

Synthesis and Characterization of a Novel Polyoxometalate Gel Electrolyte

Limei Ai, Zeqing Wang, Fengwei He and Qingyin Wu*

School of Biomedical and Chemical Engineering, Liaoning Institute of Science and Technology, Benxi 117004, Liaoning, China

*Email: qywu@lnist.edu.cn

Abstract. A novel polyoxometalate gel electrolyte was synthesized by 1-(3-sulfonic group) propyl-3-methyl imidazolium (abbreviated as MIMPS) and $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$. The synthesized gel electrolyte was successfully characterized by infrared spectra (IR), ultraviolet spectra (UV) and X-ray diffraction (XRD). The results of the characterization indicate that existence of Keggin structure heteropolyanion in the tungstovanadosilicate-based ionic liquid gel. The change from crystal to amorphous was observed in the XRD patterns, before and after the cation (MIMPS) added.

1. Introduction

Ionic liquids (ILs) are special salts which are normally composed of relatively large organic cations and inorganic anions. They have special properties that remain in the liquid state at low temperatures.[1] Recently, more and more ionic liquids have been synthesized. They possess some excellent properties such as thermodynamic stability, electrical conductivity and electrochemical properties.[2-5]

Heteropolyacids and polyoxometalate, a class of discrete, negatively charged early transition metal oxide clusters, are formed based on inorganic metal-oxygen cluster anions. Some research in material science area pay more attention to the electrochemical performance of these compounds since they are perfect electron acceptors.[6-10] The electrochemical performance of polyoxometalate will provide insights into developing electrochemical electrolytes based on heteropolyacids or polyoxometalate, such as phase transformation electrolytes.

In the past decade, polyoxometalate-based organic-inorganic hybrid gel-type complexes show more perfect properties than the pure acid in some application. Thus more and more researchers interest in design and synthesis of these polyoxometalate derivatives. Polyoxometalate-based ionic liquids, which consist of heteropoly anions and appropriate organic cations, were paid more attention to many researchers, and more and more new family of ionic liquids were synthesised.[11, 12] They have emerged as compounds with the most potential for applications in catalysis, electrochemistry and nanotechnology.[13-16]

Here, we report novel hybrid gel electrolyte which consists of 1-(3-sulfonic group) propyl-3-methyl imidazolium (MIMPS) and inorganic $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ and synthesized by an ionic self-assembly method. In addition, we also report some characteristic of the hybrid gel electrolyte, such as IR, UV, and XRD.



2. Experimental section

2.1 Instruments and reagents

Infrared (IR) spectra were conducted on a WQF-510 FT/IR spectrometer during the wavenumber range 400–4000 cm^{-1} using KBr pellet. X-ray powder diffraction (XRD) patterns were conducted on a Rigaku D/max-rB X-ray diffractometer using a Cu tube at the conditions: at 40 kV and 40 mA in the range of $2\theta = 4\text{--}40^\circ$ at a rate of 0.02°s^{-1} . The UV absorption spectra of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ and $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$ were monitored by a Specord TU-1901 UV-vis spectrophotometer. All chemicals were of analytical grade and used without further purification.

2.2 Synthesis of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$

$\text{K}_8[\text{SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ was synthesized by a method according to recent literature. 20 mL aqueous solution of sodium metavanadate (0.54g NaVO_3) was added to 30 mL aqueous solution of $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$ (11 g $\text{K}_8[\text{SiW}_{11}\text{O}_{39}]\cdot 13\text{H}_2\text{O}$). The mixture was adjusted to pH=2.5 by adding sulphuric acid (1:1) solution. Subsequently, it is boiled for 1.5 h and allowed to stand at ambient temperature for half an hour. The cooled solution was extracted with ether in a sulfuric acid medium. The orange powder was obtained after the ether was removed in vacuum dryer.

