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# Physicochemical characterization of paramagnetic ionic liquids 1-vinyl-3alkylimidazolium tetrahalogenidoferrate(III) [VRIM][FeCl<sub>m</sub>Br<sub>4 – m</sub>]

# Yimei Tang<sup>a</sup>\*, Xiaoling Hu<sup>a</sup>, Ping Guan<sup>a</sup>, Xiangping Lin<sup>a</sup> and Xiaoqian Li<sup>a</sup>

Using microwave-assisted synthesis method, a series of paramagnetic ionic liquids comprising 1-vinyl-3-alkylimidazolium VRIM<sup>+</sup> cation and tetrahalogenidoferrate (III) FeCl<sub>m</sub>Br<sub>4 - m</sub><sup>-</sup> anion were designed and synthesized. The structure was analyzed using <sup>1</sup>H NMR and Raman spectroscopy. Ultraviolet-visible absorption spectra, thermal stability, magnetic susceptibility, viscosity, ionic conductivity, and solubility were characterized. Results show that elongation of the alkyl chain leads to replacement of bromides with a small amount of chlorides in the anion, shifting of UV maximum absorption peaks to shorter wavelengths, reduction of ionic conductivity, and solubility in polar solvents, as well as increase in fluidity, magnetic susceptibility, and solubility, and solubility in nonpolar solvents. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: 1-vinyl-3-alkylimidazolium; magnetic ionic liquids; physicochemical properties; tetrahalogenidoferrate

# INTRODUCTION

A new class of solvents, which are often fluid at room temperature and consist entirely of ionic species especially used in chemical materials,<sup>[1–5]</sup> synthesis,<sup>[6,7]</sup> and separations,<sup>[8–10]</sup> has elicited much attention. This interest is ascribed to their unique material characteristics, such as low vapor pressure, high thermal stability, high ionic conductivity, and wide electrochemical stability window<sup>[11–13]</sup>; ability to dissolve organic, inorganic, and polymeric compounds<sup>[12]</sup>; and physicochemical properties that vary extensively on structural composition (anion or cation).<sup>[14]</sup> Thus, these materials are labeled as "designer solvents"<sup>[15]</sup> or commonly known as ionic liquids (ILs).

Magnetic ILs (MILs), which comprise magnetic inorganic or organic ions, are an exceptional subclass of ILs not only because of their unique properties but also due to their magnetic properties. MILs containing magnetic inorganic anions, such as  $Fe^{IIX4^-}(X = CI, Br)$ ,<sup>[16-20]</sup>  $Mn^{II}X_4^{2-}(X = CI, Br)$ ,<sup>[20,21]</sup>  $Mn^{II}(Tf_2N)^{3-,[21]}$   $Co^{II}X_4^{2-}(X = CI, NCS, NCSe, N(CN)_2)$ ,<sup>[20,22,23]</sup>  $Dy^{III}(SCN)_{8-x}(H_2O)_x^{(5-x)-}(x=0-2)$ ,<sup>[24]</sup> and  $Gd^{III}CI_6^{3-,[20]}$ , have been revealed consecutively since the first discovery in 2004.<sup>[25]</sup> Tilve *et al.*<sup>[26]</sup> studied the successful function of the [BMIM]Cl/FeCl<sub>3</sub> IL system as a solvent and catalyst in stereo-controlled glycosidation of 3,4,6-tri-Oacetyl-D-glucal with different alcohols. Sun et al.[27] demonstrated the use of the [BMIM]Cl/FeCl<sub>3</sub> system for the alkylation of deuterated benzene with ethylene. Given their strong response to external magnetic fields, MILs have been used as raw materials to prepare magnetically responsive materials of single-walled carbon nanotubes,<sup>[28]</sup> electron paramagnetic resonance spin probes in typical achiral diamagnetic ILs,<sup>[29]</sup> and magnetic ion gels.<sup>[30]</sup> MILs have also been applied in magnetic separation of materials,<sup>[31]</sup> in magnetic resonance imaging as contrast agents for medical diagnostics,<sup>[32]</sup> in flow batteries,<sup>[33,34]</sup> in poly (3,4-ethylenedioxythioxythiophere) nanosphere synthesis,[35] and

in various polypyrrole and poly(N-methylpyrrole) nanostructures.<sup>[36]</sup> In addition, interest in the polymeric forms of ILs has been increasing.<sup>[37,38]</sup> Their potential as a new class of polymers lies in their novel properties with improved mechanical durability and dimensionality combined by polymerization. Therefore, a series of 1-vinyl-3-alkylimidazolium tetrahalogenidoferrate (III) [VRIM] [FeCl<sub>m</sub>Br<sub>4-m</sub>] (R=*n*-butyl, m=2,3,4; R=*n*-pentyl, m=3,4; R=*n*hexyl, m=3,4) bifunctional materials with olefinic bonds and magnetic groups were designed and synthesized.

