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Physicochemical Properties of Tungstate-Based Room-Temperature Ionic Liquids

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Tungstate-functionalized room-temperature ionic liquids (ILs), 1-alkyl-3-methylimidazolium tungstates $[RMIm]_2[WO_4]$ (R = C_6H_{13} or $C_{12}H_{25}$), were synthesized and the IL's structure has been proved by NMR, Fourier transform IR, and elemental analysis. The physicochemical characteristics of the tungstate-based ILs have been determined by using methods of conductivity, viscosity, and cyclic voltammetry measurements, in comparison with those of the conventional ILs such as 1-hexyl-3-methylimidazolium methanesulfonate and 1-hexyl-3-methylimidazolium hexafluorophosphate. The influences of anions and the length of alkyl chain linked to the imidazolium ring on physicochemical properties of the ILs were examined in detail. All ILs owned higher conductivities and lower viscosities at higher temperatures. The strong intramolecular hydrogen bonds were found in the tungstate-based ILs. Cyclic voltammograms of the functionalized ILs illustrated that they were quite electrochemically stable. In general, the understanding of electrochemical properties of imidazolium ILs can facilitate their possible applications in electrochemistry.

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Ionic liquids (ILs) are receiving increasing attention from both industry and academics, and research involving ILs is expanding to many different areas of knowledge.^{1,2} There are so many attractive physical and chemical properties of the ILs,^{3,6} including a negligible vapor pressure, low inflammability, high thermal stability, liquidity over a wide temperature range, easy recycling, and being a good solvent for a wide variety of organic and inorganic chemical compounds.

Of all the imidazolium room-temperature ionic liquids (RTILs), most of them are air- and water-stable and with higher thermal stability compared to other kinds of ILs. The imidazolium RTILs, which are "designable" as structural modifications in both cations (especially the 1 and 3 positions of the imidazolium ring) and anions, permit the tuning of properties such as electrochemical stability,⁵ miscibility with water and/or organic solvents,⁷ melting point, viscosity,⁴ etc. Recently, the discovery of new imidazolium RTILs by the suitable choice of the anion initiates intensive research efforts toward the potential application.⁸⁻¹²

Electrochemistry of imidazolium RTILs is a very attractive area of research, which is due to their chemical and electrochemical stability, wide electrochemical windows, high electrical conductivities, and ionic mobilities.^{4,5,13-16} Electrochemical applications of imidazolium RTILs as electrolytes are found in, e.g., fuel cells,¹⁷ electrodeposition,¹⁸ capacitors,¹⁹⁻²¹ solar cells,^{22,23} batteries,²⁴ and water electrolysis for hydrogen generation.²⁵ These ILs usually consist of an inorganic or organic anion, whereas the most commonly used IL anions include halide ions, tetrachloroaluminate (AlCl₄), tetrafluoroborate (BF₄), hexafluorophosphate (PF₆), and bis[(trifluoro-methyl)sulfonyl]imide anion (CF₃SO₂)₂N⁻ [also known as bistriflylimide (Tf₂N⁻)].

Needless to say, understanding the physicochemical properties of ILs is important to provide information about their application scope.^{26,27} Herewith, novel tungstate-based RTILs 1-hexyl-3-methylimidazolium tungstate $[HMIm]_2[WO_4]$ and 1-dodecyl-3-methylimidazolium tungstate $[DMIm]_2[WO_4]$ can be obtained by a simple anion exchange of imidazolium bromide with silver tungstate, and then the physicochemical properties of these RTILs, including the temperature dependency of the dynamic ionic conductivity, viscosity, and the electrochemical stability of these RTILs, are determined and analyzed according to the nature of the cations and/or anions in detail, which are also compared with those of the

conventional RTILs 1-hexyl-3-methylimidazolium methanesulfonate $[HMIm][CH_3SO_3]$ and 1-hexyl-3-methylimidazolium hexafluorophosphate $[HMIm][PF_6]$. This study mainly discusses the electrostatic interaction, the hydrogen bonding, and van der Waals interactions in these RTILs and attempts to enable many structure– property trends to be identified, including the effect of both cations and anions.

