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Comparison between Dicationic and Monocationic Ionic Liquids: Liquid Density, Thermal Properties, Surface Tension, and Shear Viscosity

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S *Supporting Information*

ABSTRACT: We report the data of liquid density, thermal properties including glass transition temperature, melting point, and decomposition temperature, surface tension, and shear viscosity for imidazolium-based dicationic ionic liquids with the anions of bis(trifluoromethylsulfonyl)amide, bis(pentafluoroethylsulfonyl)amide, tetrafluoroborate, and nitrate. To find the unique and general features of the dicationic ionic liquids, data of their corresponding monocationic ionic liquids are also summarized. The results of the dicationic ionic liquids showed that the density was high; the glass transition temperature and melting point were high, and they were thermally stable. Also the surface tension was large, and the shear viscosity was high in comparison with the reference monocationic ionic liquids. The data of the physical properties including liquid density, surface tension, and shear viscosity of the ionic liquids were also compared with that of alkanediols and alkyl alcohols to find the alkyene-linker and alkyl-group dependences in the ionic liquids and alcohols.

INTRODUCTION

Ionic liquids (ILs) are molten salts at room temperature.[1] The salts are purely composed of cations and anions, but they have extremely low melting points as salts. Since the possible number of combinations of cations and anions is large, the physical and chemical properties of ILs are greatly tunable by choosing a suitable cation and anion combination. Consequently, ILs are very attractive research targets in chemistry, physics, and materials science and technology.[2−10]

To date, most research target ILs are monocationic types. When we consider ILs for material and industrial applications, it is important to understand the relations between physical and chemical properties and ionic species. By changing an ionic species and leaving a counterion unchanged, the properties of ILs can be systematically examined. Because extensive efforts in this research strategy have been made, the relationships between properties and ionic species or structure now are rather clarified.[1−3,11] Recently, effects of the replacement of an atomic element in an ionic species on the physical and chemical properties of ILs have also been reported.[12−22] Changes in IL properties, such as shear viscosity, liquid density, and surface tension, by an atom substitution are not very large compared to a whole ion exchange, while the atom replacement could be useful for a fine and sophisticated control for the properties of ILs.

On the other hand, the understanding of dicationic ILs, which consists of one dication and two monoanions, is lacking relative to that of monocationic ILs because of much fewer reports on dicationic ILs than monocationic ILs. Actually, dicationic ILs would be rather fascinating research targets. Since the number of possible combinations of cation and anion in dicationic ILs are greater than that in monocationic ILs, a broader variability of the properties of dicationic ILs than monocationic ILs would be possible. Recently, Engel and co-workers have prepared and characterized several ammonium-based dicationic phosphate salt liquids.[23−27] Some imidazolium-based dicationic ILs have been synthesized by Ohno and co-workers.[28] They have also synthesized pyridinium- and ammonium-based dicationic ILs having a polyether linker.[29] Armstrong and co-workers have characterized some properties including thermal stability and shear viscosity, of 39 ILs (imidazolium and pyrrolidium cation based ILs).[30] Interestingly, the thermal stability is higher in the dicationic ILs than the monocationic ILs. Other than the above works, the conductivity, glass transition temperature, melting point, and crystalline structure (at solid state) in some dicationic ILs have also been reported, while the number of dicationic ILs is limited.[31−33] Unsymmetric dicationic ILs whose cation has two different cation moieties have also been synthesized by several groups, and the thermal stabilities of the unsymmetric dicationic ILs keep high compared to monocationic ILs, as well as symmetrical (or conventional) dicationic ILs.[34−36] On the basis of their advantages in dicationic ILs, some applications of dicationic ILs have also been explored, such as stationary phases for gas chromatography,[37−39] solvents for high-temperature organic reactions,[40] high-temperature lubricants,[41−44] electrolytes in secondary batteries,[45] and dye sensitized solar cells.[46,47] However, it is no doubt that the deeper and broader knowledge of physical and chemical properties of dication ILs is necessary to find the unique and general features and to control their properties.

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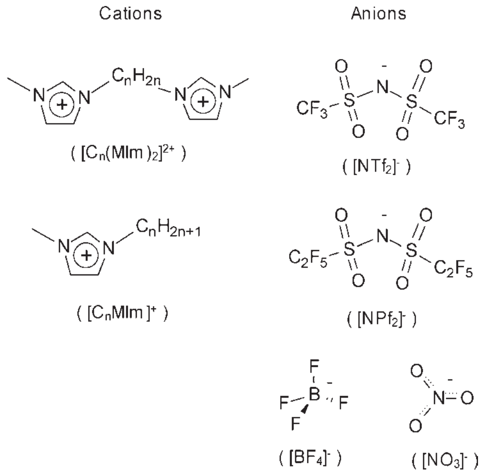

Figure 1. Structures of the cations and anions for the ILs used in this study. Abbreviations are also given.

