

Study on the Performance of the Ionic Liquids [Emim]CH₃SO₃ and [Emim]PF₆ to Prepare the Biosensor of the Detection of Heavy Metals in Seawater

Xuhui Ma, Shipeng Zhao and Shuping Zhang*

College of Science, University of Shanghai for Science and Technology, Shanghai 200093, China

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Abstract: Electrochemical sensors can detect the heavy metal ions in seawater quickly, conveniently and accurately with the advantages such as the fast detection speed, the simple operability and the low cost. The ionic liquid [Emim]CH₃SO₃ showed excellent electrochemical performance and could meet the initial application requirements as electrochemical sensors. The characters of the ionic liquids [Emim]CH₃SO₃ and [Emim]PF₆ which include IR, LC-MS, conductivity, electrochemical window and viscosity were detected. The influence of trace impurity on the conductivity of the ionic liquids was investigated. Results suggested that the conductivity of the ionic liquids increased with the concentration of the added organic solvents. In addition, though the conductivity of the ionic liquids increased with temperature, there is no significant difference in the influence of the same impurity at varying temperatures. Multi Walls Carbon Nanotubes (MWCNTs) are appropriate materials which are commonly used materials for electrochemical sensor applications. The effect of the imidazolium-based ionic liquids on the performance of the conductivity of the MWCNTs was studied. It was found that Ionic liquid is an excellent extraction agent for metal ions and its presence in the sensor system improves significantly the detection of heavy metal ions.

Keywords: heavy metal ions, sea water, ionic liquid; conductivity; electrochemistry

1. INTRODUCTION

An ionic liquid is also called as a room temperature molten salt, an organic ionic liquid, or a room-temperature ionic liquid, etc. It refers to a salt in the liquid state, completely constituted by ions under room temperature. It is another environmentally friendly solvent system following water and supercritical carbon dioxide. An ionic liquid is generally colorless and usually composed by nitrogen, phosphorus organic cations and large inorganic anions[1] In comparison with common solvents, It has incomparable advantages: (1)Extremely small vapor pressure; (2)Excellent ability to dissolve Inorganic and organic materials; (3)Non-volatility, non-flammability and low toxicity; (4)Lewis acidic and physico-chemical properties which can be adjusted through changing the composition ratio; (5)High conductivity and wide electrochemical window[2].

In 1914, Walden[3] unintentionally mixed concentrated nitric acid with triethylamine, gaining nitrate ethyl ammonium[EtNH₃][NO₃] with melting point of 12 °C which was generally

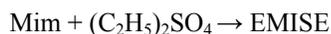
liquid at room temperature. This was the first research about ionic liquids, but it did not receive the attention of other researchers. In 1948, Wier and Hurley synthesized the first chloroaluminate ionic liquid while conducting aluminum-plating experiments. In 1951, Wier and Hurley[4] synthesized a kind of room-temperature ionic liquid N-ethyl pyridine tetrachloro aluminum salts by mixing anhydrous aluminum chloride with N-butyl-bromo pyridine salt. This ionic liquid was used for metal electrodeposition with good effects. The research of ionic liquids didn't develop rapidly until 1992 when Wilkes[5] synthesized 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid with hydrolysis-resistance, and its excellent properties including low melting point and high stability attracted a lot of interest from the research area. At present stage, the study of ionic liquids mainly includes the characterization of physicochemical properties, the synthesis of new functional ionic liquids, the electrodeposition and the roles of being electrolytes played in electrochemical applications.

As to the great varieties of ionic liquids, lots of favourable properties of them can be devised by changing their make-ups of cations and anions[6]. Generally, ionic liquids consist of tiny inorganic anions and asymmetric organic cations with bigger sizes. Ac-

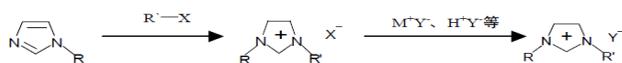
*To whom correspondence should be addressed:
Email: zhang_lucy9999@vip.126.com
Phone: +0086 13371935893

cording to different organic cations, Four kinds of ionic liquids have been divided: alkyl quaternary ammonium ions; alkyl quaternary phosphonium ions; alkyl-substituted imidazolium ions; alkyl-substituted pyridinium ions[7]. With an example of 1-butyl-3-methylimidazolium ions, the alkyl-substituted imidazolium ions have received more attraction from the research fields than the other three.

Currently, one-step synthesis and two-step synthesis are the dominated choices to prepare aimed ionic liquids with specific structures and composition. Nitro ethalimine ionic liquids can be synthesized in the neutralization reaction between nitric acid and ethalimine solution through one-step approach[8]. 1-ethyl-3- methylimidazolium sulfate ionic liquids[9] can be gained using the same path as follow:



The preparation of imidazolyl ionic liquids can be taken for an example of two-step synthesis[10,11]: intermediates containing aimed cations can be produced before the process of ionic exchange, replacement reaction, complexation, electrolyzation etc. After the aimed anions Y^- replacing the initial anions X^- , this synthesis will be ending with the wanted ionic liquids as follow:



In general, melting point occurs when ionic liquids are characteristic of strong intermolecular forces, nonuniform distribution of positive-negative charges, and good structural symmetry[12], exemplified by 2-Methylimidazole born with relatively high melting point resulted from fine symmetry.