ILs are designer solvents,<sup>[15]</sup> which implies that their properties can be varied to suit the requirements of a particular process. In this study, through cation change, the relationships between structure and physicochemical properties (e.g. anionic structure, melting point, viscosity, density, and hydrophobicity) were discussed in detail to obtain some parameters for their actual applications.

# **MATERIALS AND METHODS**

#### Materials

The reagents used for the synthesis of ILs were 1-vinylimidazole (w > 0.990; Alfa), C<sub>4</sub>H<sub>9</sub>Br (w > 0.980; Aladdin), C<sub>5</sub>H<sub>11</sub>Br (w > 0.970; Aladdin), C<sub>6</sub>H<sub>13</sub>Br (w > 0.980; Aladdin), FeCl<sub>3</sub> · 6H<sub>2</sub>O (w > 0.990; Yaohua Reagent Factory, Tianjin, China), hydrochloric acid (w = 0.370; Third Chemical Reagent Factory, Tianjin, China), acetonitrile (w > 0.995; Kemiou Reagent Tianjin,

<sup>\*</sup> Correspondence to: Yimei Tang, School of Natural and Applied Science, Northwestern Polytechnical University, The Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, Xi'an 710072, China. E-mail: tangymhkf@163.com

a Y. Tang, X. Hu, P. Guan, X. Lin, X. Li

School of Natural and Applied Science, Northwestern Polytechnical University, The Key Laboratory of Space Applied Physics and Chemistry, Ministry of Education, Xi'an 710072, China

China), and acetic ether (w > 0.995; Hedongquhongyan Reagent Factory). All chemicals were of analytical grade and used without any purification.

#### Methods

#### Apparatus

The structures of the samples were characterized by <sup>1</sup>H NMR using a Bruker AVANCE 300 MHz spectrometer and by Raman spectroscopy using inVia Raman Microscope (RENISHAW). The absorption spectra were recorded on a Shimadzu UV-2550 spectrometer. Thermal analysis was performed by thermogravimetric analysis (TGA) on Q1000DSC+LNCS+ FACEQ600 SDT (FA, USA). Magnetic susceptibility was verified using MPMS-XL-7 SQUID (USA) at 298.15 K. The viscosities  $\eta$  of [VRIM][FeCl<sub>m</sub>Br<sub>4</sub> m] were determined using a rotational viscometer. Ionic conductivity was measured using conductivity meter DDS-307.

# Synthesis of 1-vinyl-3-alkylimidazolium tetrahalogenidoferrate (III) $[VRIM][FeCI_mBr_{4-m}]$

A mixture of 100 mmol bromoalkane and 100 mmol 1-vinylimidazole was placed in a microwave reactor. After vigorous shaking for 2 min, the mixture was microwave heated at 189 W for 40 s and then cooled to room temperature naturally. This process was repeated a few times until the mixture was translucent. The considerably viscous liquid was collected by rinsing with ethyl acetate, after which it was concentrated using reduced pressure distillation. This liquid was vacuum dried at 303.15 K for 48 h and naturally cooled to room temperature. The final product was verified to be 1-vinyl-3-alkylimidazolium bromide [VRIM]Br using <sup>1</sup>H NMR and IR before subsequent use. The respective yields of [VBIM]Br, [VPIM]Br, and [VHIM]Br are 84.7%, 84.6%, and 82.6%.

One hundred millimoles of FeCl<sub>3</sub>· $6H_2O$  and 100 mmol equivalent of [VRIM]Br were added in a flask that was stirred at 298.15 K. A yellow, viscous liquid was formed after 8 h, which was obtained by rinsing the solution with hydrochloric acid for 6 s and concentrated using reduced pressure distillation. The final product (Scheme 1) was further collected by vacuum drying at 308.15 K for 48 h and then naturally cooled to room temperature before it was analyzed. The yields (in weight) of [VBIM]FeX<sub>4</sub>, are 81.6%, 76.8%, and 82.3%, respectively.

