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Physicochemical Properties of Halogen-free 1, 3-Dialkylimidazolium Ionic Liquids Based on the Sulfonate Anions

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Abstract Ten halogen-free ionic liquids (ILs) based on 1, 3-dialkylimidazolium cations and methanesulfonate [MS]⁻ or *p*-toluenesulfonate [TS]⁻ anions were synthesized via one-step reaction, and their physicochemical properties such as aggregation behavior, surface property, thermal property, density, viscosity, refractive index and electrochemical properties have comparatively been studied. The results showed that ion cluster behavior was observed for the methanesulfonate anion ILs. The emission spectra of neat [BEim]MS only gave relatively weak fluorescence, whereas [BEim]TS exhibited strong emission behavior under same conditions. Ten studied ILs displayed five different phase behaviors, of which [C₁₂Mim]MS exhibited a liquid crystal behavior. The [TS]⁻ based ILs showed high refractive indices of > 1.51.

Key words Sulfonate; Ionic liquids; Halogen-free; Synthesis; Physicochemical property

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In general, organic molten salts containing ions (ionic cluster) and with a melting point of below 100 °C are defined as “ionic liquids” (ILs)^[1]. Different from molecular liquids, ILs have many peculiar properties, including wide liquid range, negligible vapor pressure, higher thermal stability, and good ionic conductivity. Hence, over the past decade, the potential applications of ILs have spread rapidly to numerous fields, such as catalysis^[2], electrochemistry^[3], separation^[4], polymer^[5], synthesis^[6], material^[7] etc. However, further development of the ILs’ applications was encountered some obstacles due to the difficulty in acquiring the highly pure ILs, especially in those fields sensitive to halogen ions. Presently, the most widely used route to prepare ILs still employs a two-step method, i.e., a quaternization reaction with the aim of forming an IL precursor containing a target cation, and followed by a metathesis process leading to the desired

product. This method inevitably introduces the contamination of trace amounts of halide ion^[8-9], thereby resulting in the uncleanness of the target ILs. Now it has been recognized that in some transition-metal catalyzed reactions, even ppm quantities of halide in ILs can poison expensive catalysts, rendering them useless^[10]. On this account, to develop halogen-free routes to ILs has been one of the hot topics in current IL synthesis.

To achieve the goal of synthesizing halogen-free ILs, great endeavor has been made and several halogen-free synthetic approaches including one-step alkylation of N-alkylimidazole by using alkyl sulfates^[11], carbonates^[12], or phosphates^[13] etc. as alkylating agent have been developed. Among them, the method utilizing alkyl sulfonates to target ILs, i.e. one-step alkylation of N-alkylimidazole with alkyl sulfonates (e.g. methanesulfonate ester, *p*-toluenesulfonate ester, etc.), has attracting great interest. Recently, Dupont

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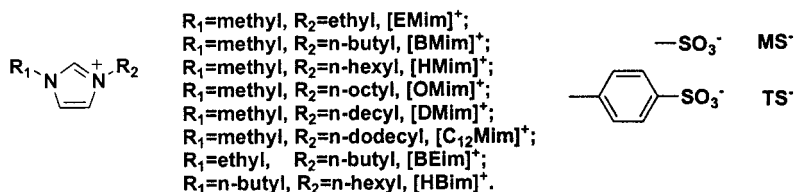
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et al reported that the anions of the alkanesulfonate-based ILs can be easily substituted by a series of other anions such as $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, and $[\text{NTf}_2]^-$ etc.^[14]. That is, these methanesulfonate (mesylate) or *p*-toluenesulfonate (tosylate) based ILs can be used as important “intermediate ILs” like $[\text{BMim}]\text{Cl}$ and $[\text{EMim}]\text{Br}$ to prepare the target ILs with other anions, which thereby supports an alternative approach to synthesize halogen-free ILs based on conventional fluorinated anions. On this account, these $[\text{MS}]^-$ and $[\text{TS}]^-$ based ILs should be given much more attention, especially considering their importance to some halogen-free ILs. And, acquiring the detailed properties of these dialkylimidazolium salts based $[\text{MS}]^-$ and $[\text{TS}]^-$ anions is also necessary. Up to now, however, the studies on these $[\text{MS}]^-$ and $[\text{TS}]^-$ based ILs are still relatively limited, and the in-depth explorations of their properties and its comparative study with the $[\text{BF}_4]^-$ ILs have been lacking yet. In this work, an

attempt was made to systematically characterize a series of 1, 3-dialkylimidazolium $[\text{MS}]^-$ or $[\text{TS}]^-$ based ILs and a detailed study on their physicochemical properties such as ion aggregation, fluorescence, surface property, thermal property, density, viscosity, refractive index and electrochemical property.