Experimental

General remarks.— All manipulations involving air-sensitive materials were carried out using standard Schlenk line techniques under an atmosphere of nitrogen. CH_2Cl_2 and Et_3N (analytic reagent grade) were distilled from CaH_2 before use. Commercially available ethyl acetate, diethyl ether, 1-hexanol, 1-methylimidazole, 1-bromohexane, 1-bromododecane, silver nitrate, sodium tungstate, and methanesulfonyl chloride were purchased from Sinopharm Chemical Reagent Co. Ltd. and used without further purification.

The IL samples were dried further at 70°C under vacuum for 2 h before conducting thermogravimetric analysis (TGA) and electrochemical measurements. All NMR spectra were recorded on a Bruker Advance 500 instrument (500 MHz¹H, 125 MHz¹³C) using chloroform-D (CDCl₃) and tetramethylsilane as solvent and reference, respectively. Chemical shifts (δ) were given in ppm and coupling constants (J) in hertz. Fourier transform infrared (FTIR) spectra were recorded at room temperature on a Nicolet FTIR spectrometer (Magna 550). The elemental analysis of C, H, and N was performed on an Elementar Vario EI III Elementa and inductively coupled plasma-atomic emission spectroscopy analysis of W on a TJA IRIS 1000 instrument. The water content of the dried ILs was determined by Karl Fischer titration using a KF-1B Karl Fischer coulometer (Shanghai, China). A Perkin-Elmer Pyris Diamond was used in the current study for the TGA measurements. A constant heating rate of 10° C min⁻¹ and high purity nitrogen purge $(100 \text{ mL min}^{-1})$ was used for all the measurements. The standard material used for calibrating the equipment was α -sapphire powder (Perkin-Elmer). The rheological (viscosity) measurements were performed on a Physica MCR 501 (Anton Paar GmbH) rheometer with 25 cm parallel plate geometry and a gap of 1 mm. The temperature was controlled by a Peltier plate. Conductivity experiments were carried out on a DDS-307 conductivity meter (Shanghai Jingke, China). Electrochemical experiments were carried out on a CHI 430A electrochemical workstation (Shanghai Chenhua, China) with a three-electrode system, a glassy carbon electrode as the working electrode and a platinum counter electrode as the auxiliary electrode.

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A nonaqueous Ag/AgCl reference electrode was used in all measurements. It consists of a AgCl-coated Ag wire, which was immersed in the IL in a sealed glass tubing with an ion porous Vycor glass tip. The cyclic voltammetry (CV) measurement was carried out at room temperature.

The synthesis of 1-hexyl-3-methylimidazolium bromide.— 0.05 mol 1-methylimidazole (4.10 g) and 0.05 mol 1-bromohexane (8.25 g) were stirred at 90°C under 1.0 MPa nitrogen atmosphere in a stainless steel autoclave (50 mL) for 24 h, cooled to room temperature and washed with ethyl acetate (3×15 mL), and then dried under reduced pressure to afford 1-hexyl-3-methylimidazolium bromide ([HMIm]Br) as a colorless, viscous product (11.62 g, 94%).

The synthesis of silver tungstate (Ag_2WO_4) .— The aqueous solution of 0.05 mol AgNO₃ (8.49 g) was added to the solution of 0.025 mol Na₂WO₄ (8.25 g) in the dark, and then a pale yellow precipitate was produced immediately and washed with deionized water three times.

The synthesis of $[HMIm]_2[WO_4]$.— The aqueous solution of 0.047 mol [HMIm]Br (11.62 g) was added to the freshly prepared Ag₂WO₄. The color of the precipitate changed obviously from pale yellow to yellow and, simultaneously, the particle size became bigger. The reaction mixture was stirred for an additional period of 0.5 h and filtered, and then the transparent colorless filtrate was concentrated and dried under reduced pressure to afford the colorless liquid product [HMIm]_2[WO_4] (12.72 g, 93%). The as-synthesized IL contained no residue of Ag⁺ or Br⁻ ions by elemental analysis, and water content in the IL is 0.8% by Karl Fischer titration. [Found: C, 38.25; H, 6.88; N, 8.86; W, 29.74%. C₂₀H₃₈N₄O₄W requires C, 38.84; H, 6.85; N, 9.06;W, 29.73%. $\delta_{\rm H}$ (500 MHz, CDCl₃): 0.79 (3H, t, CH₃), 1.22 (6H, m, C₃H₆), 1.81 (2H, m, CH₂), 3.82 (3H, s, CH₃), 4.14 (2H, t, CH₂), 7.41 (1H, s, CH), 7.70 (1H, s, CH), 9.90 (1H, s, CH).]