## **RESULTS AND DISCUSSIONS**

# <sup>1</sup>H NMR

1-Vinyl-3-butylimidazolium tetrahalogenidoferrate (III) [VBIM] [FeCI<sub>m</sub>Br<sub>4 - m</sub>]: <sup>1</sup>H NMR (ppm, DMSO-d<sub>6</sub>,  $\delta$ ): 10.68 (s, 1H, CH), 7.83 (s, 1H, CH), 7.47–7.55 (dd, 2H, CH), 5.31–6.13 (m, 2H, CH<sub>2</sub>), 4.42 (t, 2H, CH<sub>2</sub>), 1.91–2.04 (m, 2H, CH<sub>2</sub>), 1.23 (m, 2H, CH<sub>2</sub>), 0.96 (t, 3H, CH<sub>3</sub>).

1-Vinyl-3-pentylimidazolium tetrahalogenidoferrate (III) [VPIM] [FeCl<sub>m</sub>Br<sub>4 - m</sub>]: <sup>1</sup>H NMR (ppm, DMSO-d<sub>6</sub>, δ):10.70 (s, 1H, CH), 7.77 (s, 1H, CH), 7.47–7.55 (dd, 2H, CH), 5.29–6.11 (m, 2H, CH<sub>2</sub>), 4.43 (t, 2H, CH<sub>2</sub>), 1.95–2.04 (m, 2H, CH<sub>2</sub>), 1.19–1.35 (m, 4H, CH<sub>2</sub>), 0.89 (t, 3H, CH<sub>3</sub>).

1-Vinyl-3-hexylimidazolium tetrahalogenidoferrate (III) [VHIM] [FeCl<sub>m</sub>Br<sub>4-m</sub>]: <sup>1</sup>H NMR (ppm, DMSO-d<sub>6</sub>, δ):10.77 (s, 1H, CH), 7.73 (s, 1H, CH), 7.47–7.55 (dd, 2H, CH), 5.29–6.10 (m, 2H, CH<sub>2</sub>), 4.42 (t, 2H, CH<sub>2</sub>), 1.92–2.04 (m, 2H, CH<sub>2</sub>), 1.20–1.33 (m, 4H, CH<sub>2</sub>), 0.89 (t, 3H, CH<sub>3</sub>)

The results of <sup>1</sup>H NMR indicate that the cation structure for the title substance is 1-vinyl-3-alkylimidazolium.

#### Raman spectra

Figure 1 shows the Raman spectra of [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>].<sup>[39]</sup> The strong band assigned to the totally symmetric stretching vibration of Fe–Cl bond<sup>[40]</sup> is observed at *ca*. 331 cm<sup>-1</sup> in the spectra of the three ILs, demonstrating that [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (R=*n*-butyl, *n*-pentyl and *n*-hexyl; m=4) has FeCl<sub>4</sub><sup>-</sup>. The peaks observed at *ca*. 269 cm<sup>-1</sup> correspond to FeCl<sub>3</sub>Br<sup>-</sup> in the spectra of [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (R=*n*-butyl, *n*-pentyl or *n*-hexyl; m=3). A band located at about 243 cm<sup>-1</sup> is only observed in the spectra of [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (R=*n*-butyl, m=2), corresponding to FeBr<sub>2</sub>Cl<sub>2</sub><sup>-</sup>.

Under identical reaction conditions, anionic differences in Raman spectra can be explained using electron-donating and volume effects. All chemical reactions turn toward a relatively



**Figure 1**. Raman spectra of a, [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 2, 3, 4); b, [VPIM] [FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4); c, [VHIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4)





n=4, 5, 6 m=2, 3 or 4

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stable state of resultants. Elongation of the alkyl chain increases the electron-donating ability of alkyls, causing the electropositivity of VRIM<sup>+</sup> cation to successively decrease with the elongation of alkyl (*n*-butyl, *n*-pentyl, and *n*-hexyl) chain on cation. If the resultants need to be stable, the anion must be closer to the cation and balance positive and negative charges better. With the elongation of the alkyl chain to the 3-position of the imidazole ring, bromide should be replaced with chloride in FeCl<sub>m</sub>Br<sub>4-m</sub><sup>-</sup> to make the anion smaller and closer to the cation. The theoretical analysis is in accordance with the Raman spectra results (Fig. 1, Supplemental Figs. 1 and 2). Thus, under identical reaction conditions, [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] and [VHIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] have no FeBr<sub>2</sub>Cl<sub>2</sub><sup>-</sup> anion.