Ionic liquids have exhibited good solubility to inorganic matter, organics and polymer. This nature are influenced by alkyl groups existing within ionic liquids which can be accounted for through the fact that lengthening side chains of quaternary ammonium cations will weaken ionic liquids' polarity[13]. Anions are significantly relevant to this nature as well. We can see it from the phenomena that both [Emim]CF₃SO₃ and [Emim]CF₃CO₂ are utterly mixed with water while [Emim]PF₆ and [Emim] (CF₃SO₂)₂N are merely

mixed with water partly. The percentage of saturated water in [Emim] (CF₃SO₂)₂N is only 1.4% at 20°C[14].

With the help of high conductivity, broad electrochemical windows and thermostability, ionic liquids have displayed great potential for applications in sensors. Sun Jie, Li Yan etc. designed a type of hydrazinebiosensors based on room-temperature ionic liquid and studied the electrochemical behavior of hydrazine in room temperature ionic liquid by cyclic voltammetry[15]. Martina Nadhera, Frantisek Opekar etc. successfully tested a new ionic liquid-polymer electrolyte in the planar amperometric solid-state sensor sensitive towards nitrogen dioxide, concluding that the sensor response was linear in the NO₂ concentration range 0.3–1.1 ppm and was reproducible and long-term stable[16]. Six imidazolium-based ionic liquids (ILs) [17] were synthesized, employed as sensing materials coated on quartz crystal microbalance for the detection of organic vapors.

There is a bigger interaction over van Edward force category between anion and cation imidazole ionic liquid with MWCNTs. So it can overcome the Van Edward force between MWCNTs, reduce the reunion, so as to improve the effective area and conductivity of MWCNTs. It has good application prospects in the preparation of electrochemical sensors. Ionic liquid is an excellent extraction agent for metal ions, the interaction between the cations and the anions of ionic liquids is involved in the metal ions. Because of its environmental protection, high efficiency and easy recovery, ionic liquid is very suitable for the extraction of metal ions, which is also a hot field in the research of ionic liquids at home and abroad.

2. EXPERIMENTAL

2.1. Reagents

The experimental reagents are as shown in Table 1. Unless otherwise noted, water is onized water in this study.

2.2. Instruments and devices

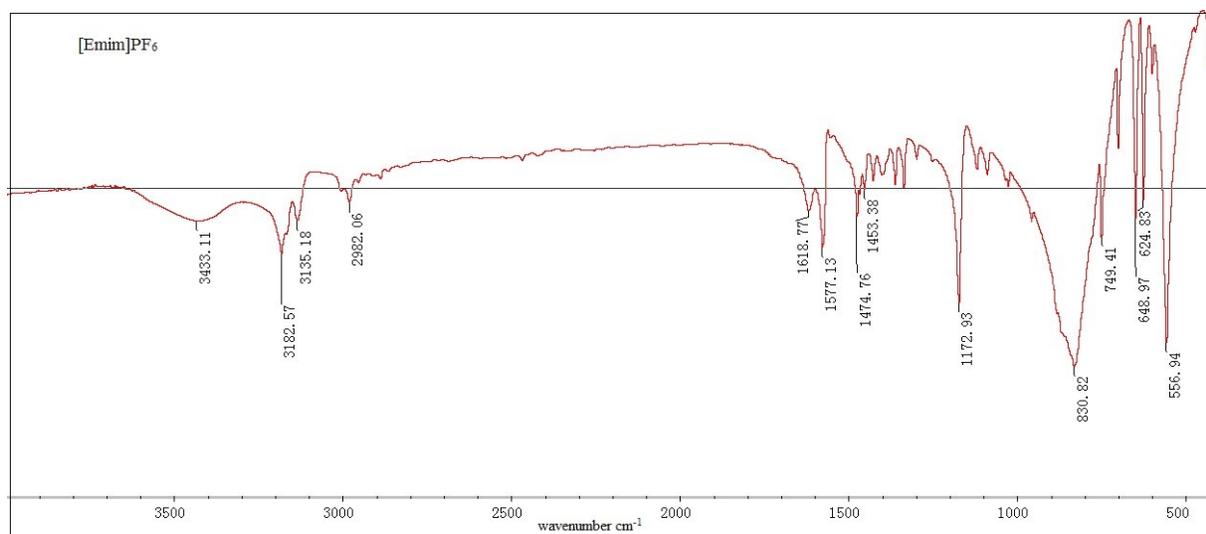
The experimental Instruments and devices are as shown in Table 2.

Table 1. Main experimental reagents

| Name | Source | Specification |
|---------------------------------------|--------------------------------------|------------------|
| CH ₃ CN | Sinopharm Chemical Reagent Co., Ltd. | Analytical grade |
| CH ₃ OH | Sinopharm Chemical Reagent Co., Ltd. | Analytical grade |
| C ₂ H ₅ OH | Sinopharm Chemical Reagent Co., Ltd. | Analytical grade |
| [Emim]CH ₃ SO ₃ | Alfa Aesar Reagent Co., Ltd. | 99% |
| [Emim]PF ₆ | Alfa Aesar Reagent Co., Ltd. | 99% |

