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The invertible electrochemical properties and thermal reponse about a series of gel-type ionic liquids based on polyoxometalate

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A series of vanadium-substitutive Dawson-structure POM-type ionic liquids, [TEAPS]₇P₂W₁₇VO₆₂ and [TEAPS]₉P₂W₁₅V₃O₆₂, bearing of sulfo-group grafted ammonium (TEAPS) and Dawson-type polyoxoanions are formed to reversible-thermal-response type gels. These gel-type compound exhibit the phase transition from a quasi-solid gel phase to an isotropic sol phase. What's more, these series of hybrid compounds can process reversible electrochemical reactions in Dimethyl Formamide (DMF) owing to the reduction of the vanadium in POM anions as a simple anion, which is unlikely to happen in water solution because of water protonation.

Introduction

Gels as a type of important soft materials are a result of the entrapment and adhesion of molecular self-assemblies and they usually have some unique structures.¹ These self-assembled fibers or other shaped objects of small molecular gelators are usually formed through some kinds of secondary interactions such as metal ion coordination, electrostatic interaction and hydrogen bonding,² and they have been explored in many areas such as catalysis and electrochemistry.³ In many cases, these kinds of gels can form many different complexes, and these organic-inorganic hybrid gel-type complexes have attracted a lot of attentions recently.⁴

Heteropoly acids (HPAs) and Polyoxometalate (POM), a class of discrete, negative charge early transition metal oxide clusters, are formed by inorganic metal–oxygen cluster anions and they can be applied in wide areas.^{5–11} An aspect of the research in materials science has been reported the electrochemical performance of these compounds.^{12–14} Therefore, to conduct research on the detail of these compounds in some particular applications such as electrochemical capacitors, fuel cell and phase transformation electrolyte will provide insights in developing electrochemical electrolytes based on POM.¹⁵ Besides the application of pure POMs, recently POMs have been dispersed in organic polymer matrices¹⁶ or formed various salts with some other cations such as organic ammonium to prepare many novel kinds of gel-type hybrid materials¹⁷ which are much easier to machine than the pure POM.

These POM-based organic–inorganic hybrid gel-type complexes usually show more perfect properties than pure acids in the electrochemical application.¹⁸ The design and synthesis of these POM derivatives are of great interest for their potential applications in catalysis, medicine, electrochemistry and nanotechnology.¹⁹ Among the variety of routes described to prepare these kinds of hybrid materials, ionic self-assembly is a successful method of organizing POM with some kinds of organic ammonium cations in solution physically into ordered organic-inorganic assemblies gelator.²⁰

In fact, the nature of cations has a great influence on the dynamic equilibrium of protonic species, secondary structure of heteropoly compounds, and characteristics of POM.²¹ In this context, this kind of POM-based hybrid gel-type material can be concluded as a novel POM-type ionic liquid, and they also have some significant physical properties such as reversible thermal response. Therefore it is believed new kind of ionic liquid based on POM can also be applied in many potential areas.²²

We now choose a kind of sulfo-group grafted organic ammonium, 1-(3-sulfonic group) triethylamine (TEAPS) and vanadium-substituted Dawson-type heteropolyanion (P₂W₁₇VO₆₂⁷⁻ and P₂W₁₅V₃O₆₂⁹⁻) to prepare a novel electrochemical-active gel-type ionic liquid based on POM and organic ammonium through ionic self-assembly method. We also report the phase transformation, the structure and some electrochemical characters about these series of POM-based gel-type compound.

