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Unsymmetrical Dicationic Ionic Liquids: Manipulation of Physicochemical Properties Using Specific Structural Architectures

Tharanga Payagala, Junmin Huang, Zachary S. Breitbach, Pritesh S. Sharma, and Daniel W. Armstrong*

Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, Texas 76019

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Geminal dicationic liquids have been shown to possess superior physical properties in terms of thermal stability and volatility compared to traditional ionic liquids (ILs).[1] Consequently, they have been proposed as novel high-temperature lubricants,[2] solvents in high-temperature reactions,[3] and ultrastable separation phases[4] and have potential in extractions similar to monocationic liquids[5] and mass spectrometry where ordinary ILs fail.[6] However, they possess the same desirable solvation properties as the more common singly charged ionic liquids.[7] They are able to dissolve all manner of polar and nonpolar molecules, including some proteins, peptides, polymers, and simple organic molecules. In some instances, geminal dicationic liquids exhibited higher melting points than their monocationic analogues, sometimes even extending beyond the accepted IL region of 100 °C.[8] The most common methodology applied to lower the melting point is changing the counteranion. But this alters the solvation properties of the IL, and even in cases where optimal anions (e.g., NTf_2^-, PF_6^-, BF_4^-, etc.) are used, some dicationic salts remained solids. We have found that the melting point and other physical properties can be altered and engineered by manipulating the cationic moieties, thereby forming unsymmetrical dicationic liquids. The "tunability" of ILs (i.e., the ability to alter, control, and tailor their structure as desired) had been touted as one of their virtues. Here, we demonstrate that dicationic liquids and their properties can be "tuned", controlled, or altered to a greater extent than more conventional ILs. This approach is exclusive to dicationic liquids or other multifunctional ions. In fact, it appears that an advantage of dicationic ionic liquids over monocationic ionic liquids is that they provide more opportunities to fine-tune their physical and chemical properties.

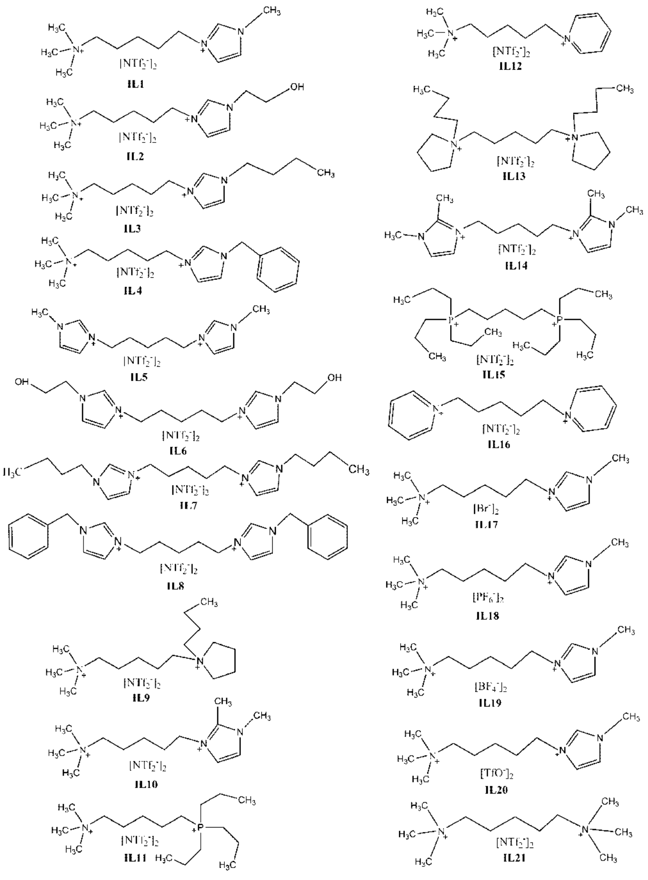

Figure 1. Structures of dicationic ionic liquids synthesized.

Each structure contains two cationic moieties and two anionic moieties that can be varied with respect to each other. To understand the structural change that corresponds to a particular physical property, we synthesized and investigated a series of related compounds with systematic structural variations (see Figure 1). The structural variations investigated include the effect of symmetry of the cationic fragment (i.e., having identical or dissimilar cationic moieties), the length of the alkyl chain substituted at the third position of the imidazole ring, and the type of accompanying anions. The anions studied include bis(trifluoromethylsulfonyl)imide, bromide, hexafluorophosphate, tetrafluoroborate, and trifluoromethanesulfonate (NTf_2^-, Br^-, PF_6^-, BF_4^-, and TfO^-, respectively). The spacer alkyl chain length between the two cationic moieties was set to be five carbons. This value was chosen on the basis of previous research in our group.[1] It has been shown that if the chain length is short (∼3), ILs tend to be solids at room temperature regardless of their other structural features. Similarly, when longer chain lengths were chosen (9,12), most ILs tend to be liquids at room temperature because of high conformational degrees of freedom.