1 Experimental Section

Materials Most of the chemicals used in this work were of analytical grade and were used without further purification. *p*-Toluenesulfonyl chloride or methanesulfonyl chloride and all alcohols were purchased from Shanghai Reagent Co. Ltd. and Tianjin Reagent Co. Ltd., respectively. *N*-Methylimidazole (99%) and *N*-ethylimidazole (99%) were purchased from Aldrich. *N*-hexylimidazole was prepared according to the approach reported previously^[8]. For the purpose of comparison, $[\text{BMim}]\text{BF}_4$ and $[\text{BMim}]\text{PF}_6$ with high purity were purchased from Merck.



Scheme 1 Structure and abbreviations of cations and anions employed in this work

1.1 Synthesis and Characterization

All alkylmethanesulfonates, alkyl *p*-toluenesulfonates and the ILs (Scheme 1) were prepared according to the literature procedures with slight modification^[15]. For example, 1-butyl-3-methylimidazolium mesylate ($[\text{BMim}]\text{MS}$) was prepared with high yield from the reaction of *N*-methylimidazole and butylmethanesulfonate in an appropriate solvent such as acetonitrile under mild conditions. $[\text{EMim}]\text{MS}$, $[\text{HMim}]\text{MS}$, $[\text{OMim}]\text{MS}$, $[\text{DMim}]\text{MS}$, $[\text{C}_{12}\text{Mim}]\text{MS}$, $[\text{BEim}]\text{MS}$, $[\text{HBim}]\text{MS}$, $[\text{BEim}]\text{TS}$, $[\text{HBim}]\text{TS}$ were prepared similarly via the quaternization reactions of corresponding *N*-alkylimidazole with alkyl sulfonate or alkyl *p*-toluenesulfonate. We used the method which was described in literature^[16] to monitor the end-point of the alkylation reaction and determine the levels of unreacted *N*-methylimidazole to < 0.2 mol%. All the samples were washed with diethyl ether for five times

and then treated under reduced pressure ($10^{-2} \sim 10^{-3}$ mbar) at 80 °C for 12 h to remove the organic impurities or water. The purified ILs were stored in a desiccator wrapped by aluminum foils under dry nitrogen. In order to ensure that the ILs were free from volatile impurities such as water, they were purified again before physicochemical property testing. The water content in ILs was determined by means of a Karl-Fischer titration (Mitsubishi CA-06 Moisturemeter) to be less than 400 ppm. ¹H NMR spectra were recorded on a Bruker AMX FT 400 MHz NMR spectrometer. Electrospray ionization (ESI) mass spectrometry was recorded on a Bruker Daltonics APEX II 47e Fourier transform mass spectrometer. The fluorescence spectra were recorded at 25 °C on a Hitachi model F-7000 FL spectrophotometer at a scan speed of 1200 nm/min and PMT voltage 700 V. The excitation and emission slit width were kept at 5.0 nm and 2.5 nm, respectively. The X-ray

photoelectron spectroscopy (XPS) analyses were performed with a VG ESCALAB 210 instrument (Mg K α , 150 eV) by depositing IL on the Au substrate. Measurements of phase-transition temperatures, melting and freezing points were carried out on a Mettler-Toledo differential scanning calorimeter, model DSC822 $^{\circ}$, and the data were evaluated using the Mettler-Toledo STARe software version 7.01. The samples were heated up to 120 $^{\circ}$ C and maintained 30 min for further purification because of their strong hydrophilic properties. The scanning rate was 10 $^{\circ}$ C/min. Melting points and glass-transition temperatures were obtained from the second heating curve. The samples for TG/DTA measurements were sealed tightly in Al $_2$ O $_3$ pans and analyzed with a Beijing WCT-2C TG/DTA analyzer. The thermal decomposition temperature (T_d) with 5% weight loss was obtained with a heating rate of 10 $^{\circ}$ C/min under nitrogen atmosphere. The density (ρ) was measured at 25 $^{\circ}$ C using a 10 mL volumetric flask calibrated with water by mass method. The viscosity was measured on a Brookfield DV-III ULTRA Programmable Rheometer. Measurement of refractive index was conducted with a WAY-2s Abbe refractometer. The conductivity was measured using a Mettler-Toledo Seven Multimeter. The cyclic voltammetry was conducted using a CHI 660A Electrochemical Work Station with a GC working electrode and an Ag wire pseudoreference electrode.