The synthesis of $[DMIm]_2[WO_4]$.— The synthesis route of 1-dodecyl-3-methylimidazolium bromide ([DMIm]Br) was very similar to that of [HMIm]Br. The product [DMIm]Br was obtained as a colorless, viscous product in high yield (96%).

The synthesis of $[DMIm]_2[WO_4]$.— The aqueous solution of 0.048 mol [DMIm]Br (15.90 g) was added to the freshly prepared Ag₂WO₄. The color of the precipitate changed immediately to yellow and the reaction mixture was continuously stirred at 60°C for 12 h. The precipitate was filtered. Then the transparent yellow filtrate was evaporated and dried under reduced pressure to afford the yellow liquid $[DMIm]_2[WO_4]$ (16.58 g, 92%). The as-synthesized IL contained 17.7 ppm Ag⁺ and a trace of Br⁻ by elemental analysis, and water content in the IL was 0.7% by Karl Fischer titration. [Found: C, 49.58; H, 8.60; N, 7.20; W, 21.46%. C₃₂H₆₂N₄O₄W requires C, 48.85; H, 8.46; N, 7.12; W, 23.37%. $\delta_{\rm H}$ (500 MHz, CDCl₃): 0.86 (3H, t, CH₃), 1.11 (2H, m, CH₂), 1.23 (16H, m, C₈H₁₆), 1.84 (2H, m, CH₂), 4.11 (3H, s, CH₃), 4.22 (2H, t, CH₂), 7.26 (1H, s, CH), 7.52 (1H, s, CH), 9.85 (1H, s, CH).]

The synthesis of $[HMIm][CH_3SO_3]$.— $[HMIm][CH_3SO_3]$ was synthesized according to our previously reported procedure.²⁸ Briefly, the reaction of 1-methylimidazole with hexyl methane-sulfonate afforded $[HMIm][CH_3SO_3]$ in high yield (>95%).

Hexyl methanesulfonate was synthesized by the following steps: A solution of 1-hexanol (4.09 g, 40 mmol) and triethylamine (7.8 mL, 56 mmol) in dichloromethane (30 mL) was cooled in an ice bath as methanesulfonyl chloride (3.6 mL, 46 mmol) in dichloromethane (10 mL) was added dropwise. An external water bath was used to control the reaction mixture temperature between 10 and 20°C. After addition, stirring was continued for another 2 h. Then water (25 mL) was added; the aqueous layer containing the triethylammonium chloride by-product was separated; the organic layer was washed sequentially with a saturated solution of NaHCO₃ and



Figure 1. FTIR spectra of the different ILs.

water, and finally dried with sodium carbonate. The organic solvent was evaporated under reduced pressure to afford the desired hexyl methanesulfonate as a colorless liquid (6.60 g, 92%). $\delta_{\rm H}$ (500 MHz, CDCl₃): 1.28 (3H, t, CH₃), 1.34 (4H, m, C₂H₄), 1.75 (2H, m, CH₂), 3.00 (3H, s, CH₃), 4.22 (2H, t, CH₂).

Hexyl methanesulfonate (6.60 g, 36.8 mmol) was mixed with 1-methyl-imidazole (3.00 g, 37 mmol) and the reaction mixture was kept at room temperature for 12 h, then the reaction temperature was raised to 60°C for 48 h with vigorous stirring. After the reaction, the product was recrystallized at 0°C three times using ethyl acetate as a solvent (20 mL). Then after vacuum drying, a pale yellow liquid [HMIm][CH₃SO₃] was obtained as a slightly yellow liquid (8.54 g, 89%). The water content in the IL was 0.02% by Karl Fischer titration. [Found: C, 50.32; H, 8.47; N, 10.63; S, 12.25%. C₁₁H₂₂N₂O₃S requires C, 50.36; H, 8.45; N, 10.68; S, 12.22%. $\delta_{\rm H}$ (500 MHz, CDCl₃): 0.79 (3H, t, CH₃), 1.21 (6H, m, C₃H₆), 1.80 (2H, m, CH₂), 2.68 (3H, s, CH₃), 3.97 (3H, s, CH₃), 4.18 (2H, t, CH₂), 7.41 (1H, s, CH), 7.55 (1H, s, CH), 9.68 (1H, s, CH).]