Experimental section

Instrument and reagent

Infrared (IR) spectrum was recorded on a NICOLET NEXUS 470 FT/IR spectrometer over the wave number range 400–4000 cm⁻¹ using KBr pellet. X-ray powder diffraction analysis was obtained on a BRUKER D8 ADVANCE X-ray diffractometer using a Cu tube operated at 50 kV and 200 mA in the range of 2θ = 4–40° at

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a scanning rate of $0.02^\circ \text{ s}^{-1}$. The thermal stability of the sample was investigated through simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) techniques from room temperature to 600° C . TG-DTA measurement was conducted on a SHIMADZU thermal analyzer in a Nitrogen stream, with a heating rate of $10^\circ \text{ C} \cdot \text{ min}^{-1}$. The texture of these samples was observed through an Axioskop 40 polarizing microscope (Carl Zeiss Light Microscopy, Germany) equipped with a LINKAM THMS 600 hot stage and a LINKAM CI 94 temperature controller. The cyclic voltammetric studies were conducted on CHI650C electrochemical workstation in dimethyl formamide (DMF). The density of substrate was 0.25 mM and 0.2 M NaClO_4 was assigned as supporting electrolyte. The working electrode was glass carbon which is 5 mm in diameter and the counter electrode was Pt. The surfaces of electrodes were pretreated to fresh before experiment. The reference electrode was saturated calomel electrode. The solution was deaerated by nitrogen before experiment. All reagents were analysis grade.

20 Synthesis of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$

TEAPS was synthesized according to recent literature.²³ $\text{H}_7\text{P}_2\text{W}_{17}\text{VO}_{62} \cdot n\text{H}_2\text{O}$ ($\text{P}_2\text{W}_{17}\text{V}$) and $\text{H}_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62} \cdot n\text{H}_2\text{O}$ ($\text{P}_2\text{W}_{15}\text{V}_3$) was synthesized according to the method from recent literature available,^{7,14} which are both collected through ion-exchange process of the potassium salt. The pre-synthesized TEAPS and $\text{P}_2\text{W}_{17}\text{V}$ and $\text{P}_2\text{W}_{15}\text{V}_3$ were taken in 7:1 or 9:1 mole ratio to give one mole of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$. TEAPS (1.5 g) was added to an aqueous solution of $\text{P}_2\text{W}_{17}\text{V}$ (4.33 g) or $\text{P}_2\text{W}_{15}\text{V}_3$ (3.17 g), and then the mixture was stirred for 24 h at room temperature. The solvent water was firstly evaporated at 50° C and then it was removed in vacuum to give the product as orange oily gel-type compounds. These series of compounds are highly insoluble in tetrahydrofuran, acetone or ethyl acetate, but they are soluble in N, N-dimethylformamide, dimethyl sulfoxide and water.

Results and discussion

FT/IR spectroscopy studies

Infrared spectroscopy is an effective measurement for polyoxoanions systems and hydrogen bonds system study. These two compounds have been investigated by FT/IR spectroscopy in Fig. S1, and the detail of these compounds are in the Table.1.

Table. 1 The assignment of the vibration modes in IR spectra of the complexes and pure acids

Vibrations	Wavenumber (cm^{-1})			
	$[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$	$\text{H}_7\text{P}_2\text{W}_{17}\text{VO}_{62}$	$[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$	$\text{H}_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$
O-H stretching	3423	3432	3446	3570
-CH ₂ stretching	2985	-	2983	-
H-O-H bending	1657	1631	1650	1624
-CH ₂ scissoring	1487	-	1493	-
-CH ₂ twisting	1398	-	1394	-

S=O bending	1220	-	1223	-
S=O bending	1164	-	1179	-
P-O _a stretching	1099	1088	1091	1086
M-O _d stretching	957	963	948	952
M-O _b -M stretching	889	919	903	916
M-O _c -M stretching	801	792	792	786

From Table.1, we can find it that compared with pure acids, the characteristic bands of polyoxoanions have shifted somewhat. In fact, compared with pure acids, the M-O_d vibrations are considered as pure stretching vibration, and frequencies have decreased when TEAPS ammoniums have been adding with HPA to make gel-type compounds because anion-anion electrostatic interactions are weakened as anion-anion distances increase so it can bring about significant influence of anion-anion interactions, so M-O_d asymmetrical stretching vibrations frequencies have decreased. M-O_b-M and M-O_c-M are different from M-O_d stretching, and they are not pure and cannot be free from bending character, there are perhaps competitions of opposite effects, for M-O_c-M asymmetrical stretching vibration increases while M-O_b-M asymmetrical stretching vibration decreases.