Table 2. Main experimental instruments and devices

| Instruments | Manufacturer | Specification |
|---|---|---|
| FTIR Spectroscopy | Nicolet | 380 |
| Liquid chromatography - mass spectrometry | Agilent | 1100 LCMSD SL |
| Electrochemical analyzer | Shanghai Chen Hua Instruments | CHI800 |
| Three-electrodes system | Shanghai Chen Hua Instruments | Working electrode: glassy carbon electrode Reference electrode: saturated calomel electrode Auxiliary electrode: platinum electrode |
| Electronic analytical balance | Mettler-Toledo Instr(Shanghai)Ltd. | AB104-N |
| Ultrasonic cleaner | Kunshan Ultrasonic Instrument Co., Ltd. | KQ218CQ-250 |
| Drying oven | Shanghai Jing Hong Laboratory Equipment Co., Ltd. | DHG-9053A |
| Stirring hot plate | Gongyi Yingyuyuhua Instrument Factory | DF-101S |
| Cryogenic refrigerator | Sanyo Electric | MDF-382EN |
| Digital viscometer | Shanghai Jingtian Electronic Instrument Co., Ltd. | NDJ-5S |
| conductivity meter | Shanghai Dapu Instrument Co., Ltd. | DDS-307 |

Figure 1. IR spectra of [Emim]PF₆

2.3. Experimental procedures

2.3.1. IR spectra of [Emim]CH₃SO₃ and [Emim]PF₆

Infrared Spectroscopy was used to characterize the functional groups such as imidazole ring, alkyl and anions in the ionic liquids. The IR spectrum was given by Nicolet 380 infrared spectrometer with the determination of wave number ranged from 4000 to 400cm⁻¹, and the specimens were prepared by KBr pellet method.

2.3.2. Liquid mass spectra of [Emim]CH₃SO₃

Liquid Chromatograms were given by Agilent 6410 Chromatograph. Agilent C18 column(4.6x150mm) was the chromatographic column. The mobile phase of LC was acetonitrile and water (0.1%HCOOH) which rose from 10% acetonitrile to 95% acetonitrile in 20 min. Conventional electrospray ionizing acquisition of positive and negative ions was employed to detect mass spectra.

2.3.3. The solubility of ionic liquids of [Emim]CH₃SO₃ and [Emim]PF₆

Ionic liquids of [Emim]CH₃SO₃ and [Emim]PF₆ were mixed with water, methanol, ethanol, ether, chloroform, acetone, benzene, hexane respectively to observe dissolution conditions.

2.3.4. Determination of electrical conductivity and electrochemical window of [Emim]CH₃SO₃

Electrical conductivity was measured by DDS-307 digital conductivity meter produced by Shanghai Dapu Instrument Co., Ltd. which contained a temperature sensor and automatic temperature compensation. The electrochemical window was determined by three-electrodes system of CHI800 electrochemical analyzer which was produced by Shanghai Chen Hua Instruments.

2.3.5. Determination of viscosity of [Emim]CH₃SO₃

The dynamic viscosity was directly measured by the NDJ-5S digital viscometer which was produced by Shanghai Jingtian Electronic Instrument Co., Ltd. Kinematic viscosity was measured by capillary viscometer with constant. The general formula is as follows,

$$V=CT$$

In the formula, V-Kinematic viscosity mm²/s)

C-Viscometer constant mm²/s²)

T-Flow time(s)

At the same time we used the water bath to conserve the temperature of ionic liquids [Emim] CH₃SO₃. Kinematic viscosity at different temperatures was also determined.

2.3.6. Hygroscopic determination of [Emim]CH₃SO₃

Excessive amount of saturated salt solution could generate a steady relative humidity and water vapor pressure in a closed space. The general formula is as follows,