2 Results and Discussion

Ten [MS] $^-$ and [TS] $^-$ based ILs were prepared according to the similar method reported previously, i.e., one-step alkylation of N-alkylimidazole with organic sulfonate ester. The purity of each treated IL was verified by NMR spectroscopy to check for residues of unreacted reactants or residual solvents, and the analysis results indicated that these compounds had been completely eliminated. Among the ten ILs, seven of them (i.e., [EM in]MS, [HM in]MS, [OM in]MS, [BE in]MS, [HB in]MS, [BE in]TS and [HB in]TS) are liquids at room temperature (25 $^{\circ}$ C), whilst the other ILs (i.e., [BM in]MS, [DM in]MS and [CM in]MS) are white solids. Except that [C $_2$ M in]MS is partly soluble in water, all other ILs are miscible with water and the hydrophilicity gradually decreased as the alkyl chain length on the cation increased. Owing to their hygroscopicities, the ILs still contained water content of 200~400 ppm, even after rigorous drying. For example, the water content in [EM in]MS was 380 ppm, that in [BE in]MS was 388 ppm, that in [HB in]MS was 300 ppm, respectively. Duplicate measurements were performed on each sample with results agreeing to within 5%. Before each physicochemical property testing, the ILs were purified again.

Electrospray ionization (ESI) mass spectrometry in both positive and negative modes has been successfully applied to characterize the behavior of cationic or anionic supramolecular aggregates of ILs $^{[17-19]}$. The acquired information is of great value for understanding intrinsically on nature of ILs, and therefore, it is helpful to understand some unique properties. Here the ion cluster behavior of these [MS] $^-$ and [TS] $^-$ based ILs were also estimated by positive ESI mass spectrometry, and two representative positive ion spectra were provided in Fig. 1.

2.1 Ion aggregation behavior

Electrospray ionization (ESI) mass spectrometry in both positive and negative modes has been successfully applied to characterize the behavior of cationic or anionic supramolecular aggregates of ILs $^{[17-19]}$. The acquired information is of great value for understanding intrinsically on nature of ILs, and therefore, it is helpful to understand some unique properties. Here the ion cluster behavior of these [MS] $^-$ and [TS] $^-$ based ILs were also estimated by positive ESI mass spectrometry, and two representative positive ion spectra were provided in Fig. 1.

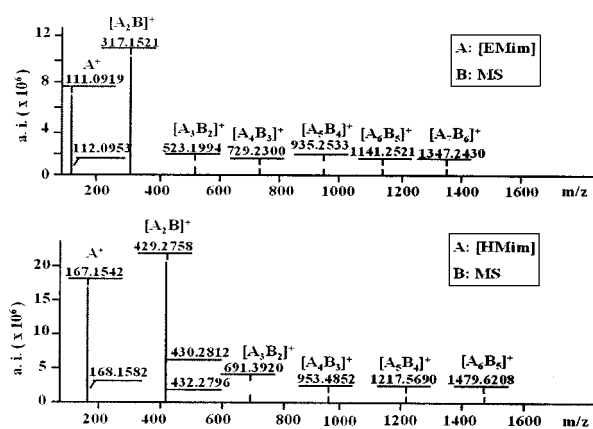


Fig. 1 The positive ion ESI mass spectra of [EM in]MS and [HM in]MS

All the peaks corresponding to the aggregates of cations and anions conform very favorably with the theoretical values, thus confirming their identities. For the [EM in]MS, in addition to observing the parent cation [EM in] $^+$ (m/z 111), the positively charged ion clusters ($[A_n^+ B_{n-1}^-]$, $2 \leq n \leq 6$, A is the cation, B is the anion), and the isotope patterns can also

be detected clearly. The cluster $[(EM\ in)_7(MS)_6]^+$ (m/z 1347) was also found clearly from Fig. 1, and no larger clusters was observed perhaps because their signals were too weak to be detected. Additionally, the relative abundances of positively charged ion clusters indicated that the dimer cluster in $[EM\ in]MS$ is easier to form than other larger cluster, even much richer than the parent cation $[EM\ in]^+$. As to $[HM\ in]MS$, its spectrum was similar to that of $[EM\ in]MS$. For $[DM\ in]MS$ and $[C_{12}M\ in]MS$, only parent cation was detected, which was caused mainly by the difficulty of both ILs in forming larger clusters along with increasing the cation size.