What's more, we can also find it that there are some other characteristic peaks of TEAPS ammoniums such as $\nu_{\text{S=O}}$, $\nu_{\text{C-H}}$ of CH₂. Compared with pure acids, the O-H stretching decreases and H-O-H stretching increases, which looks like hybrid materials based on organic polymer and HPA.²⁵ So we conclude that these complexes can form hydrogen bonds systems among TEAPS ammoniums and Dawson-type polyoxoanions. (Fig.1)

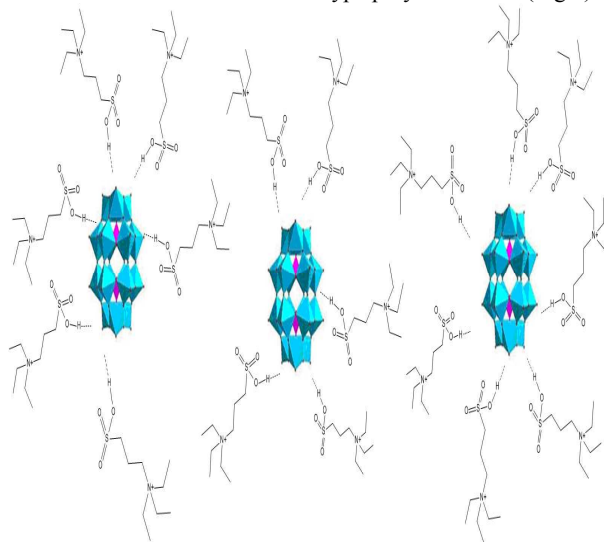


Fig.1 The image of the hydrogen bonds system among TEAPS ammoniums and Dawson-type POM anions

Thermal Studies

$[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ are investigated by polarized optical microscopy (PM) (Fig. 2.). Upon heating, these compounds show similar phenomenon: more and more slice structure occur through heating but in high temperature there are fewer slice structure.

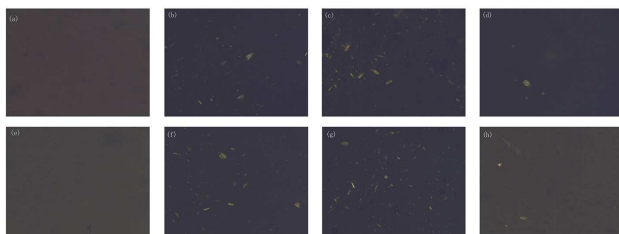


Fig. 2. PM images of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ at (a) 27 °C, (b) 70 °C, (c) 95 °C and (d) 132 °C, and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ at (e) 28 °C, (f) 74 °C, (g) 93 °C and (h) 129 °C (magnification: $\times 200$).

Actually, these phenomenons are along with the phase transformation of these compounds when considered TG and DTA curves of these compounds in phase transformation that are showed in Fig.3.

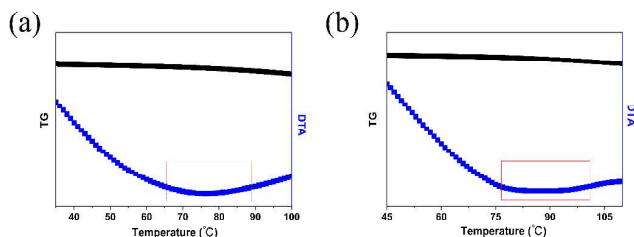


Fig. 3. TG and DTA curves of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ (a) and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ (b) in the low temperature.