$$RH=A \exp(B/T)$$

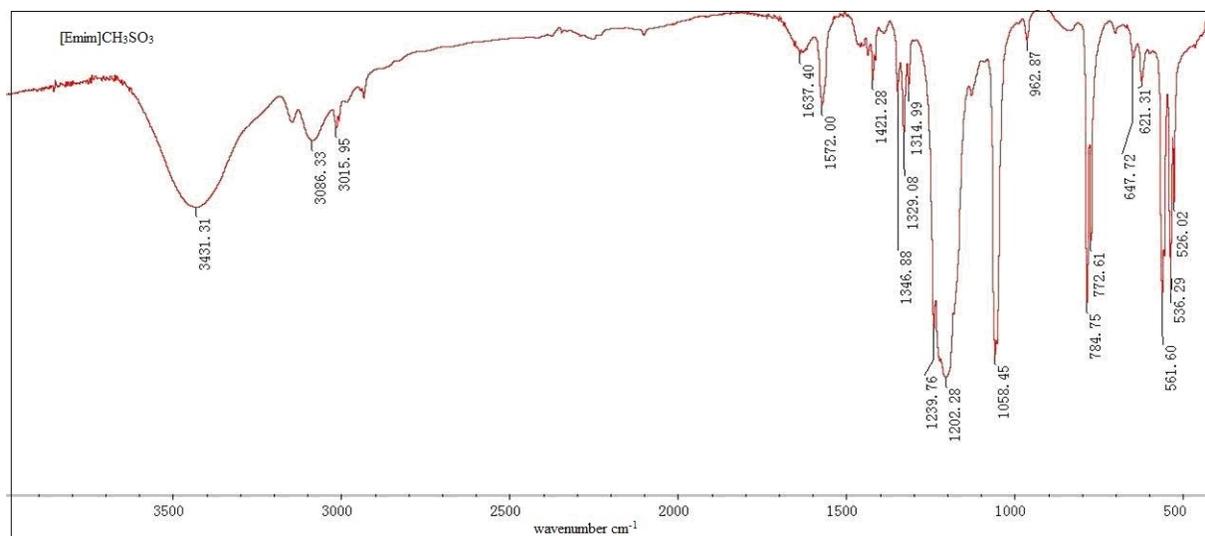
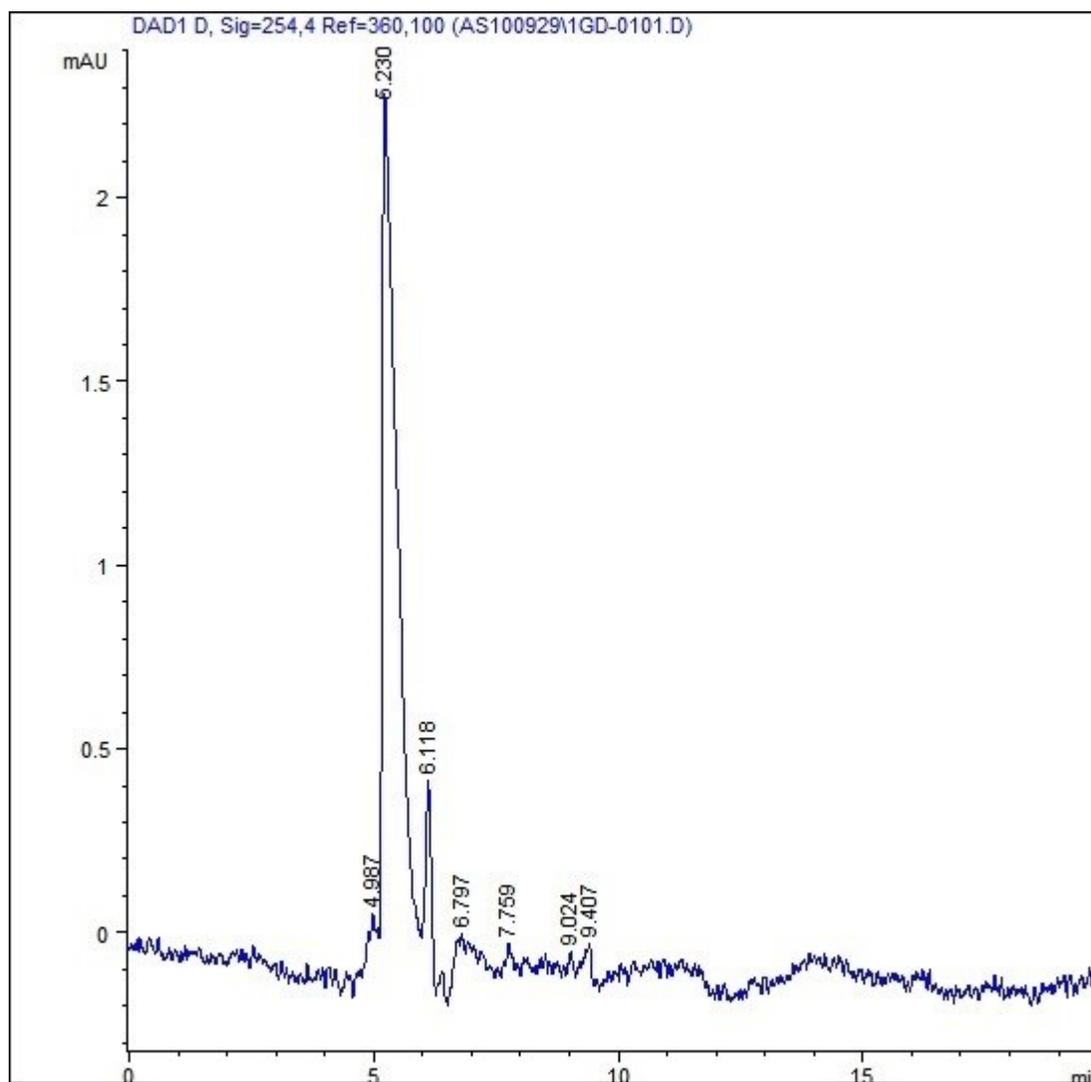
In the formula, RH means relative humidity(generally accurate to ± 2%); T means Kelvin degree; A and B are constants, A and B vary for different compounds.

2.3.7. Determination of corrosivity of [Emim]CH₃SO₃ to biosensor elements

The corrosivity of [Emim]CH₃SO₃ to biosensor elements was mainly determined by weight-loss methods. 5 different sensor elements were put in [Emim]CH₃SO₃ and the changes of their quality were measured after a certain period of time.

2.3.8. The conductivity of [Emim]CH₃SO₃ and [Emim]PF₆ in different solvents

4 gram of ionic liquid [Emim]CH₃SO₃ was dissolved in acetonitrile after being dried and purified, then metered in a 50ml volumetric flask. Mixed acetonitrile ionic solutions with the concentration of 0.008, 0.016, 0.024, 0.032, 0.04, 0.048, 0.056, 0.064, 0.072, 0.08g/ml could be gained separately by put 1, 2, 3, 4, 5, 6, 7, 8, 9, 10ml of solution abovementioned into 10ml acetonitrile with transfer pipette. Homogeneous liquids formed by fully oscillation at room temperature. Changes of the electrical conductivity values of

Figure 2. IR spectra of [Emim]CH₃SO₃Figure 3. Liquid mass spectra of [Emim]CH₃SO₃