We report here the data of some physical properties such as liquid density, thermal properties (e.g., melting point, glass transition temperature, and decomposition temperature), surface tension, and shear viscosity of imidazolium-based dicationic ILs, as well as the data of the reference monocationic ILs to reveal the unique, specific, and general natures of the dicationic ILs. We also compare the data of the ILs with that of the alcohols to find the features of the ions or molecules having two functional groups.

EXPERIMENTAL SECTION

Chemical structures of the cations and anions for the sample ILs are shown in Figure 1. Abbreviations of the cations and anions are also given in the figure. As shown in the figure, typical four anions are chosen in this study: bis(trifluoromethylsulfonyl)amide ($[NTf_2]^-$); bis(pentafluoroethylsulfonyl)amide ($[NPf_2]^-$); tetrafluoroborate ($[BF_4]^-$); and nitrate ($[NO_3]^-$). The ILs were prepared according to the standard preparation procedures.[2,11,48,49] The ILs were assigned by ^{1}H NMR and elemental analysis. Besides water and solvent, no extra peak was found in the ^{1}H NMR spectra. The obtained values for the elemental analysis were less than ± 0.3 % of the calculated values. The sample ILs were dried under vacuum at 308 K for 3 days before measurements. The water content of the ILs was estimated by Karl Fischer titration using a Mettler Toledo Karl Fischer coulometer (model DL32). The water content of the ILs was within the range of 176 ppm to 256 ppm. The water content of the ILs was quite reproducible (approximately ± 30 %) when the drying conditions were similar. While some physical properties of ILs depends on the water content,[50−57] data of several ILs studied here have been already reported by other groups, and they are quite similar.[11,30,32,36,49,50,58−63] Details of the synthesis procedures for the ILs and all of the analysis data are summarized in Supporting Information. Reference alcohols were purchased from Aldrich and Kanto Chemicals and used from an unopened bottle without further purification.

Differential scanning calorimetry and thermogravimetry measurements were perfomed using a Rigaku Thermo plus EVO/DSC8230 to estimate the melting points (T_m), glass transition temperatures (T_g), and decomposition temperatures (T_d) of the ILs. The scan rate was 10 $K \cdot min^{-1}$. The decomposition temperature was defined as the temperature at the 10 wt % loss. Liquid densities (d) of the ILs were measured using a density meter (Anton Paar, DMA 4500) at 297 ± 0.3 K. Surface tension (γ) measurements were made by a du Noüy tensiometer (Yoshida Seisakusho) at 297 ± 0.5 K. A reciprocating electromagnetic piston viscometer (Cambridge Viscosity, ViscoLab 4100) with a circulating water bath (Yamato, BB300) was used for the shear viscosity (η) measurements at 297 ± 0.4 K.

RESULTS AND DISCUSSION

Liquid Density and Molar Volume. Table 1 summarizes the values of formula weights (FW) and the data of liquid densities and molar volumes at 297 K of the dicationic and monocationic ILs. The molar volumes (V) were estimated from the liquid densities and formula weights ($V = FW/d$). It is clear from the table that the liquid density for the dicationic ILs is approximately 4 % higher than that for the monocationic ILs when the dicationic ILs are compared to the monocationic ILs with the identical anions and the cations having the corresponding alkyl groups (e.g., C_6 for a dicationic IL and C_3 for a monocationic IL). The similar feature was also confirmed in the alcohols: The liquid density in alkanediols was higher than that in the corresponding alkyl alcohols, though the difference in density in the cases of alcohols was much larger than that in the cases of ILs (Supporting Information).