For this matter, it is obvious during the process of the phase transformation, there are many slice structures so these compounds can be regarded as a liquid-crystal type of ionic liquids which exist in the process of phase transformation that starts from a crystal phase to an isotropic phase (Fig.4), so in this case these series of compounds can be considered as a novel type of ionic liquid.²⁶

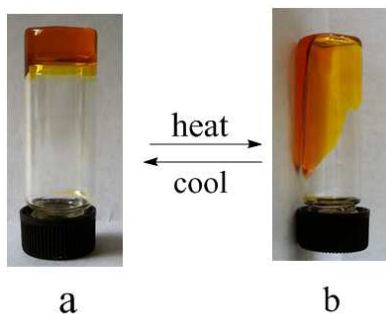


Fig. 4. Photographs of these kind of POMs at room temperature (a) and 85 °C (b).

XRD patterns

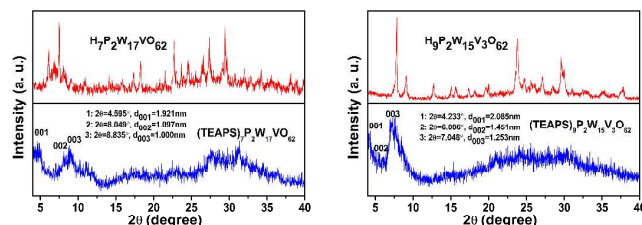


Fig. 5. XRD patterns of $\text{H}_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$, with $\text{H}_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$.

The phase and structure of these heteropoly compounds are further identified by using powder X-ray diffraction (XRD) in Fig. 5. The XRD pattern peak of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ are a series of marked contrast with that of pure heteropoly acids^{7,14} and consistent with the smectic-state appearance of this sample,²⁷ while pure acids are usually powders indeed.²⁷ According to the recent paper²⁸ and inspired from intense peaks in XRD patterns of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ in small angles area, we can assume that a organized layer-type structure exists in these series of compound just like the image in Fig. 6, and we can calculate the height of each layer based on intense peaks. Meanwhile, a wide diffraction peak appears in the wide-angle region while there are still some strong intense peaks in the patterns of pure acids, indicating that this compounds do not have identified shape in total like pure acid but has a smectic gel-type phase at room temperature exists instead,²⁹ which is caused by weak connections of among the layers and hydrogen bonds system just like in Fig. 1.

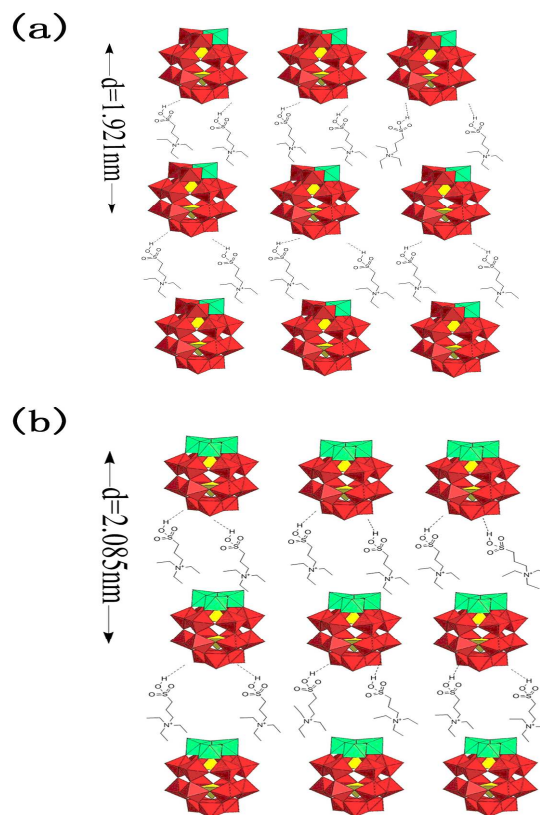


Fig. 6. The image of the layer-structure about $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ (a) and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ (b).