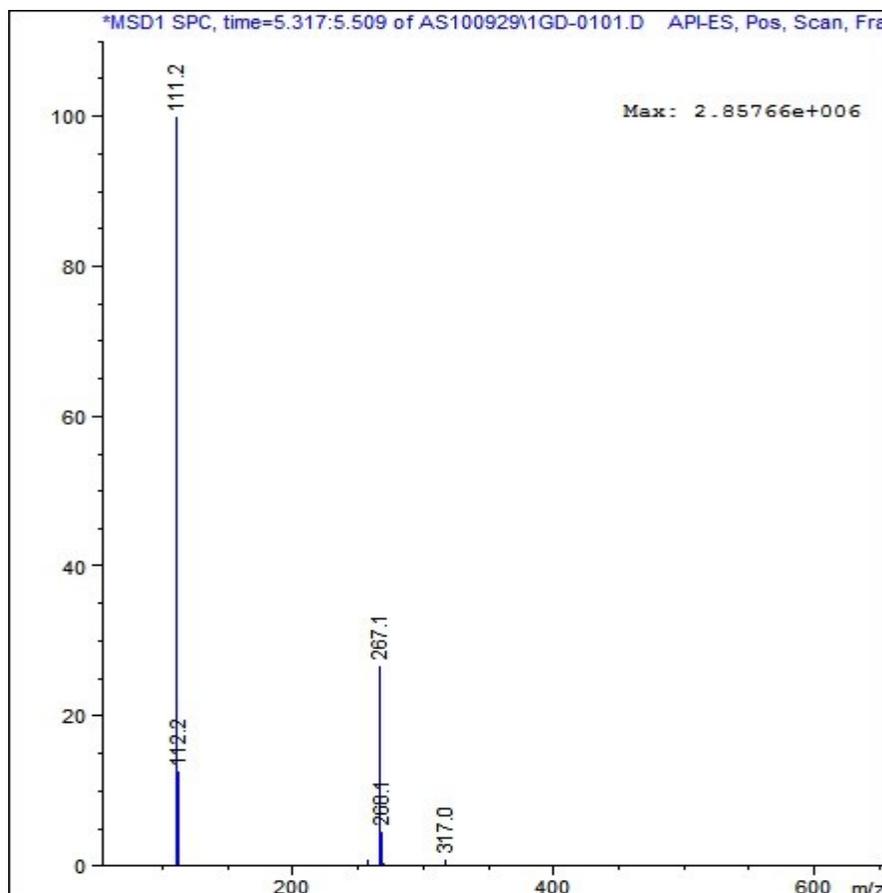


Figure 4. The mass spectra isolated at 230min

[Emim]CH₃SO₃ and acetonitrile were measured by conductivity meter under different temperatures. The same measurement was repeated on [Emim]PF₆ and acetonitrile. Corresponding tests were conducted for the electrical conductivity of [Emim]CH₃SO₃ and methanol under different concentration and temperatures, and that under different concentration and low temperature of -40°C, as well as the changes of electrical conductivity of solution mixed by ionic liquid [Emim]CH₃SO₃ and water with volume ratio of 8:7 under different temperatures.

3. RESULTS AND DISCUSSION

3.1. IR spectra contrast of [Emim]CH₃SO₃ and [Emim]PF₆

IR spectra of ionic liquid [Emim]PF₆ is shown in Figure 1. Crest appears at 3433 cm⁻¹ which is characteristic absorption band of -OH. The presence of a small amount of water can be known for that the crest is not very high. 3182 cm⁻¹ is the C-H-stretching vibration peak on the imidazole ring. 2982 cm⁻¹ is the C-H-stretching vibration peak of aliphatic series. Stretching vibration of C=C, C=N bond on imidazole ring appears at 1577 cm⁻¹. Skeleton vibration peak on imidazole ring appears at 1172 cm⁻¹. Strong absorption peak presents at 830 cm⁻¹ which is known as the stretching vibration frequency region of PF₆. IR spectra of [Emim]CH₃SO₃ is shown in Figure 2. Crest appears at 3431 cm⁻¹ which is characteris-

tic absorption band of -OH. The presence of a large amount of water can be known for that the crest is very high. 3085 cm⁻¹ is the C-H-stretching vibration peak on the imidazole ring. Stretching vibration of C=C, C=N bond on imidazole ring appears at 1573 cm⁻¹. Skeleton vibration peak on imidazole ring appears at 1202 cm⁻¹. Strong absorption peak presents at 1058 cm⁻¹ which must be the stretching vibration frequency region of S=O bond.

3.2. Liquid mass spectra of [Emim]CH₃SO₃

Liquid mass spectra of [Emim]CH₃SO₃ is shown in Figure 3 and Figure 4 below. The 5.230min is the main peak of liquid phase separation. Fragment peak of 111 is the single fragment of imidazole cation [Emim], but 112 is isotopic peak. 267 is a peak combined by two imidazole cations [Emim] and a -COOH. 317 is exactly combined by two imidazole cations [Emim] and an anion CH₃SO₃.