The MILs were obtained by rinsing with hydrochloric acid for 6 s. A series of supplementation experiments (Supplemental Data) shows that a portion of the Br content has been substituted by Cl during rinsing and a thermodynamic equilibrium (rinsing with HCl for different durations) has been reached upon comparison with the Raman spectra and MS (Supplemental Figs. 1 and 2) of the solutions.

#### **Electronic absorption spectra**

Figure 2 shows the absorption spectra of [VRIM][FeCl<sub>m</sub>Br<sub>4-m]</sub> in acetonitrile. For [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], the observed bands with maxima at ca. 361, 312, and 234 nm, which are similar to those of [EMIM][FeCl<sub>4</sub>],<sup>[17]</sup> are readily assigned to the lowest energy charge transfer transition  ${}^{6}A_{1} \rightarrow {}^{6}T_{2}$  of tetrahalogenidoferrate (III)<sup>[41]</sup>. The maximum absorption peaks move into the direction of shorter wavelength upon elongation of the alkyl chain to the 3-position of imidazole ring. Due to the replacement of a portion of bromides with chlorides in FeCl<sub>m</sub>Br<sub>4-m</sub><sup>-</sup> anion observed in the Raman spectra (Fig. 1), the ligand field strength (\Delta) known by the spectrochemical sequence, which follows the order  $I^- < Br^- < CI^- < F^- < H_2O < C_2O_4^{-2-} < NH_3 < NO_2 < CN^-$ , increases. The transition energies are also expected to increase. Thus, a blue shift of the absorption peak can be observed (Fig. 2). Combining the results of Raman spectra, the covalency in Fe-X (X = Cl or Br) bonds also decreases with the replacement (Br is more nephelauxetic than Cl in the expected order), so the



**Figure 2**. Electronic absorption spectra of a, [VBIM][FeCl<sub>m</sub>Br<sub>4 - m</sub>] (m = 2, 3, 4); b, [VPIM] [FeCl<sub>m</sub>Br<sub>4 - m</sub>] (m = 3, 4); c, [VHIM] [FeCl<sub>m</sub>Br<sub>4 - m</sub>] (m = 3, 4) in acetonitrile

energy of the excited levels is strengthened and the factor is dominant in the observed spectra.

#### TGA

The thermal stabilities of  $[VRIM][FeCl_mBr_{4-m}]$  (R = n-butyl, m = 2, 3, 4; R = n-pentyl, m = 3, 4; R = n-hexyl, m = 3, 4) in nitrogen atmosphere were performed at a heating rate of  $283 \text{ K} \cdot \text{min}^{-1}$ . This process was repeated until the weight of the sample remained constant. Figure 3 shows that [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] is stable up to 573 K, and the loss of weight is sufficiently close to 0% below 573 K. This result indirectly indicates that the title substance has high purity. The thermal decomposition process includes two steps. The first one is rapid, and the weight losses are ca. 58.0%, 61.0%, and 57.0%, respectively. This degradation indicates the dissociative nature of the decomposition process without the participation of oxygen. The respective mass losses in the second step are ca. 13.0%, 14.0%, and 15.0%, showing the predominance of residual carbon oxidation. Thus, the anion for [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] is either FeCl<sub>4</sub><sup>-</sup> or FeBrCl<sub>3</sub><sup>-</sup>. Based on this assumption, the weight percentage of the cation is calculated (Table 1). Experiments indicate that the weight losses in the first decomposition are within the range of the above-calculated value, which reveals that the first step is cationic decomposition<sup>[42]</sup> and the final residue may be  $FeCl_mBr_{4-m}^{-}$  debris.<sup>[29]</sup>

#### Magnetism

Magnetic susceptibility ( $\chi_g$ ) exhibits a linear field dependency over the applied magnetic field range of -10,000 to 10,000 Oe, which corresponds to paramagnetic behavior (Fig. 4). Most of the ILs containing FeCl<sub>4</sub><sup>-</sup> exhibit a paramagnetic temperature dependence of  $\chi_g$ , with only small deviations from the Curie–Weiss law at low temperatures, thereby showing very weak antiferromagnetic interactions.<sup>[43]</sup>  $\chi_g$  of [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], [VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], and [VHIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] is  $33.3 \times 10^{-6}$ ,  $36.8 \times 10^{-6}$ , and  $36.9 \times 10^{-6}$  cm<sup>3</sup> · g<sup>-1</sup>, respectively. With the elongation of alkyl chain in the imidazole ring, the  $\chi_g$  of the title substance increases.