The synthesis of $[HMIm][PF_6]$.— [HMIm][PF₆] was simply synthesized by an anion exchange reaction between [HMIm][CH₃SO₃] and KPF₆ in water. The precipitate was washed with water three times and then dried under vacuum, and then [HMIm][PF₆] was obtained as a colorless liquid. The water content in the IL was 0.01% by Karl Fischer titration. [Found: C, 38.49; H, 6.16; N, 8.96; P, 9.84; F, 36.48%. C₁₀H₁₉N₂PF₆ requires C, 38.47; H, 6.13; N, 8.97; P, 9.92; F, 36.51%. $\delta_{\rm H}$ (500 MHz, CDCl₃): 0.88 (3H, t, CH₃), 1.32 (4H, m, C₂H₄), 1.56 (2H, m, CH₂), 1.87 (2H, m, CH₂), 3.93 (3H, s, CH₃), 4.15 (2H, t, CH₂), 7.25 (1H, s, CH), 7.26 (1H, s, CH), 8.56 (1H, s, CH).]

Results

Characterization of $[HMIm]_2[WO_4]$ and $[DMIm]_2[WO_4]$.— The structures of as-synthesized $[HMIm]_2[WO_4]$ and $[DMIm]_2[WO_4]$ were first confirmed by ¹H NMR and elemental analysis. In addition, FTIR and TGA have also been utilized to prove the existence of anions and determine the thermal stability of the ILs, respectively. The FTIR bands of $[HMIm]_2[WO_4]$ and $[DMIm]_2[WO_4]$ are shown in Fig. 1; obviously they were very similar. The characteristic bands of alkyl groups in imidazolium rings were observed around 2958, 2930, 2860, 1466, and 1380 cm⁻¹. The bands around 1650 and 1570 cm⁻¹ were due to C=N and C=C ring vibrations of the imidazolium cation part of two ILs.²⁹ The typical large absorption band of the WO₄²⁻ anion from ~700 to 900 cm⁻¹, ³⁰⁻³² which was reported to be ascribed to the W–O stretching vibration in the WO₄ tetrahedron, is shown in



Figure 2. The TGA trace of [HMIm]₂[WO₄] and [DMIm]₂[WO₄].

both ILs. Meanwhile, the pronounced bands of the 1-hexyl-3methylimidazolium cation of both ILs [HMIm][PF₆] and [HMIm][CH₃SO₃] were clearly observed in FTIR. Also, the feature bands of PF₆ anion³³ in 839.0 cm⁻¹ as well as the bands of CH₃SO₃ anion³⁴ in 1192.4, 1043.0, and 773.3 cm⁻¹ significantly existed in [HMIm][PF₆] and [HMIm][CH₃SO₃]. Although the typical bands of WO₄²⁻ and PF₆⁻ were overlapped in the low wavenumber region, as shown in Fig. 1, the tungstate-based ILs were not produced from PF₆-based ILs, so the presence of WO₄²⁻ in [HMIm]₂[WO₄] and [DMIm]₂[WO₄] was confirmed very clearly. In combination with NMR spectra and the elemental analysis (ICP), it can be seen that the as-synthesized ILs were very pure.

The thermal stability of the two ILs ($[HMIm]_2[WO_4]$ and $[DMIm]_2[WO_4]$) was investigated using the TGA method. As shown in Fig. 2, both ILs were decomposed by two successive weight-loss regions: The weight-loss region above 220 and 400°C can be attributed to the gradual decomposition of the imidazolium cation part (63.3% loss for $[HMIm]_2[WO_4]$ and 70.5% loss for $[DMIm]_2[WO_4]$).³⁵ No further decomposition was observed up to 450°C. Two ILs with different alkyl chain lengths nearly had the same thermogravimetric–differential thermal analysis curves, which suggested that the imidazolium cation had insignificant effects on the thermostability of the ILs.