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* Corresponding author. E-mail: sec4dwa@uta.edu.

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Table 1. Physicochemical Properties of Dicationic ILs Synthesized

ionic liquid	MW (g/mol)	melting point (°C)	D[c] (g/cm^3)	refractive index	viscosity[e] (cSt)		thermal stability[f] (°C)		miscibility with heptane[g]	miscibility with water[g]
					30 °C	50 °C	99% w	95% w		
IL1	771.2	−51.5[a]	1.54	1.431	357	190	301.5	407.6	I	I
IL2	801.2	−54.2[a]	1.54	1.435	398	225	132.9	398.6	I	I
IL3	813.2	−53.0[a]	1.47	1.433	527	192	389.0	409.8	I	I
IL4	847.3	−36.2[a]	1.50	1.458	1217	352	328.0	385.5	I	I
IL5	794.2	−61.0[a]	1.57	1.441	251	119	365.2	431.1	I	I
IL6	854.2	−65.0[a]	1.58	1.456	241	106	257.4	322.2	I	I
IL7	878.3	−62.0[a]	1.44	1.433	355	101	375.8	421.3	I	I
IL8	946.3	−34.5[a]	1.55	1.486	1209	372	291.1	379.2	I	I
IL9	816.3	30–32	1.46			357	356.8	396.7	I	I
IL10	785.2	42–45	1.53			236	297.9	389.8	I	I
IL11	849.3	33–35	1.02[d]	1.435[d]	373[d]	144	177.0	380.0	I	I
IL12	768.2	39–40	1.56			218	335.0	384.0	I	I
IL13	884.4	36–38	1.47			337	309.5	379.5	I	I
IL14	822.2	62–63	1.60				392.1	440.4	I	I
IL15	950.4	71–72	1.30				391.4	421.7	I	I
IL16	788.2	53–54	1.62				332.7	374.8	I	I
IL17	371.1	115–116	1.37				90.5	190.7	I	M
IL18	501.3	86–88	1.57				312.4	345.2	I	I
IL19	385.0	>50, < 80[b]					336.9	355.0	I	M
IL20	509.5	153–156	1.50				315.9	358.2	I	M
IL21	743.2	86–88	1.33				363.7	399.6	I	I

[a] Determined by the peak position in DSC. [b] Amorphous solid; does not show a sharp melting point. [c] Measured using a pycnometer. [d] Measured at a supercooled state. [e] Measured using a capillary viscometer. [f] Thermogravimetric analysis (TGA), 99% w = temperature at 1% mass decrease sample. [g] I = immiscible, M = miscible.

Therefore, 5 is the best chain length for this study because of the melting point's sensitivity to the changes in the rest of the structure. The physicochemical data obtained for each ionic liquid is summarized in Table 1.

The melting point of an ionic compound is determined by the crystal lattice energy between the cation and the anion. This lattice energy is controlled by 3 main factors:[9,10] (1) intermolecular forces, (2) molecular symmetry, and (3) conformational degrees of freedom. Comparing IL1 to IL3 and IL5 to IL7, the chain length of the substituent group at the 3-position of the imidazole ring increases. The accompanying melting point decrease can be attributed to the added conformational degrees of freedom of IL3 and IL7. IL4 and IL8 have somewhat higher melting points compared to the comparable structures (IL1–IL8). This may be attributed to the added π–π interactions of the aromatic ring substituent. Of the seventeen NTf$_2^-$ salts synthesized, IL21 with bis(trimethylammonium) groups has the highest melting point. This is a result of two main factors, high intermolecular attraction due to localized charged density on quaternary amine nitrogen and the inherent symmetry of the dicationic moiety. When the symmetry component is removed in IL1–IL4, the melting point decreases by about 140 °C compared to IL21. When the bis(trimethylamino) moieties are removed, thereby removing the high intermolecular attraction component, as in IL5-IL8, remarkably lower melting points are obtained despite the symmetry of the cationic fragments.