The  $\chi_g$  is approximately constant for the three compounds, whose relationship is given by  $\chi_M = \chi_g \times M$ , where M is molecular weight,  $\chi_g$  is expected to increase with the decrease of molecular weight, where  $M_{\text{[VBIM][FeCImBr4-m]}} > M_{\text{[VPIM][FeCImBr4-m]}}$ . This result demonstrates the increase in bromide substitution in [VRIM][FeCI\_mBr4-m] with the elongation of alkyl chain in the imidazole ring based on Raman spectra results.

Assuming that the anion  $FeCl_mBr_{4-m}^-$  is either  $FeCl_4^-$  or FeBrCl<sub>3</sub><sup>-</sup>, the effective magnetic moments ( $\mu_{eff}$ ) at 298.15 K are estimated to be in the range 4.89  $\mu_{\rm B}$  to 5.28  $\mu_{\rm B}$  for [VBIM] [FeCl<sub>m</sub>Br<sub>4-m</sub>], 5.64  $\mu_B$  to 5.98  $\mu_B$  for [VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], and 5.76  $\mu_B$  to 6.09  $\mu_B$  for [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>]. These results agree with the expected values from the S = 5/2 high-spin electronic state of iron (III), where the spin-only value is 5.92  $\mu_{\rm B}$ . Due to the replacement of bromide with chloride, the slight increase in  $\mu_{\text{eff}}$  is explained in terms of the lower ligand field strength D in FeCl<sub>m</sub>Br<sub>4-m</sub><sup>-</sup> (here, Br appears before Cl in the spectrochemical series) as  $\mu_{\rm eff} = \mu_0 (1 - 2\lambda/D)$ , where  $\mu_0$  is the spin-only value, and I is the spin-orbit coupling constant of the tetrahalogenoferrate (III) anion. In addition,  $\mu_{eff}$  for [VBIM]  $[FeCl_mBr_{4-m}]$  is far above the spin-only value 5.92  $\mu_B$  because of the assumption that the anion  $FeCl_mBr_{4-m}^-$  is either  $FeCl_4^$ or FeBrCl<sub>3</sub><sup>-</sup>. In fact, the anions for [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] are FeCl<sub>4</sub><sup>-</sup>, FeBrCl<sub>3</sub><sup>-</sup>, and FeBr<sub>2</sub>Cl<sub>2</sub><sup>-</sup>.



Figure 3. TGA of (a) [VBIM][FeCImBr4 - m] (m = 2, 3, 4); (b) [VPIM][FeCImBr4 - m] (m = 3, 4); (c) [VHIM][FeCImBr4 - m] (m = 3, 4);

#### Viscosity

Figure 5(a) shows the viscosities that follow the order [VPIM]  $[FeCl_mBr_{4-m}] < [VHIM][FeCl_mBr_{4-m}] < [VBIM][FeCl_mBr_{4-m}],$ with respective values of 89.0, 47.0, and 60.5 mPa · s at 298.15 K. High viscosities for ILs are mainly derived from hydrogen bond interaction and van der Waals force. Upon elongation of the alkyl chain, hydrogen bond interaction and van der Waals force follow the order [VBIM][FeCl\_mBr\_{4-m}] > [VPIM][FeCl\_mBr\_{4-m}] >  $[VHIM][FeCl_mBr_{4-m}]$  and  $[VBIM][FeCl_mBr_{4-m}] < [VPIM][FeCl_mBr_{4-m}]$ < [VHIM][FeCl<sub>m</sub>Br<sub>4-m</sub>]. Theoretical analysis and experimental results show that the change in viscosity behavior given by  $[VPIM][FeCl_mBr_{4-m}] < [VHIM][FeCl_mBr_{4-m}] < [VBIM][FeCl_mBr_{4-m}]$ is caused by the combined effect of hydrogen bonding and van der Waals force. As the temperature rises, ionic kinetic energy increases, which enables the ion to overcome the effect of assembly and hydrogen bonding interaction; the internal structure of ILs is similar to that of a macromolecule.<sup>[44]</sup> Figure 5(b) shows the Arrhenius plot of  $\eta$  for [VRIM][FeCl\_mBr\_{4-m}] in the temperature range of 293.15 K to 253.15 K. The trend of function  $ln(\eta)$  is almost linear with  $1000 \cdot T^{-1}$ , with all linear correlation coefficients  $R^2$ greater than 0.99. The temperature dependence of  $\eta$  is given by the Arrhenius equation