2.2 Fluorescence behavior

Although fluorescence behavior of many imidazolium-based ILs has been extensively studied^[21, 21], the reports on fluorescence behavior of $[MS]^-$ and $[TS]^-$ anions based dialkylimidazolium ILs have been not available yet. In this work, fluorescence properties of neat $[BE\ in]MS$ and $[BE\ in]TS$ were studied. Fig. 2

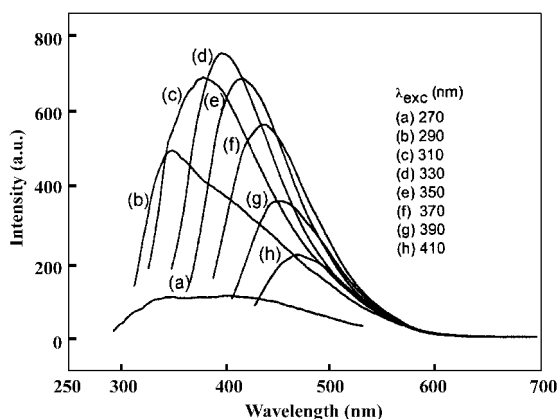


Fig. 2 Excitation wavelength-dependent emission behavior of neat $[BE\ in]MS$

and Fig. 3. The results showed that the fluorescence behavior of both ILs was strongly dependent on the excitation wavelength. For $[BE\ in]MS$, its maximum excited wavelength was 334 nm, and the fluorescence became very weak (intensity < 100) when excited wavelengths were below 250 nm or over 470 nm. Similar to $[BE\ in]MS$, the fluorescence behavior of $[BE\ in]TS$ was also dependent on the excitation wavelength (Fig. 3), and its maximum excited wavelength was 397 nm. Different from $[BE\ in]MS$, the intensity of $[BE\ in]TS$ (intensity > 2600) was much stronger

than the former. According to previous report by our group, the $[MS]^-$ based ILs from caprolactam have no

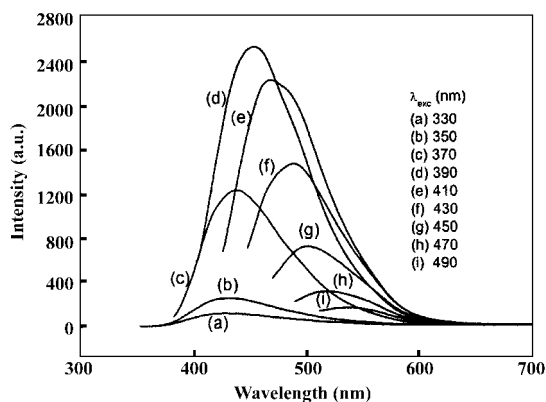


Fig. 3 Excitation wavelength-dependent emission behavior of neat $[BE\ in]TS$

fluorescence while the $[TS]^-$ based ILs from caprolactam exhibited weak fluorescence behavior^[15]. That is, the weak fluorescence behavior of $[BE\ in]MS$ should be attributed to the imidazolium moiety, and for the $[BE\ in]TS$ both $[BE\ in]^+$ cation and $[TS]^-$ anion made the respective contributions, and the anion made greater contribution to the wholly fluorescence behavior.

2.3 Surface property

In comparison with the widely studied “bulk” properties such as thermal, soluble, and electrochemical properties, etc., the study of the surface properties for ILs are still very limited, it has attracted more and more attention owing to its great value for understanding the surface science of ILs. Here the surface studies of these $[MS]^-$ and $[TS]^-$ based ILs utilizing XPS were performed. The survey scan XPS spectra for the five ILs ($[EM\ in]MS$, $[BM\ in]MS$, $[OM\ in]MS$, $[BE\ in]MS$, $[BE\ in]TS$) showed that the expected elements O, N, C, S were detected, no evidence of impurities by other elements (such as halogen, metal) and any substrate (Au) related spectral features was found. The high resolution spectra of $[BE\ in]TS$ showed that all the O 1s or N 1s core level spectrum were fitted with only one sharp peak, and the S 2p core transition curve can be fitted with two components due to the contribution of 2p_{1/2} and 2p_{3/2} respectively^[22]. The electron emissions from O 1s, N 1s and S 2p were well resolved for all ILs and the high resolution

spectra didn't change with alkyl chain length^[23], the binding energies (B. E.) were 531.0 ± 0.2 (O1s), 401.6 ± 0.2 (N1s), 167.5 ± 0.2 (S2p 3/2), respectively. Due to the presence of C in various chemical environments, the structure of C1s was as expected,

more complicated. The spectrum for C1s core level can be fitted with at least three different curves^[24]. The atomic ratio (A. R.) for each element in the ILs was listed in Table 1. The experimental A. R. O/S, N/S, C/S for all mesylate ILs was higher than the