Discussion

Hydrogen bonding formation in [HMIm][PF₆], [HMIm] $[CH_3SO_3]$, $[HMIm]_2[WO_4]$, and $[DMIm]_2[WO_4]$. An important aspect of RTILs is the nature of the interactions among the ions present, and questions of particular interest include how the interaction affects the properties. In the present work, we first used ¹H NMR to investigate the alkyl chain length in the imidazolium ring and the anion effects on the trend of forming hydrogen bonds in this class of ILs. The three protons in the IL imidazolium ring were distinguished by the commonly adopted annotation H2, H4, and H5 as reported.³⁶⁻³⁸ H2 hydrogen represented the substituent at the carbon between the two nitrogens. H4 denoted the hydrogen substituent at the imidazole ring carbon close to the methyl group, whereas H5 hydrogen was the substituent at the ring carbon in the vicinity of the long alkyl chain. The proton NMR chemical shift data of the ILs are shown in Table I. From the listed ILs in Table I, the chemical shift variations in H4 and H5 were not significant, but H2 exhibited a much broader chemical shift variation than either H4 or H5, with 9.68 in the IL [HMIm][CH₃SO₃], 8.56 in the IL [HMIm][PF₆], and about 9.90 in [HMIm]₂[WO₄]. This can be explained such that H2 was more acidic and more sensitive to anion effects than H4 or H5,³⁹ which also implied that the more basic $CH_3SO_3^-$ and WO_4^{2-} anions show a stronger interaction with H2 proton than PF_6^- anion.

Table I. The chemical shifts of H2, H4, and H5 in ¹H NMR spectra for the different ILs.

IL	H2	H4	Н5
[HMIm][CH ₃ SO ₃]	9.68	7.55	7.41
[HMIm] ₂ [WO ₄]	9.90	7.70	7.41
[DMIm] ₂ [WO ₄]	9.85	7.52	7.26
[HMIm][PF ₆]	8.56	7.26	7.23

Together with the fact that the H2 proton normally moved significantly downfield with increasing acidity,⁴⁰ the hydrogen bond was more pronounced at the H2 protons than at the H4 and H5 protons. Considering the H2 chemical shift data in the three ILs, the hydrogen bonding decreased in the following order: [HMIm]₂[WO₄] > [HMIm][CH₃SO₃] > [HMIm][PF₆]. This can be explained by the fact that the electrostatic interaction in [HMIm]₂[WO₄] was stronger than that in [HMIm][CH₃SO₃] and [HMIm][PF₆] because of a higher negative charge WO₄^{2–} anion, and the higher charge density should result in a stronger hydrogen bonding interaction.

Vibrational spectroscopy is another versatile tool in probing the hydrogen bonding of both liquid and solid compounds or their solutions. Hence, the IR spectra of the four ILs are given in Fig. 1 and confirmed the structures of the ILs. The peaks between 3100 and 3200 cm⁻¹ can be attributed to the vibration of the imidazolium ring C-H stretch vibration, whereas those between 2800 and 3000 cm⁻¹ can be attributed to aliphatic C-H stretches. The imidazolium ring C-H stretch vibration of [HMIm][PF₆] appears in 3172.1 and 3120.9 cm⁻¹, which are much higher frequencies than those of 3150.5 and 3106.0 cm⁻¹ in [HMIm][CH₃SO₃] as well as 3143.5 and 3102.8 $\,\,\mathrm{cm^{-1}}$ in $[\,\mathrm{HMIm}]_2[\,\mathrm{WO}_4].$ Upon formation of the hydrogen bond, the C-H bond was weakened and, thus, the frequency of its stretching vibration is normally decreased.³⁹ Therefore, the strength of the hydrogen bond between the H2 proton and anions decreased in the order $WO_4^{2-} > CH_3SO_3^- > PF_6^-$, which agreed well with the ¹H NMR characterization.

Because ILs $[HMIm]_2[WO_4]$ and $[DMIm]_2[WO_4]$ gave no significant differences from the characterization of the FTIR and ¹H NMR chemical shift (Fig. 1 and Table I), the length of the alkyl chain in the imidazolium ring most possibly had no obvious effect on the hydrogen bond formation.