3.3. The solubility of ionic liquids of [Emim]CH₃SO₃ and [Emim]PF₆

Table 3 shows the solubility of [Emim]CH₃SO₃ and [Emim]PF₆ in different solvents. We can see that [Emim]CH₃SO₃ and [Emim]PF₆ can be both dissolvable in polar solvents while undissolvable in some solvents which are low polar or nonpolar. Therefore, the solubility of the ionic liquids has great relevance with

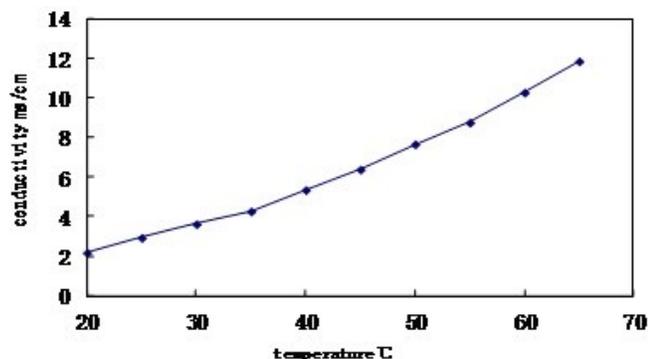


Figure 5. The conductivities of [Emim]CH₃SO₃ at different temperatures

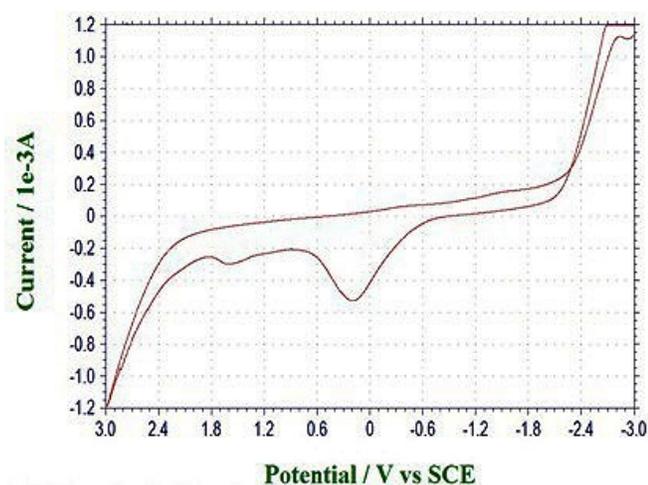


Figure 6. Cyclic voltammety curves of [Emim]CH₃SO₃

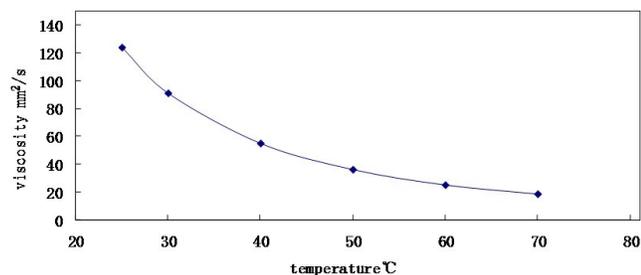


Figure 7. The viscosity-temperature property of [Emim]CH₃SO₃

anions. It will be of great significance to promote the application of ionic liquids in chemical reactions and catalytic synthesis through solubility experiments and the investigation of ionic liquids' solubility in organic solvents.

Table 3. The solubility of [Emim]CH₃SO₃ and [Emim]PF₆ in different solvents

| | Water | Benzene | Ether | N-hexane | Methanol | Ethanol | Acetone | Chloroform |
|---------------------------------------|-----------|-----------|-----------|-----------|----------|---------|---------|------------|
| [Emim]CH ₃ SO ₃ | Soluble | Insoluble | Insoluble | Insoluble | Soluble | Soluble | Soluble | Soluble |
| [Emim]PF ₆ | Insoluble | Insoluble | Insoluble | Insoluble | Soluble | Soluble | Soluble | Soluble |

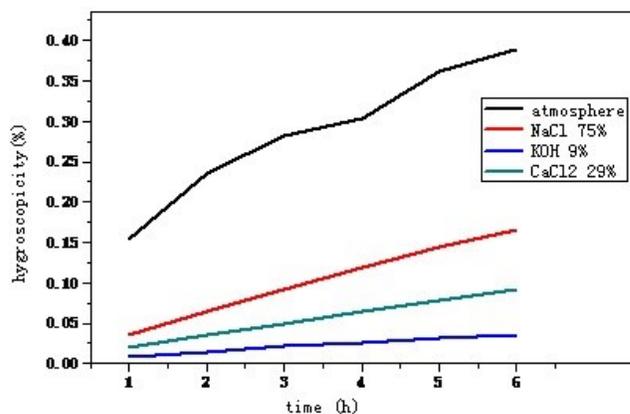


Figure 8. Hygroscopicity of [Emim]CH₃SO₃ under different humidity

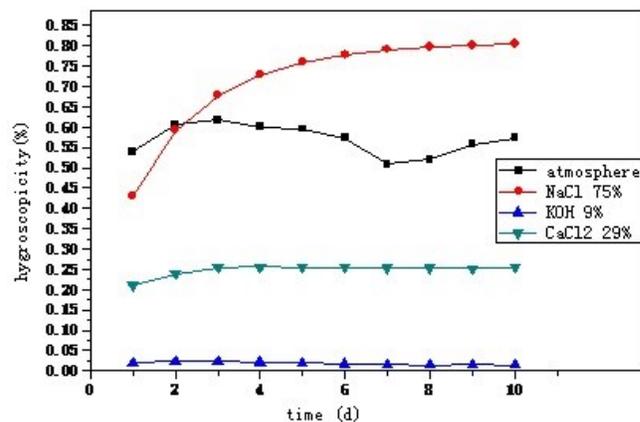


Figure 9. Hygroscopicity of [Emim]CH₃SO₃ under different humidity

3.4. Conductivity and electrochemical window of [Emim]CH₃SO₃

Conductivity changes of ionic liquid [Emim]CH₃SO₃ under different temperatures is shown in Figure 5 below. The figure tells that the conductivity continuously becomes larger with the increase of the temperature. Figure 6 indicates that the electrochemical window of [Emim]CH₃SO₃ is about 4.8V, which can be obtained by measuring the cyclic voltammety curves with three-electrode system of electrochemical analyzer.