Table 1 The B. E. (eV) and A. R. for each element in the studied ILs

	[EM in]MS		[BM in]MS		[OM in]MS		[BE in]MS		[BE in]TS	
	B. E.	A. R. (Cal)	B. E.	A. R. (Cal)	B. E.	A. R. (Cal)	B. E.	A. R. (Cal)	B. E.	A. R. (Cal)
O	530.9	3.9(3.0)	530.9	3.7(3.0)	531.1	4.1(3.0)	530.8	3.7(3.0)	531.2	3.85(3.0)
N	401.5	2.2(2.0)	401.4	2.2(2.0)	401.6	2.0(2.0)	401.4	2.2(2.0)	401.8	2.2(2.0)
C	285.0	9.4(7.0)	285.0	9.6(9.0)	285.0	14.6(13.0)	285.0	11.0(10.0)	285.0	15.8(16.0)
S	167.4	1.0(1.0)	167.4	1.0(1.0)	167.5	1.0(1.0)	167.3	1.0(1.0)	167.7	1.0(1.0)

A. R.: atomic ratio O/S, N/S, C/S

corresponding theoretical value, this result suggested that some O- and C-containing contaminations should exist in these ILs, which may be introduced during the synthesis and purification procedures^[22, 24] or during XPS analysis.

2.4 Thermal property

The phase behavior of ten ILs based [MS]⁻ and

[TS]⁻ anions such as melting and freezing points (T_m, T_f), crystal-crystal transition (T_c), glass phase transition (T_g), melting entropy change (ΔS_m) were investigated with DSC (Table 2).

Similar to those [BF₄]⁻ and [PF₆]⁻ ILs, relatively complicated phase behavior were exhibited for these [MS]⁻ and [TS]⁻ based salts, and four types

Table 2 Thermal properties of dialkylimidazolium organic sulfonate ILs

Entry	ILs	T _f	T _m	T _g	T _c	ΔC _p	ΔH _m	ΔS _m	T _d
1	[EM in]MS		37.9	-62.6	-9.2	0.373	7.81	25.1	342
2	[BM in]MS	-22.4	76.6	-55.0	-17.8	0.420	24.03	68.7	330
3	[HM in]MS		44.3	-52.5	10.1	0.348	11.87	37.4	325
4	[OM in]MS		40.4	-54.0	-7.9	0.431	28.82	91.9	322
5	[DM in]MS	6.3	62.3				38.28	114.1	330
6	[C ₁₂ M in]MS	23.2	69.8				48.67	141.9	323
7	[BE in]MS			-62.3		0.358			318
8	[BE in]TS			-43.9		0.335			328
9	[HB in]MS			-52.4		0.308			324
10	[HB in]TS			-42.3		0.413			343

T_f(°C): freezing point, T_g(°C): glass transition, T_m(°C): melting point, T_d(°C): decomposition temperature, T_c(°C): cold crystal temperature, ΔC_p(J g⁻¹ K⁻¹): heat capacity change during the glass transition, ΔH_m(kJ mol⁻¹): melting enthalpy change, ΔS_m(JK⁻¹ mol⁻¹): calculated from ΔH_m/T_m is the entropy change during the melting

of DSC thermograms and phase diagrams were observed (Fig. 4). Among them, except that [DM in]MS and [C₁₂M in]MS have only a T_m and T_f in a heating and cooling cycle, other ILs all exhibit a glass transition in

both heating and cooling processes. For [EM in]MS, [HM in]MS and [OM in]MS in the heating process, a phase transition from the glass state to a cold crystal occurred at -9.2°C, 10.1°C and -7.9°C, respec-

tively. The transitions of melting enthalpy (ΔH_m) and entropy (ΔS_m) have been calculated over those ILs with a melting point. Obviously, both ΔH_m and ΔS_m values were remarkably affected by changing the length of alkyl chain for the ILs. For example, except for

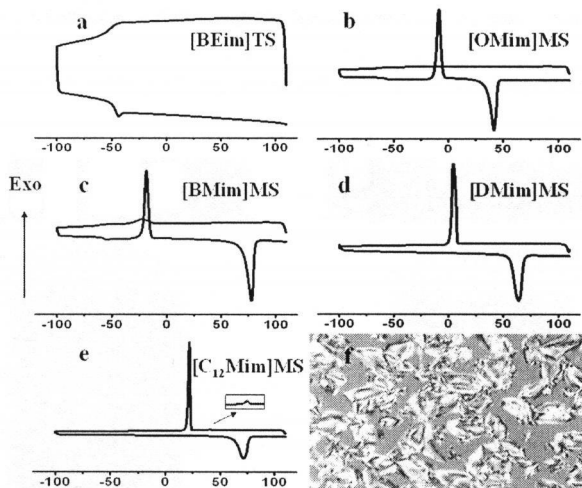


Fig. 4 DSC curves of five ILs (a~ e) and POM picture of $[C_{12}Mim]MS$ (f magnification: $40\times$)