$$\eta = \eta_0 \exp(E_a(\eta)/\kappa_B T)$$

<b>Table 1.</b> The cationic percentage of weight under the supposition				
Anion	VBIM+ (w%)	VPIM+ (w%)	VHIM+ (w%)	
FeCl <sub>4</sub> <sup>-</sup>	59.34 38.45	60.92	62.37	
<sup>a</sup> FeBr <sub>2</sub> Cl <sub>2</sub>	30.43	40.09	42.55	

where  $\eta_0$  and  $\kappa_B$  are constants, and  $E_a(\eta)$  is the activation energy for viscous flow.  $E_a(\eta)$  is estimated from the slope of the best fit curve as  $E_a(\eta) = \text{slope} \times \kappa_B$ . Due to hydrogen bond interaction and van der Waals force, the respective activation energies  $E_a(\eta)$  for [VBIM][FeCl\_mBr\_4\_m], [VBIM][FeCl\_mBr\_4\_m], and [VBIM][FeCl\_mBr\_4\_m] are 20.68, 23.89, and 22.64 kJ·mol<sup>-1</sup>.

#### **lonic conductivity**

lonic conductivity ( $\sigma$ ) varies with the cationic species, as observed for viscosity. Figure 6(a) shows that  $\sigma$  increases with rising temperature and decreases with elongating alkyl chain in the cation. In particular, the respective  $\sigma$  values for [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>],



**Figure 4**. Relationship between the magnetization of [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] and the applied magnetic field. Experimental point: **•**, [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 2, 3, 4);  $\circ$ , [VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4); **▲**, [VHIM] [FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4)



**Figure 5**. Temperature dependence of viscosity for [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], (a)  $\eta$  vs. T plot and (b) ln  $\eta$  vs. 1000 ·  $T^{-1}$  plot. Experimental point: **a**, [VBIM] [FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 2, 3, 4); •, [VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4); •, [VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4);



**Figure 6**. Temperature dependence of ionic conductivity for [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], (a)  $\sigma$  vs. T plot and (b)  $\ln\sigma$  vs.1000 ·  $T^{-1}$  plot. Experimental point: **a**, [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 2, 3, 4); •, [VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4); •, [VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] (m = 3, 4);

[VPIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], and [VHIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] are 5.1, 3.8, and 3.5 S · m<sup>-1</sup> × 10<sup>-3</sup> at 298.15 K, which are nearly similar to those of [BMI][FeCl<sub>4</sub>].<sup>[16]</sup> Figure 6(b) shows the Arrhenius plots of  $\sigma$  for [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], in which the trend of ln( $\sigma$ ) is almost linear with 1000 ·  $T^{-1}$  ( $R^2 > 0.99$ ) for the temperature range 293.15 K to 353.15 K. The conductivity can be expressed using the Arrhenius equation

$$\sigma = \sigma_0 \exp(-E_a(\sigma)/\kappa_B T)$$

where  $\sigma_0$  and  $\kappa_B$  are constants, and  $E_a(\sigma)$  is the activation energy for ionic conduction.  $E_a(\sigma)$  is estimated from the slope of the

best fit curve as  $E_a(\sigma) = \text{slope} \times \kappa_B$ , which is found to be 20.80, 22.21, and 22.95 kJ·mol<sup>-1</sup> for [VBIM][FeCl\_mBr<sub>4-m</sub>], [VBIM] [FeCl\_mBr<sub>4-m</sub>], and [VBIM][FeCl\_mBr<sub>4-m</sub>], respectively. The key influential factors of electrical conductivity are liquid density, molecular weight, viscosity, and ionic size. Higher viscosity implies poorer electrical conductivity, but the behavior of liquid density on ionic conductivity is opposite that of viscosity on ionic conductivity. For ILs with similar viscosities and densities, molecular weight and ionic size are important in ionic conductivity. Generally, a smaller ion implies better ionic conductivity. The viscosity for [VRIM][FeCl\_mBr<sub>4-m</sub>] follows the order  $\eta_{\text{[VBIM][FeCl_mBr_4-m]} > \eta_{\text{[VHIM][FeCl_mBr_4-m]} > \eta_{\text{[VHIM][FeCl_mBr_4-m]} > \eta_{\text{[VHIM][FeCl_mBr_4-m]}}$  and the density follows the