To understand the difference in free volume for the dicationic and monocationic ILs, we calculated the van der Waals volumes (V_{VDW}) of the ILs by the van der Waals increments[64,65] and examined the ratios of the van der Waals volume and molar volume V_{VDW}/V. The ratio, V_{VDW}/V, is a measure of how much a molecule (or pair of ions) occupies the unit space. The values of V_{VDW}/V of the ILs are summarized in Supporting Information. For the ILs, V_{VDW}/V in the dicationic ILs is approximately 3 % larger than that in the monocationic ILs when the ILs having the same anions and the cations with the comparable alkyl groups are compared. The same is true for the alcohols (Supporting Information). However, the difference in the value V_{VDW}/V between the dicationic and monocationic ILs is much smaller than that between the alkanediols and alkyl alcohols. Also, V_{VDW}/V in the alkyl alcohols becomes larger with the longer alkyl group, while V_{VDW}/V in both the monocationic and dicationic ILs decreases slightly with the longer alkylene linker/alkyl group. The hydrogen-bonding interaction (or bond) is sensitive to the direction between the interaction sites, but the ionic interaction is not dependent on the orientation of the ions if the ion is spherical. Surely the present system is not the case of a spherical shape, while it would be plausible that the ionic or molecular orientation is more critical in the case of hydrogen-bonding interaction than the case of interionic interaction. As well as the interionic interaction, the van der Waals interaction is also rather insensitive to the orientation between the molecules. Alkyl alcohols having a shorter alkyl group would favor to align making hydrogen-bonding network because of the higher density of hydroxyl group, though it might not be a very suitable for the space filling. On the other hand, hydrogen-bonding network does not so expand in alkyl alcohols with a longer alkyl group because of the larger hydrophobic alkyl group, and thus it is favorable for the space filling. Anyway, the fact regarding the larger V_{VDW}/V for the dicationic ILs than the monocationic ILs implies that the interionic interaction of the dicationic ILs could be stronger than that of the monocationic ILs.

Table 1. Formula Weights FW, Liquid Densities d, and Molar Volumes V at 297 K for the Dicationic and Monocationic ILs

cation	FW				d^a (g·cm^{-3})				V (cm^3·mol^{-1})			
	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$
$[C_4(MIm)_2]^{2+}$	780.6	980.7	393.9	344.3	–	–	–	–	–	–	–	–
$[C_5(MIm)_2]^{2+}$	794.6	994.7	408.0	358.4	1.570	1.639	–	–	506.1	606.9	–	–
$[C_6(MIm)_2]^{2+}$	808.7	1008.8	422.0	372.4	1.546	1.615	–	–	523.1	624.6	–	–
$[C_8(MIm)_2]^{2+}$	836.7	1036.8	450.0	400.4	1.500	–	–	–	557.8	–	–	–
$[C_9(MIm)_2]^{2+}$	850.7	1050.9	464.1	414.5	1.479	1.553	1.255	–	575.2	676.7	369.8	–
$[C_{10}(MIm)_2]^{2+}$	864.8	1064.9	478.1	428.5	1.462	1.536	1.240	–	591.5	693.3	385.6	–
$[C_{12}(MIm)_2]^{2+}$	892.8	1092.9	506.1	456.5	1.428	1.503	1.209	–	625.2	727.1	418.6	–
$[C_2MIm]^+$	391.0	491.4	198.0	173.2	1.520	1.594	1.279	–	257.2	308.3	154.8	–
$[C_3MIm]^+$	405.0	505.4	212.0	187.2	1.476	1.552	1.237	1.184	274.4	325.6	171.4	158.1
$[C_4MIm]^+$	419.0	519.4	226.0	201.2	1.438	1.514	1.201	1.153	291.4	343.1	188.2	174.5
$[C_5MIm]^+$	433.1	533.4	240.1	215.3	1.403	1.480	1.173	1.127	308.7	360.4	204.7	191.0
$[C_6MIm]^+$	447.1	548.4	254.1	229.3	1.373	1.450	1.155	1.103	325.6	399.4	220.0	207.9

[a] ± 0.5 %.

Table 2. Melting Points T_m, Glass Transition Temperatures T_g, and Decomposition Temperatures T_d for the Dicationic and Monocationic ILs