$[BMim]MS$, the ΔH_m and ΔS_m values of other ILs increased with increasing the alkyl chain length of the cations. And all the $[MS]^-$ and $[TS]^-$ based salts which have the glass transitions gave the heat capacity changes (ΔC_p) of $0.308\text{--}0.431\text{ J g}^{-1}\text{ K}^{-1}$, which were slightly lower than $[BMim]BF_4$ ($1.66\text{ J g}^{-1}\text{ K}^{-1}$)^[15]. Thermodynamic properties of these salts were indicated that the ability to vitrify and to crystallize among the studied ILs strongly depends on the alkyl chain length in the imidazolium ring and anions. Additionally, during the cooling process from $150\text{ }^\circ\text{C}$ to $-100\text{ }^\circ\text{C}$, a phase transition of $[C_{12}Mim]MS$ firstly occurred from a liquid to an isotropic liquid (liquid crystal) at $42.2\text{ }^\circ\text{C}$, followed by a crystallization from an isotropic liquid to a solid at $23.2\text{ }^\circ\text{C}$. However, no liquid crystal phenomenon was observed during the heating process, which suggested that $[C_{12}Mim]MS$ was monotropic liquid crystal^[25]. Fig. 4f gave the POM (Polarizing Optical Microscopy) picture of $[C_{12}Mim]MS$ under conditions of anisotropic crystal phase at $42.2\text{ }^\circ\text{C}$. Except for $[C_{12}Mim]MS$, no liquid crystalline phase was observed for other nine ILs.

Fig. 5 showed the change trend of the melting points for ten $[C_nMim]BF_4$ and $[C_nMim]MS$ salts with

increasing the alkyl chain lengths. It can be seen that different from the trend exhibited by the $[BF_4]^-$ salts (*i.e.* the ILs' T_m values decreased with increasing the alkyl chain from C_2 to C_4 and C_6)^[26], the T_m values obviously increased from $37.9\text{ }^\circ\text{C}$ of $[EMim]MS$ to $76.6\text{ }^\circ\text{C}$ of $[BMim]MS$ when the alkyl chain length was increased from the ethyl to the butyl. If further increasing the alkyl from butyl to hexyl or octyl, the T_m values of $[HMim]MS$ and $[OMim]MS$ decreased to $44.3\text{ }^\circ\text{C}$ and $40.4\text{ }^\circ\text{C}$, respectively. Anyway, it was difficult to conclude a regular rule since the phase behaviors of the ILs depend on many factors. For these

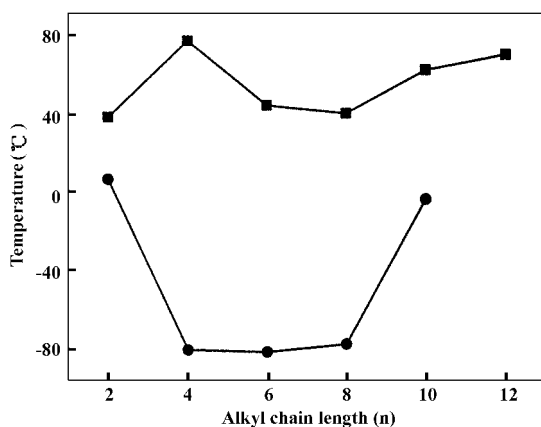


Fig. 5 T_m change trends of $[C_nMim]^+$ with $[BF_4]^-$ ^[26] (circle) and $[MS]^-$ as anions (square)

ten ILs, obvious characteristic was that all those ILs based $[C_nMim]^+$ cation have a melting point and all those ILs based $[BEim]^+$ or $[HBim]^+$ only exhibit a glass transition in their heating and cooling cycles; most of these ILs showed a strong trend to be supercooling.

According to the thermogravimetric curves of these ILs, the thermal decomposition temperatures (which were listed in Table 2) of ten ILs were ranged of $318\text{--}343\text{ }^\circ\text{C}$, which was slightly affected by the carbon number of the alkyl chain and anions. $[TS]^-$ anion based ILs gave higher thermal stability than that of corresponding $[MS]^-$ ILs. Although it was lower than those in imidazolium $[BF_4]^-$ or $[PF_6]^-$ salts (*ca.* $400\text{ }^\circ\text{C}$)^[26], it is stable enough for normal usage, *i.e.* as solvent, extract and catalyst, etc. Among all the studied ILs, $[HBim]TS$ exhibited the highest thermal stability ($T_d = 343\text{ }^\circ\text{C}$) and $[BEim]MS$ gave the lowest ther-

mal stability ($T_d = 318\text{ }^\circ\text{C}$).