The conductivity of [HMIm][PF₆], [HMIm][CH₃SO₃], $[HMIm]_2[WO_4]$, and $[DMIm]_2[WO_4]$.— The ionic conductivity is a transport property and is governed by the degree of dissociation of the ion, which is related to ion mobility, ionic charge, and ion number involved in the conduction process. Figure 3 shows the conductivities of ILs [HMIm][PF₆], [HMIm][CH₃SO₃], [HMIm]₂[WO₄], and [DMIm]₂[WO₄] at different temperatures. The conductivity values of [HMIm][PF₆] measured in this work agreed well with those reported,⁴³ which indicated that the present data were reliable. The same conductivity-temperature correlation was observed for all the four ILs. Higher temperatures resulted in higher conductivities. Furthermore, a small increase in conductivity was observed in the lower temperature range and a large increase was observed in the higher temperature range. Temperature at the intersection of the low and high temperature range dependent on conductivity was defined as $T_{\rm is}$, which indicated that the transport processes were differently affected below and above this temperature (Table II). Further, the conductivity of [HMIm][PF₆] was the highest among ILs at the same temperature, whereas the conductivities of $[HMIm]_2[WO_4]$ were higher than that of [DMIm]₂[WO₄]. The conductivity of [HMIm][CH₃SO₃] was slightly lower than that of [HMIm][PF₆] but much higher than that of the corresponding tungstate anionbased IL [HMIm]₂[WO₄].

For the imidazolium ILs, the positive charge is normally delocalized on the imidazolium ring, that is, the long alkyl side chain fa-



Figure 3. Conductivities of the ILs at different temperatures.

cilitates dispersive interactions with the anion and intermolecular binding. Further, van der Waals interactions become more attractive when the length of the alkyl group is increased. Therefore, the fact that the conductivities of $[HMIm]_2[WO_4]$ were higher than $[DMIm]_2[WO_4]$ with the longer alkyl chain was expected.

electrostatic interaction between the The 1-alkvl-3methylimidazolium cation and $CH_3SO_3^-$ or PF_6^- anion was much weaker than that between the cation and the two negative charge WO_4^{2-} anion. Thus, $CH_3SO_3^{-}$ and PF_6^{-} were more mobile anions than WO_4^2 anion, which induced that the conductivity of [HMIm]₂[WO₄] was lower than that of [HMIm][CH₃SO₃] or $[HMIm][PF_6]$. Moreover, in comparison with $[HMIm][PF_6]$, [HMIm][CH₃SO₃] shows a lower conductivity, which can be attributed to the stronger hydrogen bond interaction of $CH_3SO_2^-$ with H2 proton. Figure 4 shows the Arrhenius conductivity plots of ILs $[HMIm][PF_6],$ [HMIm][CH₃SO₃], $[HMIm]_2[WO_4],$ and $[DMIm]_2[WO_4]$ as a function of temperature. All experimental data in the temperature range studied fitted well the conventional Arrhenius equation 1



Figure 4. Arrhenius conductivity plots of the ILs.

$$\ln \sigma = \ln A - (E_{a}/RT)$$
[1]

where E_a is the activation energy for electrical conduction (the energy needed for an ion to jump to a free hole), calculated from the Arrhenius formula presented in Table II. The tungstate-based ILs show higher charge-transfer activation energies. The activation energies E_a decreased in the order [DMIm]₂[WO₄] > [HMIm]₂[WO₄] > [HMIm][CH₃SO₃] > [HMIm][PF₆].

The viscosity of $[HMIm][PF_6]$, $[HMIm]_2[WO_4]$, and $[DMIm]_2[WO_4]_{--}$ Because ILs are more viscous than conventional solvents, this is an important property for possible application. Figure 5 shows the dynamic viscosities of ILs $[HMIm][PF_6]$, [HMIm]₂[WO₄], and [DMIm]₂[WO₄] at different temperatures. The viscosity values of $[HMIm][PF_6]$ in this work agreed well with those reported.⁴⁴ The viscosities of either $[HMIm]_2[WO_4]$ or $[DMIm]_2[WO_4]$ are much higher than those of the conventional IL such as [HMIm][PF₆] (Fig. 5), or 1-alkyl-3-methylimidazolium methanesulfonate, which was reported.⁴⁵ In addition, the viscosity of ILs was inversely correlated with conductivity at the same temperature. For example, the less viscous tungstate-based IL $([HMIm]_2[WO_4])$ owned the higher conductivity (Fig. 3 and 5), which agreed with phenomena previously reported.^{46,47} Because the viscosities of dialkylimidazolium ILs are dictated by a combination of electrostatics, van der Waals interactions, hydrogen bonding, ion size, and polarizability, 8,48 [HMIm]₂[WO₄] had a higher viscosity than conventional ILs such as hexafluorophosphate and methyl sulfonate anion-based ILs, which could be ascribed to a stronger electrostatic interaction between imidazolium cation and WO_4^{2-} anion.⁴⁸ Moreover, [DMIm]₂[WO₄] with a longer alkyl group possessed a higher viscosity than [HMIm]₂[WO₄] due to stronger van der Waals