cation	$T_g{}^a$ (K)				$T_m{}^a$ (K)				$T_d{}^a$ (K)			
	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$
$[C_4(MIm)_2]^{2+}$	n.o.[b]	n.o.	n.o.	n.o.	332.5	320.4	372.3	411.0	706.4	690.6	589.2	578.3
$[C_5(MIm)_2]^{2+}$	209.9	n.o.	n.o.	n.o.	n.o.	287.6	390.9	421.3	692.2	693.1	611.9	573.0
$[C_6(MIm)_2]^{2+}$	209.9	220.4	n.o.	n.o.	n.o.	278.3	403.9	444.1	700.1	687.6	639.6	583.3
$[C_8(MIm)_2]^{2+}$	212.0	220.0	n.o.	n.o.	n.o.	307.6	340.3	375.9	694.3	687.4	654.0	575.8
$[C_9(MIm)_2]^{2+}$	210.8	219.4	221.0	n.o.	n.o.	n.o.	n.o.	338.5	704.4	684.5	635.6	590.0
$[C_{10}(MIm)_2]^{2+}$	215.8	219.5	228.6	n.o.	n.o.	n.o.	n.o.	326.6	689.4	684.6	611.3	583.2
$[C_{12}(MIm)_2]^{2+}$	212.0	221.1	227.7	n.o.	n.o.	n.o.	n.o.	346.3	681.3	686.8	616.0	583.9
$[C_2MIm]^+$	183.7	n.o.	182.4	n.o.	269.9	288.2	287.8	303.9	664.3	649.6	555.9	556.6
$[C_3MIm]^+$	185.8	190.3	182.9	190.0	n.o.	n.o.	274.6	n.o.	672.0	653.5	577.3	538.1
$[C_4MIm]^+$	188.1	191.1	186.3	187.6	269.2	n.o.	n.o.	296.3	676.2	654.1	565.9	552.5
$[C_5MIm]^+$	189.6	192.5	185.9	197.0	267.1	n.o.	n.o.	n.o.	670.4	661.2	601.3	558.7
$[C_6MIm]^+$	190.4	193.4	190.0	198.6	265.9	n.o.	n.o.	n.o.	635.4	638.8	577.2	556.1

[a] ± 0.7 K. [b] n.o. denotes not observed.

Thermal Properties: Melting Point, Glass Transition Temperature, and Decomposition Temperature. Data of the melting points, glass transition temperatures, and decomposition temperatures of the dicationic and monocationic ILs are listed in Table 2. It is reported that many ILs with the anion of $[NTf_2]^-$ do not show the crystallizations and thus show only the glass transitions.[11] This is probably because the flexible structure of the $[NTf_2]^-$ anion makes difficult to crystallize. It was confirmed that the $[NTf_2]^-$ anion takes two stable forms (*cisoid* and *transoid*) in ILs.[66−69] The $[NPf_2]^-$ anion is likely similar to the $[NTf_2]^-$ anion. The existence of conformers with similar energies breaks in on crystallization. The trend of the anions in the capability of the crystallization for both the dicationic and monocationic ILs is: $[NO_3]^- > [BF_4]^- > [NPf_2]^- > [NTf_2]^-$. We also found that the melting points and glass transition temperatures of the dicationic ILs are substantially higher than that of the monocationic ILs. Namely, the liquid range in the low-temperature side is narrower for the dicationic ILs than the monocationic ILs.

To put the decomposition temperatures of the dicationic and monocationic ILs with the identical anions and the cations having comparable length of alkylene linker or alkyl group in perspective, it is obvious that the decomposition temperatures of the dicationic ILs are approximately 20 K to 40 K higher than that of the monocationic ILs (Table 2). While this feature was reported previously,[30,34−36] the broader range and more systematic data in this study strongly support this feature and would even show it as a general nature for imidazolium-based dicationic ILs. The liquid range in the high-temperature side is thus wider in the case of the dicationic ILs than the case of the monocationic ILs. The higher thermal stability in the dicationic ILs than the monocationic ILs would be related to the higher liquid density in the dicationic ILs than the monocationic ILs. It is reported that decomposition in imidazolium-based ILs occurs at C−N bonds.[70,71] Accordingly, a smaller free volume and higher shear viscosity could work for the recombination (in other words, the cage effect works effectively for the dicationic ILs compared to the corresponding monocationic ILs). Also, a small displacement of ion's vibrations due to the small free volume could suppress the decompositions of the ions. Whatever the reason, this is obviously an advantage of the dicationic ILs. The dicationic ILs are thus suitable for utilizations at high temperature conditions and applications related to local