2.5 Density, Viscosity and Refractive Index

The densities (ρ) of seven ILs which are liquids at $25\text{ }^\circ\text{C}$ were measured (Table 3), and the ρ values were ranged of $1.069\sim 1.242\text{ g/cm}^3$. The ρ values of

[EM in]MS and [BE in]MS obtained in our experiments are approximately in agreement with previously reported results^[27], which showed that our experiment results were reliable. For a given anion, with increasing the alkyl chain length, the ILs exhibited lower

Table 3 Density, viscosity, refractive index and ionic conductivity of selected ILs at $25\text{ }^\circ\text{C}$

ILs	Density(g/cm^3)	Viscosity(cp)	Refractive index	Conductivity ($\mu\text{S/cm}$)
[EM in]MS	1.242	173	1.4922	2280
[HM in]MS	1.119	906	1.4828	234
[OM in]MS	1.084	1236	1.4797	134
[BE in]MS	1.141	456	1.4844	586
[BE in]TS	1.156	2819	1.5300	97
[HB in]MS	1.069	1474	1.4776	103
[HB in]TS	1.089	4394	1.5159	25

density. For example, when the alkyl chain length was increased from the ethyl to hexyl and octyl, the densities of [EM in]MS, [HM in]MS and [OM in]MS were 1.242 g/cm^3 to 1.119 g/cm^3 and 1.084 g/cm^3 , respectively. On the other hand, when the cation is same, the ILs with a [TS]⁻ anion showed a slightly higher densities than those ILs with a [MS]⁻ anion.

The viscosities of the studied ILs were ranged from 173 cP to 4394 cP at $25\text{ }^\circ\text{C}$, which were obviously higher than that of [BF₄]⁻ salts with the same cation. Among them, [EM in]MS had the lowest viscosity of 173 cp while [HB in]TS exhibited the highest viscosity of 4394 cP. Obviously, both the cation and the anion have some effect on the ILs' viscosities. For a given anion, the viscosities of ILs increased obviously when the alkyl chain increased (e.g. from 173 cP of [EM in]MS to 906 cP of [HM in]MS to 1236 cP of [OM in]MS). When the cation was same, the [TS]⁻ based ILs exhibited higher viscosities than those [MS]⁻ based ILs, for example, the viscosities of [HB in]MS and [HB in]TS were 1474 cP and 4394 cP, respectively. Additionally, the viscosity (η) measurement under varied temperatures showed that the viscosities of all ILs were strongly dependent on the temperature. For example, the viscosity of [HM in]MS was 906 cp at $25\text{ }^\circ\text{C}$ and 45 cp at $80\text{ }^\circ\text{C}$, respectively. And it should be noted that the ILs' viscosities

were more affected at low temperature than that at high temperature.

The refractive indices (n) of seven [MS]⁻ or [TS]⁻ based ILs were ranged from 1.4776 to 1.5300 at $25\text{ }^\circ\text{C}$ (Table 3), and among the studied ILs [BE in]TS had the highest refractive index of 1.5300. Similar to the viscosity, the types of cation and anion also have obvious effect on the ILs' refractive indices. With increasing the alkyl chain of the cation, the refractive indices obviously decreased. For example, the refractive index of [EM in]MS was 1.4922 at $25\text{ }^\circ\text{C}$, and for [OM in]MS this value decreased to 1.4797. Additionally, the refractive indices of the [TS]⁻ based ILs were much higher than that of [MS]⁻ anion ILs. For example, the n value of [HB in]MS was 1.4776 while the value of [HB in]TS was 1.5159. Furthermore, the effect of temperature on the refractive index was also studied, and the n values decreased linearly with the increased temperatures.

2.6 Electrochemical Property

Electrochemical stabilities of the selected ILs such as [EM in]MS and [BE in]MS (which have the lower viscosities in our studied ILs) were evaluated by cyclic voltammetry at $25\text{ }^\circ\text{C}$. In order to test the accuracy and reliability of the electrochemical station, commercially available ILs [BM in]BF₄ and [BM in]PF₆ were firstly investigated. The data were consistent with the repor-

ted results^[28, 29]. A typical curve of cyclic voltammetry for [EM in]MS showed that it was highly pure according to the absence of other reduction or oxidation peaks and its electrochemical window (EW) is ca. 3.3 V. In comparison with [BM in]BF₄ (EW = 4.7 V) and [BM in]PF₆ (EW = 4.8 V)^[25], decreased electrochemical stabilities were mainly caused by the reduced oxidative voltages (< 1.8 V) of the electroactive anion [MS]⁻ and [TS]⁻.