Symmetry effects are more apparent in IL9–IL16. In this series, symmetrical ILs (IL13–IL16) have higher melting points than their unsymmetrical analogs (IL9–IL12). The extent to which this effect is observed depends on the type of cationic moieties utilized. If the two cationic moieties forming the unsymmetrical dication are comparable in size and charge distribution, the melting point change compared to their symmetrical analogs is smaller (compare 30 °C for IL9 to 36 °C for IL13). When the two cationic moieties are dissimilar, there is a substantial drop in melting points compared to the corresponding symmetrical ILs (compare 33 °C for IL11 and 71 °C for IL15). Substitution of a methyl group at the 2-position of the imidazolium ring (IL5 vs IL14) has a profound effect on the melting points of dicationic ILs. The melting point increased by about 123 °C (from –61 °C for IL5 to 62 °C for IL14) with this methyl substitution.

Comparison of IL5, IL13, IL14, IL15, IL16, and IL21 shows that the melting points of symmetrical dicationic salts are strongly affected by the type of cation moiety in the order trimethylammonium > tripropylphosphonium > 2,3-dimethylimidazolium > pyridinium > *N*-butylpyrrolidinium > 3-methylimidazolium (86, 71, 62, 53, 36, and −61 °C, respectively). Furthermore, it is apparent from the data obtained for IL1 and IL17–20 that for the same cation, the melting point decreases on the basis of the anion in the order: TfO$^-$ >Br $^-$ > PF$_6^-$ > BF$_4^-$ > NTF$_2^-$ (153, 115, 86, 50–80, and −51.5, respectively).

The densities of ILs range from 1.02 to 1.62 g/cm^3 for this series. The lowest density is observed for an unsymmetrical cationic ionic liquid with tripropylphosphonium and trimethylammonium cationic moieties (IL9), whereas a symmetrical ionic liquid with bispyridinium cationic moieties (IL16) has the highest density. The general trend that can be observed for the ILs listed in Table 1 is that the symmetrical cationic ILs tend to have higher densities than their corresponding unsymmetrical analogues (compare 1.54 g/cm^3 for IL1 to 1.57 g/cm^3 for IL5, 1.53 g/cm^3 for IL10 to 1.60 g/cm^3 for IL14, etc.). Furthermore, when the alkyl chain length of the substituent at the 3-position of the imidazole increases, the density decreases. For instance, the density decreases from 1.54 g/cm^3 for methyl substitution in IL1 to 1.47 g/cm^3 for butyl substitution in IL3, and from 1.57 g/cm^3

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for methyl substitution in IL5 to 1.44 g/cm^3 for the butyl-substituted IL7. Similar observations are reported for monocationic haloaluminate ILs and nonhaloaluminate ILs.[11,12]

The kinematic viscosities of this series of ILs range from 241 to 1217 cSt at 30 °C. Some dicationic liquid viscosities lie within the general monocationic ionic liquid range (IL1, IL2, IL5, IL6, IL7, and IL11 with viscosities $<$400 cSt) and some extend beyond the commonly observed values. [10–12] The viscosities are exceptionally high for ILs containing benzyl groups (1217 cSt for IL4 and 1209 cSt for IL8 at 30 °C), probably because of the added intermolecular π–π interactions. Furthermore, the viscosities were strongly dependent on the temperature. All ILs showed more than a 43% decrease in viscosity with a 20 °C increase in temperature.

Thermal stabilities for the 21 ILs as measured by thermogravimetric analysis (TGA) are reported in Table 1. It is apparent that dicationic ILs show much higher thermal stabilities than monocationic ILs.[1] Out of the 21 salts, 18 were stable up to 350 °C with only a 5% thermal degradation. IL14 carrying bis(2,3-dimethylimidazolium) cation has the highest thermal stability with only 5% thermal degradation at 440 °C.

The refractive indices of the 21 dicationic ILs are in the general region observed for monocationic ILs[11] and lie between 1.431 and 1.486. The solubility behavior of this set of dicationic ILs parallels that of monocationic ILs[11,13] in that all Br^-, BF_4^-, and TfO^- salts synthesized were soluble in water, whereas all NTf_2^- and PF_6^- salts were insoluble in water. None of the ILs were soluble in heptane.

In conclusion, we have demonstrated the effect of symmetry on the melting points and other physical properties of dicationic ionic liquids. The effect on melting point is substantial for ionic liquids containing nonimidazolium-based cationic moieties combined with trimethylammonium cationic moiety. Imidazolium-based ionic liquids have the lowest melting points within the 21 ILs synthesized. The ability to control and tune the properties of an ionic liquid to this extent is exclusive to multi-functional ionic liquids. Furthermore, using this method, we can lower the melting point without affecting the desirable solvation properties and thermal stabilities.

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Supporting Information Available: Experimental procedures and NMR data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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