Table 2. The solubility of MILs in different solvents <sup>a</sup>				
MILs Solvent mass/10 g	[VBIM][FeCImBr4 — m] (m = 2, 3, 4)	[VPIM][FeClmBr4 — m] (m = 3,4)	[VHIM][FeCImBr4 - m] (m = 3,4)	
Watar		0.22 ~(a)	0.12 (-)	
Ethanol	0.26 g(s) 0.14 g(s)	0.22 g(s) 0.13 g(s)	0.13 g(s) 0.12 g(s)	
Ethyl acetate	0.09 g(sl)	0.26 g(sl)	0.27 g(sl)	
Ethyl ether	0.003 g(i)	0.006 g(i)	0.005 g(i)	
Benzene	0.07 g(sl)	0.06 g(sl)	0.05 g(sl)	
Ethyl ether Benzene <sup>a</sup> solubility of MILs at 298.1	0.003 g(i) 0.003 g(i) 0.07 g(sl) 15 K, sl—slightly soluble; s—soluble; i-	0.006 g(i) 0.06 g(sl) —indissolvable	0.27 g(3 0.005 g( 0.05 g(s	

order  $\rho_{\text{[VBIM][FecImBr4-m]}} > \rho_{\text{[VPIM][FecImBr4-m]}} > \rho_{\text{[VHIM][FecImBr4-m]}}$ . In particular, the respective densities for [VBIM][FeCImBr4-m], [VPIM] [FeCImBr4-m], and [VHIM][FeCImBr4-m] are 1.607, 1.464, and 1.456 g·cm<sup>-1</sup> at 298.15 K. Thus, ionic conductivity follows the order  $\sigma_{\text{[VBIM][FecImBr4-m]}} > \sigma_{\text{[VPIM][FecImBr4-m]}} > \sigma_{\text{[VHIM][FecImBr4-m]}}$  with the elongation of the alkyl chain.

#### Solubility

Good solubility of title compounds in polar and nonpolar solvents is remarkable. [VRIM][FeCl<sub>m</sub>Br<sub>4 - m</sub>] is also soluble in  $H_2O$  and alcohol, slightly soluble in ethyl acetate and benzene, and insoluble in diethyl ether. Generally, salts with imidazolium cation are insoluble in water and do not hydrolyze in water. However, the trend of the title substance solubility is significantly similar to that of already known MILs, which contain tetrahalogenidoferrate (III) anions and show high solubility in polar solvents, especially in H<sub>2</sub>O. Due to the existence of a big hydrophobic grouping (imidazolium ring), salts with imidazolium cations are insoluble in water and do not hydrolyze in it. However, tetrahalogenidoferrate (III) anion is associated with water molecules through hydrogen bonding interactions, causing solubility of the title substances in H<sub>2</sub>O and alcohol. The foregoing causes the H... $\pi$  bond between benzene and ionic liquids to increase solubility in benzene.<sup>[45]</sup> Due to the different electron-donating abilities of alkyl, the elongation of the alkyl chain weakens the electropositivity of cations, which affects polarity decrease. The solubility of the title compounds in polar solvents successively lowers and improves in nonpolar solvents (Table 2) and depends on the theory of similarity and compatibility.

# CONCLUSIONS

The design and synthesis of [VRIM][FeCl<sub>m</sub>Br<sub>4-m</sub>] have been successfully accomplished. For magnetic ILs, the influence of alkyl chain length on the cation in terms of ionic association of Fe–X, anionic composition, and physical properties is analyzed. The absorption peak shifts toward lower wavelengths. Magnetic susceptibility, ionic conductivity, and solubility in polar solvents are reduced, and fluidity (except for [VBIM][FeCl<sub>m</sub>Br<sub>4-m</sub>], m = 2, 3, 4) and solubility in nonpolar solvents increase as the alkyl chain length elongates. The trend of solubility is in accordance to the theory of similarity and compatibility.

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