The conductivity of an IL is of vital importance if it is to be considered as a supporting electrolyte in electrochemical devices. According to the conclusions^[8], the ionic conductivity (κ) of an IL should be related to its viscosity (η), formula weight (FW), and density (ρ), and the radii of its cation and anion (r_a and r_c), as described by Equation (1), in which $0 < \gamma < 1$ is the degree of dissociation, F is the Faraday constant, ζ_a and ζ_c are the anion and cation microviscosity factors, respectively

$$\kappa = \gamma F^2 \rho / (6\pi N_A F W \eta) [(\zeta_a r_a)^{-1} + (\zeta_c r_c)^{-1}] \quad (1)$$

In this work, the ionic conductivities (κ) of seven ILs which are liquids at 25 °C were also measured and the κ values were ranged from 25 $\mu\text{S}/\text{cm}$ to 2.28 mS/cm. At 25 °C, [EM in]MS exhibited the highest conductivity of 2.28 mS/cm, which was obviously lower than that of [EM in]BF₄ (14 mS/cm) or [EM in]PF₆ (5.2 mS/cm)^[11], but higher than that of [BM in]BF₄ (1.73 mS/cm) or [BM in]PF₆ (1.46 mS/cm)^[30]. For a given anion, with increasing the alkyl chain, the κ value of [C_nM in]MS decreased obviously, which was similar to the change trend of the [C_nM in]BF₄ salts. For example, the κ values of [EM in]MS, [HM in]MS and [OM in]MS were 2.28 mS/cm, 234 $\mu\text{S}/\text{cm}$ and 134 $\mu\text{S}/\text{cm}$, respectively. Additionally, the [MS]⁻ based ILs had higher conductivities than those ILs with a [TS]⁻ anion. For example, the κ values of [BE in]MS, [HB in]MS were 586 $\mu\text{S}/\text{cm}$ and 103 $\mu\text{S}/\text{cm}$ at 25 °C, respectively, while only 97 $\mu\text{S}/\text{cm}$ of [BE in]TS and 25 $\mu\text{S}/\text{cm}$ of [HB in]TS were obtained. The reason might be attributed to the larger bulk of [TS]⁻. Similar to the viscosity and refractive index, the temperature had great effects on the ILs conductivities. For example, the

conductivities of [HM in]MS increased from 234 $\mu\text{S}/\text{cm}$ at 25 °C to 3.79 mS/cm at 80 °C. The conductivities of these ILs based [MS]⁻ and [TS]⁻ anions were more affected at high temperature than that at low temperature, a possible explanation was that the κ value was strongly affected by its viscosity at low temperatures, and the intrinsic structure and characteristics of the ILs may determine κ value at higher temperatures.

3 Conclusions

As an important type of “intermediates” for synthesis of many halogen-free ILs, a series of [MS]⁻ and [TS]⁻ based ILs were synthesized and characterized, and their physicochemical properties such as aggregation behavior, fluorescence, surface property, thermal property, density, viscosity, refractive index and electrochemical property were comprehensively studied. Among ten developed ILs, seven of them are liquids at room temperature (25 °C), in which [EM in]MS showed the lowest viscosity of 173 cP and the highest conductivity of 2.28 mS/cm. Ten studied ILs displayed five different phase behaviors, of which [C₁₂M in]MS exhibited a liquid crystal when cooled to 42.2 °C. The [TS]⁻ based ILs (i.e., [BE in]TS and [HB in]TS) showed the refractive indices of > 1.51, which are higher than that of dialkylimidazolium [BF₄]⁻ and [PF₆]⁻ salts. Additionally, aggregation behavior in those short alkyl chain [MS]⁻ based ILs was observed by ESI mass spectrometry, which might be explained by the reason resulting in higher viscosities and lower conductivities of these salts than that of those dialkylimidazolium [BF₄]⁻ and [PF₆]⁻ salts. Anyway, the detailed study on these [MS]⁻ and [TS]⁻ ILs will be in favor of improving understanding concerning the ILs properties and their applications, especially considering their important role as “intermediate ILs” like [BM in]Cl, [BM in]Br, and [EM in]Br.

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烷基磺酸阴离子无卤素离子液体的物理化学性质研究

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摘 要: 通过一步法合成了基于 1, 3-二烷基咪唑阳离子和甲烷磺酸或对甲苯磺酸阴离子的无卤素离子液体, 并对它们的物理化学性质如聚集行为、表面性质、热性质、密度、黏度、折光率和电化学性质等进行了详细研究. 结果表明在甲烷磺酸阴离子基离子液体中观察到离子液体中普遍存在的离子簇行为; 同等条件下 [BE_{im}][MS] 的荧光光谱强度较 [BE_{im}][TS] 弱; [C₁₂M_{im}][MS] 展现出液晶行为; [TS]⁻ 基离子液体有着较高的折光率, 大于 1.51

关 键 词: 磺酸根; 离子液体; 无卤素; 合成; 物理化学性质