Table 3. Surface Tensions γ and Shear Viscosities η at 297 K of the Dicationic and Monocationic ILs

cation	γ^a (mN·m^{-1})				η^b (cP)			
	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$	$[NTf_2]^-$	$[NPf_2]^-$	$[BF_4]^-$	$[NO_3]^-$
$[C_4(MIm)_2]^{2+}$	–	–	–	–	–	–	–	–
$[C_5(MIm)_2]^{2+}$	41.7	37.8	–	–	738.9	2601	–	–
$[C_6(MIm)_2]^{2+}$	41.1	37.4	–	–	649.5	2012	–	–
$[C_8(MIm)_2]^{2+}$	40.3	–	–	–	662.9	–	–	–
$[C_9(MIm)_2]^{2+}$	39.9	36.7	45.6	–	678.8	1935	8222^c	–
$[C_{10}(MIm)_2]^{2+}$	39.4	36.3	44.1	–	720.6	1951	12310^c	–
$[C_{12}(MIm)_2]^{2+}$	38.6	35.6	42.1	–	842.4	1958	15540^c	–
$[C_2MIm]^+$	38.0	33.9	54.4	–	30.7	81.9	61.7	–
$[C_3MIm]^+$	35.9	32.9	51.1	54.5	42.8	107.5	73.0	95.3
$[C_4MIm]^+$	34.9	31.7	46.9	50.5	49.4	115.0	101.1	166.4
$[C_5MIm]^+$	34.0	31.1	42.8	42.8	59.1	130.4	158.1	257.6
$[C_6MIm]^+$	33.8	30.3	39.5	39.9	69.3	144.7	257.2	363.8

^{a} ± 5 %. ^{b} ± 3 %. ^{c} ± 10 %.

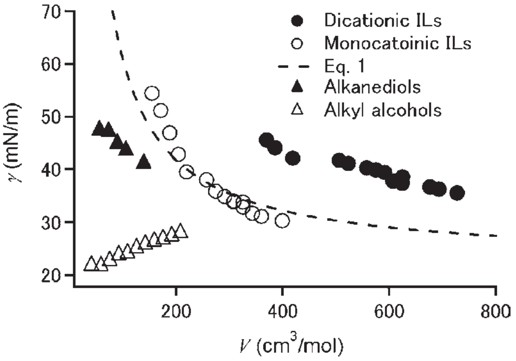

Figure 2. Plots of surface tension γ versus molar volume V. Filled circles, open circles, filled triangles, and open triangles denote dicationic ILs, monocationic ILs, alkanediols, and alkyl alcohols, respectively. The data are at 297 K. The empirical correlation (eq 1) for molten salts reported by Jin et al. (ref 61) is also shown.

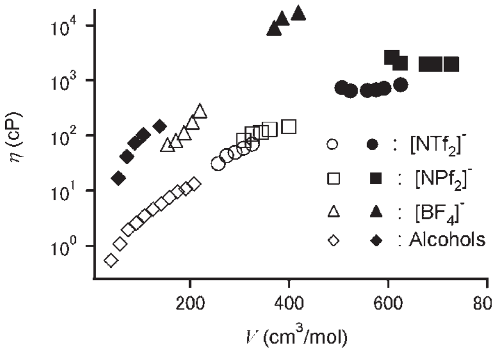

Figure 3. Plots of shear viscosity η versus molar volume V. Filled symbols indicate dicationic ILs and alkanediols, and open symbols indicate monocationic ILs and alkyl alcohols. Circles, squares, and triangles denotes the ILs with the anions of $[NTf_2]^-$, $[NPf_2]^-$, and $[BF_4]^-$, respectively, and diamonds denote the alcohols. The data are at 297 K.

heating such as lubrication rather than the corresponding monocationic ILs.[37−39,41−47]

Surface Tension. Data of the surface tensions at 297 K of the dicationic and monocationic ILs are collected in Table 3. As shown in the table, the surface tension decreases with the longer alkylene linker or alkyl group of the cations in both the cases of the dicationic and monocationic ILs when the anions are identical. As well as the liquid density, the alkylene-linker dependence on the surface tension in the dicationic ILs is the same as that in the alkanediols, while that in the monocationic ILs is opposite to that in the alkyl alcohols. The surface tension data of the alkyl alcohols and alkanediols are summarized in Supporting Information.

Jin et al. reported that molten salts including ILs showed a single correlation between the surface tension and the molar volume.[61] This empirical relation is expressed as,