2.3 Synthesis of $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$

The MIMPS was synthesized according to the literature procedure. Methyl imidazole (0.055 mol) and 1,3-propanesultone (0.05 mol) were dissolved in acetone (25 ml) and stirred at 50 $^\circ\text{C}$ for 4 h. A white precipitate (MIMPS) was obtained and washed using acetone for three times, and then dried under vacuum. Furthermore, MIMPS (0.03mol) was added into 30mL aqueous solution of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ (0.01mol), the mixture was reacted under ultrasound for 10min and stirred for 12h at room temperature. The liquid was evaporated in a water bath at 50 $^\circ\text{C}$ and then the product as gel-type was obtained

2.4 Elemental analysis of $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$

The carbon, nitrogen, sulfur, silicon, tungsten and vanadium content was analysed by elemental analysis.

$[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$: found : C: 11.25%; N: 3.91%; S: 4.20%; Si: 0.90%; W: 53.73%; V: 1.38%.

$[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$: theoretical value: C: 11.15%; N: 3.70%; S: 4.25%; Si: 0.75%; W: 53.75%; V: 1.35%.

3. Results and discussion

Table 1. The IR spectra of the compounds at 1100~600 cm^{-1}

Vibrations	$\text{H}_5\text{SiW}_{11}\text{VO}_{40}/\text{cm}^{-1}$	$[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}/\text{cm}^{-1}$
M-O _d stretching	980	970
Si-O _a stretching	923	918
M-O _b -M stretching	881	-
M-O _c -M stretching	783	795

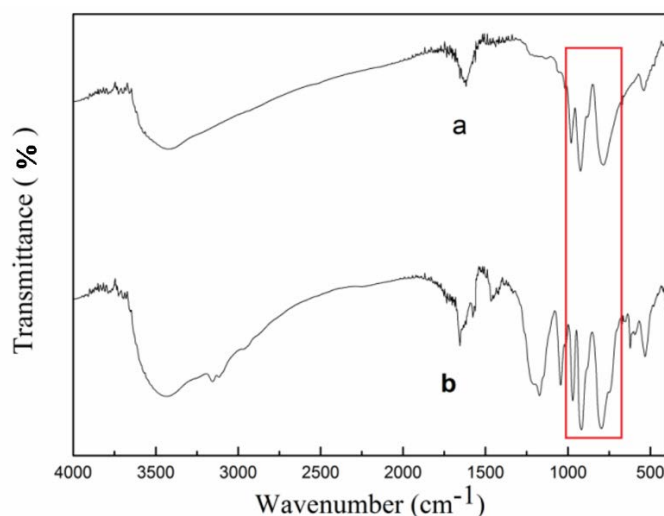


Figure 1. IR spectra of the compounds (a) $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$, and (b) $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$

The detail IR spectra of compounds at $1100\sim 700\text{ cm}^{-1}$ which is the best feature area of heteropoly compounds are shown in the figure 1 and table 1. In curve the pure heteropolyacid shows four absorption bands at 980 cm^{-1} , 923 cm^{-1} , 881 cm^{-1} , 783 cm^{-1} , corresponding to $\nu_{\text{as}}(\text{M}-\text{O}_{\text{d}})$, $\nu_{\text{as}}(\text{Si}-\text{O}_{\text{a}})$, $\nu_{\text{as}}(\text{M}-\text{O}_{\text{b}}-\text{M})$ and $\nu_{\text{as}}(\text{M}-\text{O}_{\text{c}}-\text{M})$, ($\text{M}=\text{W}, \text{V}$), respectively. These peaks could correspond to the characteristic vibrations of the Keggin polyoxoanions. In the IR spectrum of $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$, we can clearly find that these feature frequencies fall in the stretching sequence of which is referred to pure heteropolyacid character bands at $1100\sim 700\text{ cm}^{-1}$. We also find the shift of characteristic peaks of $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$ in the figure 1 and table 1 as compared with $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$. This phenomenon of vibrations frequency change results from the influence of interactions between the heteropoly anions and the organic cations. In spite of the shift of characteristic peaks of $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$, the peaks still exist, which can be found at the red zone in the figure 1. The result shows that the compound still maintains $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ structure without decomposition, when MIMPS is added.