3.5. The viscosity of [Emim]CH₃SO₃

As a result of the test, the dynamic viscosity of No.1 rotor was 160.4mpa·s when rotate speed was 12.0RPM and torque was 59.2%. The kinematic viscosity was detected by capillary viscometer attached to constants. Water bath kettle was used to control the

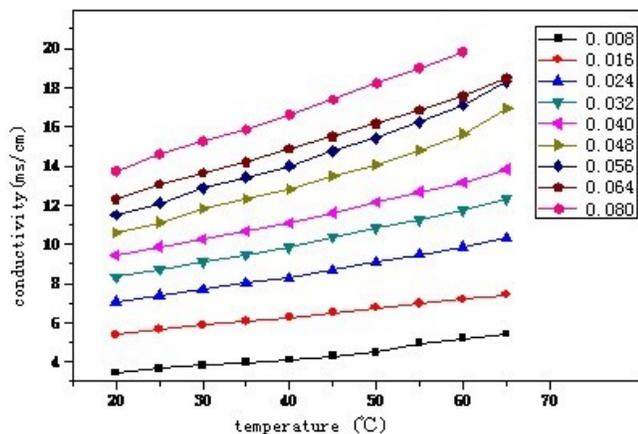


Figure 10. Changes of conductivity of [Emim]CH₃SO₃ mixed with acetonitrile under different concentration and temperatures

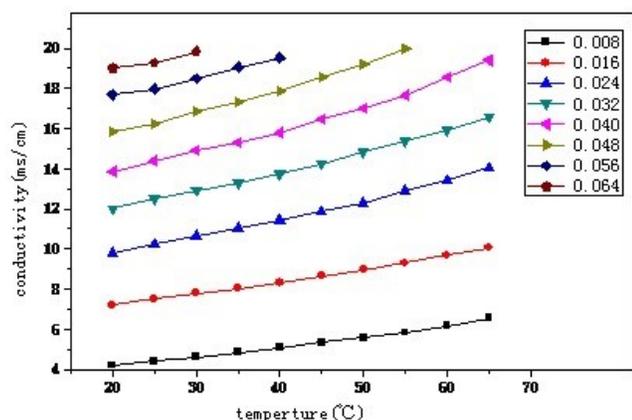


Figure 11. Changes of conductivity of [Emim] PF₆ mixed with acetonitrile under different concentration and temperatures

temperature of ionic liquid [Emim]CH₃SO₃, and kinematic viscosities at different temperatures were determined. Consequently, the kinematic viscosity of ionic liquid [Emim]CH₃SO₃ constantly reduced with the rise of the temperature. Larger viscosity of ionic liquid [Emim]CH₃SO₃ would affect its application of being the electrolytes in electrochemical biosensors.

3.6. The hygroscopicity of [Emim]CH₃SO₃

The hygroscopicities of ionic liquid [Emim]CH₃SO₃ in different humidity conditions are shown in Figure 8 and Figure 9. We found that the water absorption of ionic liquid [Emim]CH₃SO₃ had a great correlation with the humidity in the environment. In the first six hours, the amount of water absorbed in the constant humidity environment soared. After 10 days the water absorption gradually stabilized and was proportional to the environment humidity. The greater the humidity, the more the water absorbed. In the 75% humidity environment, ionic liquid [Emim]CH₃SO₃ could absorb nearly 80% of its own weight of water.

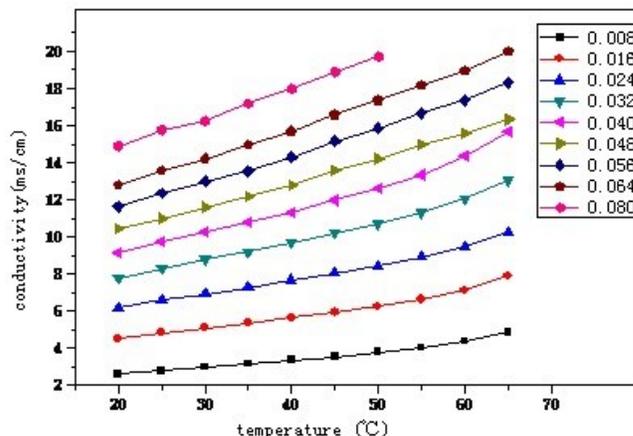


Figure 12. The changes of conductivity of [Emim]CH₃SO₃ mixed with methanol under different concentration and temperatures

3.7. The corrosivity of [Emim]CH₃SO₃ to biosensor elements

The corrosivity of [Emim]CH₃SO₃ to biosensor elements were mainly determined by weight-loss methods. 5 different sensor elements were put in ionic liquid [Emim]CH₃SO₃ and the changes of their quality were determined after a certain period of time. Experiments revealed that the corrosivity of [Emim]CH₃SO₃ to biosensor elements could be neglected.