$$\gamma = 22.77 + 3.82 \cdot 10^3/V - 1.09 \cdot 10^3/V^2 \qquad (1)$$

where γ is the surface tension in mN·m^{-1} and V is the molar volume in cm^3·mol^{-1}. Figure 2 plots the surface tension versus molar volume in the present dicationic and monocationic ILs, as well as the empirical relation of eq 1. Plots for the alkyl alcohols and alkanediols are also shown in the figure, as a reference. As shown in the figure, the data of the monocationic ILs studied here almost follow the empirical relation obtained by Jin et al.[61] However, the relation in the dicationic ILs is very different from the empirical one. Also, it is clear from the figure that the surface tension in the dicationic ILs is much higher than that in the monocationic ILs if we compare these having the similar volumes. This fact implies that the interionic interaction in the dicationic ILs is stronger than that in the monocationic ILs. On the other hand, the alkyl-group dependence of the alkyl alcohols on the surface tension is in contrast to the alkylene-linker/alkyl- group dependence of the dicationic ILs, alkanediols, and monocationic ILs on the surface tension. Actually, the surface tension of *n*-alkane becomes larger with the longer length (*n*-pentane: 15.49 mN·m^{-1}; *n*-heptane: 19.80 mN·m^{-1}; *n*-undecane: 24.21 mN·m^{-1} at 298 K).[72] The dispersion force thus seems to effectively influence the surface tension in the case of alkyl alcohols. However, the hydrogen-bonging interaction or ionic interaction is the dominant parameter for the alkanediols and the ILs, because the density of the stronger interaction sites (ion moieties and hydroxyl groups) reasonably correlates to the surface tension.

Shear Viscosity. Table 3 also summarizes the data of the shear viscosities at 297 K of the dicationic and monocationic ILs. When the dicationic ILs are compared to the monocationic ILs having the same anions and the cations of the comparable alkyl groups, the shear viscosity in the dicationic ILs is 13 to 80 times larger than that in the monocationic ILs. Similarly, the shear viscosities of the alkanediols are much higher than that of the alkyl alcohols, and the magnitude of the bifunctionalization effect on the shear viscosity in the alcohols is also quite similar to that in the ILs (Supporting Information). The fact of the increment of the shear viscosity for the dicationic ILs and alkanediols compared to the corresponding monocationic ILs and alkyl alcohols is not surprising, because the imidazolium group and hydroxyl group make strong interionic and intermolecular interactions and the alkylene linkers certainly give a low mobility.

Figure 3 illustrates the plots of shear viscosity versus molar volume of the ILs and alcohols. Overall, the shear viscosity seems to correlate with the molar volume in all of the cases of the monocationic ILs, alkanediols, and alkyl alcohols if the same series of system is focused. However, the molar volume dependence on the shear viscosity in the dicationic ILs is not large, in particular the dicationic ILs with the anions of $[\mathrm{NPf_2}]^-$ and $[\mathrm{NTf_2}]^-$ show almost no molar volume dependence. The cases of monocationic ILs, alkanediols, and alkyl alcohols are rather straightforward to understand, because the larger and heavier ions or molecules have a larger moment of inertia and the longer alkyl group might be entangled with the other alkyl groups. The unique alkylene-linker independence on the shear viscosity in the dicationic ILs could be related to the flexibility of the alkylene linker and local mobility of ionic region. Again, the difference in the alkylene-linker dependence on the shear viscosity between the dicationic ILs and the alkanediols might be due to the difference in the nature of the interionic/intermolecular interactions: Coulomb and hydrogen-bonding interactions. It seems that the stronger interionic/intermolecular interaction and longer working distance of the Coulomb interaction than the hydrogen-bonding (and the dipole−dipole) and van der Waals interactions make the differences in the physical properties between the ILs and alcohols.

■ CONCLUSIONS

We compared the liquid density, thermal properties (e.g., melting point, glass transition temperature, and decomposition temperature), shear viscosity, and surface tension between the imidazolium-based dicationic and monocationic ILs with four anions ($[\mathrm{NTf_2}]^-$, $[\mathrm{NPf_2}]^-$, $[\mathrm{BF_4}]^-$, and $[\mathrm{NO_3}]^-$) in this report. When a fair comparison (same anions and cations with the corresponding alkylene linker/alkyl group) was made, the noticeable features of the physical properties of the dicationic ILs compared to the monocationic ILs included:

(i) The density was high.
(ii) The glass transition temperature and melting point were high.
(iii) They were thermally stable.
(iv) The surface tension was large.
(v) The shear viscosity was high.

By comparing the ILs with the reference alcohols, we also found that the alkylene-linker-length dependences on the liquid density and surface tension in the dicationic ILs were qualitatively similar to that in the alkanediols, but this was not the case for the shear viscosity.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Details of the synthesis procedures of the sample ILs, van der Waals volumes V_{VDW} and ratios between van der Waals volume and molar volume V_{VDW}/V for the dicationic and monocationic ILs, and the data of the liquid densities, surface tensions, and shear viscosities of the alkyl alcohols and alkanediols. This material is available free of charge via the Internet at http://pubs.acs.org.

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