Table II. Activation energy, conductivity intersection, and linearity correlation of the ILs.						
Entry	IL	E_a^a (kJ mol ⁻¹)	E_a^{a} (eV)	T_{is}^{b} (°C)	R^2	
1	[HMIm][CH ₃ SO ₃]	42.9	0.445	48	1.000	
2	[HMIm][PF ₆]	33.9	0.351	43	0.953	
3	$[HMIm]_2[WO_4]$	66.5	0.689	56	1.000	
4	$[DMIm]_2[WO_4]$	96.5	1.000	57	0.982	

^a Activation energy calculated from the Arrhenius formula.

^b Temperature at the intersection of the low and high temperature range of the temperature-dependent conductivity.



Figure 5. Dynamic viscosities as a function of temperature for different ILs.

interactions. This behavior confirmed that, although the high electrostatic interactions between ions determined the characteristic physicochemical properties of ILs, dispersive van der Waals-type forces also played an important role and determined the way the viscosity changes with the size of the alkyl side chain. The viscosities for two tungstate-based ILs measured at different temperatures (30–80°C) gave slightly curved Arrhenius plots (Fig. 6), which has been observed in dialkylimidazolium ILs and metal complex polyether molten salts.^{49,50} A classical explanation for such behavior would involve coupling of chain motions (alkyl and polyether) with the physical transport process.⁵¹

The CV of $[HMIm]_2[WO_4]$ and $[HMIm][CH_3SO_3]$.— The potential windows for the tungstate-functionalized ILs have been measured by CV. Figure 7 shows the cyclic voltammograms of pure ILs $[HMIm][CH_3SO_3]$ and $[HMIm]_2[WO_4]$ recorded at room tempera-



Figure 6. Arrhenius viscosity plots of the different ILs.



Figure 7. Cyclic voltammogram of pure ILs $[HMIm][CH_3SO_3]$ and $[HMIm]_2[WO_4]$. The vertical coordinate [current (A)] was reduced 20 times for IL $[HMIm]_2[WO_4]$ (inset).

ture with a scan rate of 0.1 V/s. The electrochemical behavior of conventional imidazolium ILs has been well documented.⁵⁰ In the present work, there was no visible shoulder of $[HMIm][CH_3SO_3]$ or $[HMIm]_2[WO_4]$ over the range from -2 to 2 V. The reduction of imidazolium cations in the cathodic electrode may proceed initially by the reduction of ring protons to molecular hydrogen, which usually determines the cathodic window of the IL.⁵² Electro-oxidation charge-transfer processes could occur at the positive potential range, probably involving the adsorbed species formed previously on the anodic electrode.¹⁵ This suggested that the electrochemical potential window of two ILs $[HMIm][CH_3SO_3]$ and $[HMIm]_2[WO_4]$ at room temperature is found to be nearly 4 V, agreeing with previous studies.⁴ The cyclic voltammograms of $[DMIm]_2[WO_4]$ displayed a similar behavior to that of $[HMIm]_2[WO_4]$. Thus, it came to the conclusion that the novel tungstate-based ILs show nearly the same electrochemical window as the conventional ILs.

Conclusions

In summary, the synthesis of the new tungstate-based imidazolium ILs, $[HMIm]_2[WO_4]$ and $[DMIm]_2[WO_4]$, was first reported here. The ¹H NMR, FTIR, conductivity, viscosity, and cyclic voltammogram of the tungstate-based ILs were conducted to characterize the physicochemical properties of the ILs, which were then compared with those of conventional ILs such as $[HMIm][PF_6]$ and $[HMIm][CH_3SO_3]$. The effects of the anions and the length of the alkyl chain in the imidazolium ring on the electrochemical properties have been mainly investigated. The tungstate anion has a decisive influence on conductivity, viscosity, and cyclic voltammogram, as well as the intramolecular hydrogen bonding interaction, although the length of the alkyl group in the imidazolium ring also affected to some extent the electrochemical properties of ILs. The tungstatebased ILs show good electrochemical stability as the conventional ILs.

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