3.8. The conductivity of [Emim]CH₃SO₃ and [Emim]PF₆ in different solvents

As shown in Figure 10, the conductivity of ionic liquid [Emim]CH₃SO₃ mixed with acetonitrile changed under different temperatures, which was detected by conductivity meter. The changes of conductivity of [Emim] PF₆ mixed with acetonitrile under different temperatures is shown in Figure 11. As a result, adding an appropriate amount of acetonitrile could effectively improve the electrical conductivity of ionic liquid [Emim]CH₃SO₃. The conductivity of different concentrations of solution mixed by ionic liquids and acetonitrile escalated with the increasing temperature. Within a specific concentration range, the conductivity also increased with the rise of acetonitrile concentration.

Figure 12 shows the changes of conductivity of [Emim]CH₃SO₃ mixed with methanol under different concentration and temperatures. The conductivity of different concentrations of solution mixed by ionic liquids and methanol escalated with the increasing temperature. Within a certain concentration range, the conductivity was also increasing with the rise of methanol concentration. The

Table 4. The corrosivity of [Emim]CH₃SO₃ to biosensor elements under normal temperature for 1 year period of time

| | The original weight/g | The weight after one year/g |
|-----------------------|-----------------------|-----------------------------|
| PTEF | 0.2493 | 0.2569 |
| Concentric black ring | 0.1256 | 0.1257 |
| Concentric green ring | 0.1485 | 0.1487 |
| Black rubber ring | 0.1255 | 0.1256 |
| PTEF | 0.2493 | 0.2569 |

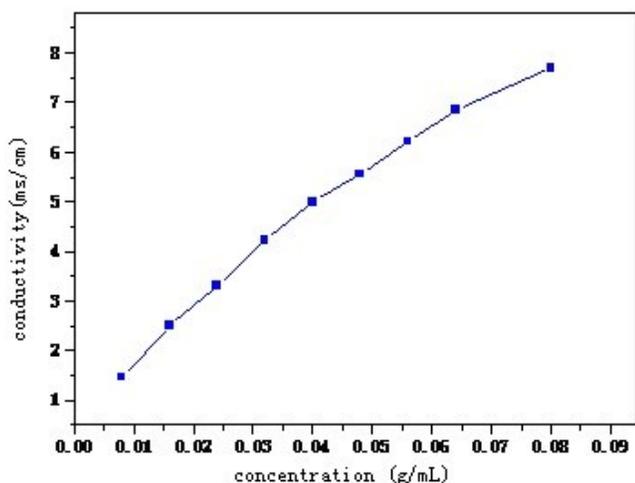


Figure 13. The changes of conductivity of [Emim]CH₃SO₃ mixed with methanol under low temperature of -40 °C and different concentrations

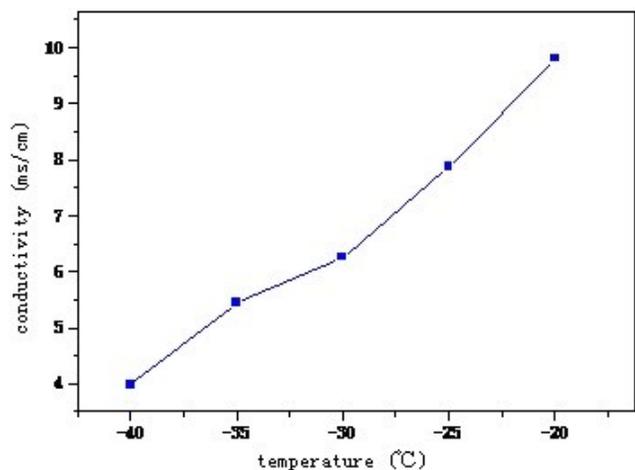


Figure 14. The conductivity of solution mixed by [Emim]CH₃SO₃ and water with a ratio of 4:3.5 under different temperatures

changes of conductivity of [Emim]CH₃SO₃ mixed with methanol under low temperature of -40°C and different concentrations were measured as well, which are shown in Figure 13. Figure 14 shows the conductivity of solution mixed by [Emim]CH₃SO₃ and water with a ratio of 4:3.5 under different temperatures. It was found that while using methanol as the solvent, the conductivity of ionic liquid [Emim]CH₃SO₃ with concentration of 0.08g/ml could reach 7.70ms/cm at -40°C.

4. CONCLUSION

The electrochemical and physic-chemical parameters of ionic liquids [Emim] CH₃SO₃ and [Emim] PF₆ including IR, LC-MS, conductivity, electrochemical widow and viscosity were determined. The influence of trace impurity on the conductivity of ionic liquids was investigated. Results explained that the ionic liquids

had high conductivity and large electrochemical window. Decreasing the viscosity of ionic liquids by adding proper amount of organic solvents would become the key to practical applications. Adding proper amount of organic solvents could effectively improve the electrochemical performance and the conductivity of the ionic liquids. On the other hand, the low freezing point of this electrolyte could effectively expand the applicable temperature range of the ionic liquid electrolyte. Different organic solvents added could produce different effects on the electrical conductivity of ionic liquids. Similarly, conductivity of the ionic liquids was significantly affected by the temperature changes. It was found that the conductivity of the ionic liquids will continue to increase with the temperature. In summary, the ionic liquid [Emim]CH₃SO₃ showed favourable electrochemical performance and could fulfill the initial application requirements as biosensor.

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