost agrees with that estimated from the $K_{\text{IP}}{}^0$ values ($[\text{BuMePyrr}]^+ \geq [\text{BuPy}]^+ > [\text{Me}_3\text{PrN}]^+ > [\text{BuMeIm}]^+$).

In Table 8, fundamental properties of the salts at 298.2 K are summarized, together with their melting point. The values of ρ and η at 298.2 K were calculated by using their temperature dependence equations. The melting point, ρ, η, and the electric conductivity (κ) values determined in this study are generally in good agreement with those in the literature,[29−33] but the η values of $[\text{Me}_3\text{PrPyra}][\text{NTf}_2]$ and $[\text{MePrPip}][\text{NTf}_2]$ are obviously greater than the literature ones. The ρ values of the salts are in narrow range from 1.396 $\text{g}\cdot\text{cm}^{-3}$ ($[\text{BuMePyrr}][\text{NTf}_2]$) to 1.438 $\text{g}\cdot\text{cm}^{-3}$ ($[\text{BuMeIm}][\text{NTf}_2]$). Hence the molar volume ($V_{\text{m}} = M_{\text{r}}/\rho$) and the molar concentration ($c = 1000/V_{\text{m}}$) are also nearly the same for all the salts. The values of ρ, V_{m}, and c have no correlation with the $K_{\text{IP}}{}^0$ value, showing that the effect of the ionicity of the ionic liquid is negligibly small for these values.

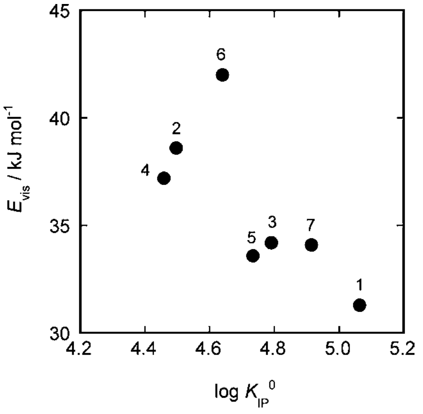

Figure 2. Relationship between the activation energy for viscous flow of pure ionic liquids and the ion pair formation constants of the salts in dichloromethane at 298.2 K. 1, $[\text{BuMeIm}][\text{NTf}_2]$; 2, $[\text{BuMe}_2\text{Im}][\text{NTf}_2]$; 3, $[\text{BuPy}][\text{NTf}_2]$; 4, $[\text{Me}_3\text{PrPyra}][\text{NTf}_2]$; 5, $[\text{BuMePyrr}][\text{NTf}_2]$; 6, $[\text{MePrPip}][\text{NTf}_2]$; 7, $[\text{Me}_3\text{PrN}][\text{NTf}_2]$.

On the other hand, the η value at 298.2 K varies considerably with the cation species as $[\text{MePrPip}]^+ > [\text{BuMe}_2\text{Im}]^+ > [\text{Me}_3\text{PrPyra}]^+ \approx [\text{Me}_3\text{PrN}]^+ \approx [\text{BuMePyrr}]^+ > [\text{BuPy}]^+ > [\text{BuMeIm}]^+$. This cation order is almost consistent with that of the E_{vis} value. Therefore, the cation dependence of the viscosity is governed by that of the E_{vis} value which is explained, as described above, by the stability of the ion pairs.

The κ values and the molar conductivities ($\Lambda = \kappa/c$, shown in Table 8) are also dependent on the cation species. It has been reported that the Walden rule for dilute electrolyte solutions is roughly applicable to pure ionic liquids.[34] If the Walden rule is valid, the product $\Lambda\eta$ should be nearly constant for the $[\text{NTf}_2]^-$ salts whose cations are similar in size. Indeed, the $\Lambda\eta$ values calculated for the $[\text{NTf}_2]^-$ salts are comparable to each other: $\Lambda\eta/(\text{S}\cdot\text{cm}^2\cdot\text{mol}^{-1}\cdot\text{mPa}\cdot\text{s}) = 59.6$, 61.3, 63.7, 64.8, 68.8, and 63.3 for $[\text{BuMeIm}][\text{NTf}_2]$, $[\text{BuMe}_2\text{Im}][\text{NTf}_2]$, $[\text{Me}_3\text{PrPyra}][\text{NTf}_2]$, $[\text{BuMePyrr}][\text{NTf}_2]$, $[\text{MePrPip}][\text{NTf}_2]$, and $[\text{Me}_3\text{PrN}][\text{NTf}_2]$, respectively. No clear correlation is observed between the values of $\Lambda\eta$ and $K_{\text{IP}}{}^0$. Therefore, it is concluded that the ion pair stability contributes to the conductivity mostly through the effect on the viscosity.

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