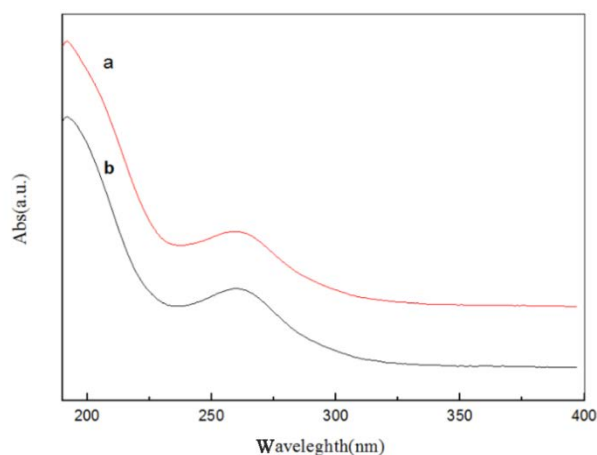


Figure 2. UV spectra of the compounds

The heteropolyacids in their non-reduced forms are generally characterized by oxygen-to-metal ($\text{O} \rightarrow \text{M}$) charge transfer bands, which appear in the UV region below 400 nm. The UV absorption spectra of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ (b) and $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$ (a) are shown in the figure 2. As shown in the figure 2, we can find that the absorption spectra of $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$ and $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ exhibit a

moderately intense peak nearly 260nm ($O \rightarrow M$). This result provides an evidence of existence of the Keggin structure unit in $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$.

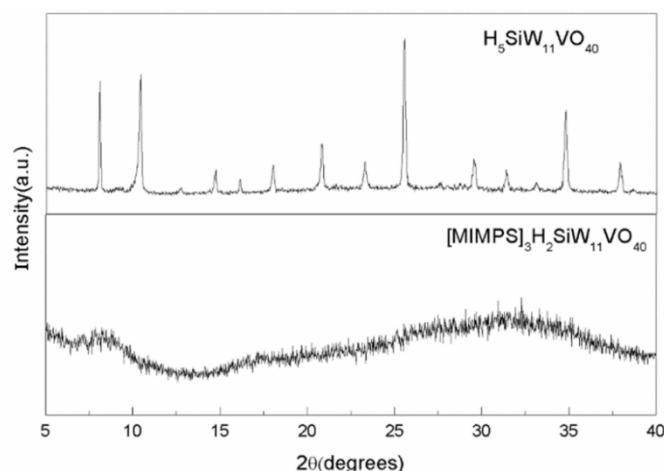


Figure 3. Wide-angle XRD patterns of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ and $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$

Wide-angle XRD pattern of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ is shown in the figure 3. The intensity of peaks is very strong in the large region of the XRD pattern of $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$. The Keggin-type of the polyoxometalate which exhibited typical peaks in the range of $2\theta = 7\text{--}11^\circ$ in the XRD patterns was found. From that phenomenon, it is clear that the pure HPA has a high crystallinity and the polyoxometalate compound was successfully prepared. However, the XRD pattern of $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$ exhibits a broad diffraction peak at $30\text{--}35^\circ$. This phenomenon shows that structure of the pure HPA changes into amorphous structure after the cation (MIMPS) added.

4. Conclusions

In this work, we have successfully synthesized novel polyoxometalate gel electrolyte by using 1-(3-sulfonic group) propyl-3-methyl imidazolium (MIMPS) and vanadium-substituted tungstosilicic acid $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$. IR and UV spectra provide an evidence of existence of the Keggin structure unit in $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$. But the interaction between the organic cation MIMPS and the heteropoly anion results out the shift of stretching vibrations of the characteristic peaks. In comparison with the original vanadium-substituted heteropolyacid $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$, the structure of tungstovanadosilicate-based ionic liquids gel changes from crystal for $\text{H}_5\text{SiW}_{11}\text{VO}_{40}$ to amorphous structure for $[\text{MIMPS}]_3\text{H}_2\text{SiW}_{11}\text{VO}_{40}$, which demonstrates that the nature of the cation greatly influences the secondary structure of the polyoxometalate derivatives.

5. Acknowledgements

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6. References

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