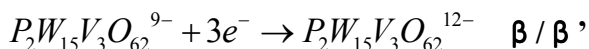
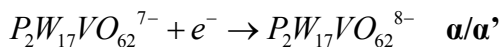
Electrochemical Properties

The Cyclic voltammetric (CV) study is a useful method in researching electrochemical characters of POM because it can indicate the variety of electrochemistry of POM, which can be applied into some other cases such as catalysis and photochemistry.³²

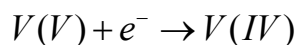
Actually, the number of electron in the electrochemical reaction can be calculated by following equation:

$$n = (E_h - E_p) / 0.0592$$

And E_h and E_p means oxidation potential and reduction potential. From Fig.7, these series of POM-based complexes can process electrochemical reduction in organic solution at certain conditions. Actually, $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ can process one step electrochemical reduced reaction in DMF:



In fact, these series of electrochemical reduced reaction can be logically referred to the reduction of the vanadium in POM anions:



This electrochemical reaction is of course unlikely to happen in water solution as a simple anion because of water protonation.

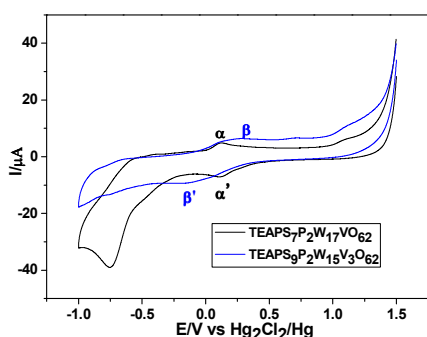


Fig. 7. Cyclic voltammetry of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ with a scanning rates of $50\text{mv}\cdot\text{s}^{-1}$ at the certain conditions in DMF : The density of substrate was 0.25mM and 0.2M NaClO_4 was assigned as supporting electrolyte. The working electrode was glass carbon which is 5mm in diameter and the counter electrode was Pt.

What's more, through further studies based on scanning rates and reduction current (Fig. 8. and Fig. 9.), we can conclude these electrochemical steps are mainly depended on the thermodynamic function more than the dynamic effect.

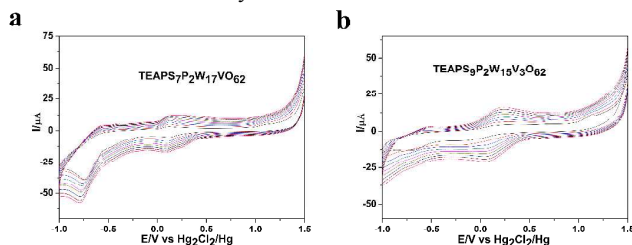


Fig. 8 Cyclic voltammetry of $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ (a) and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ (b) at different scanning rates: from inner to outer: 30, 50, 70, 90, 110, 130, 150, 170 and $190\text{mv}\cdot\text{s}^{-1}$.

In fact, from Fig. 10, we can find it that the scanning rates and reduction current follow this equation:

$$I \propto \nu^{0.5}$$

So these series of electrochemical reactions can be regarded as a type of reversible reaction somewhat, ³⁰ which is useful in the application of cell or electrochemical catalysis. ³¹

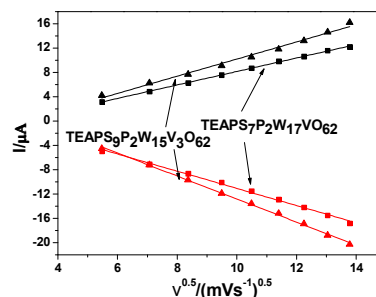


Fig. 9. Dependence of cathodic and anodic peak currents of the first reduction and oxidation waves as a function of the scan rate.

Unlike Keggin-type POM anion, ³³ the Dawson-type POM anion seems to be more stable in electrochemical reductions so only the vanadium in the structure can process reduction while the whole Dawson-type POM structure seem to keep stable during electrochemical reactions. This matter can be explained as the TEAPS cations and solvent DMF which are both playing roles in coordination with POM anions and the intermediate of Dawson structure seems more stable and hard to be reduced because of its high charge number that will attract more TEAPS cations. In addition, the anhydrous environment can role out the influence of the proton, which is an important influence in these electrochemical reactions in water solution, especially for Dawson-type POM, ³⁴ for protonated POM will be active and then it might reduce to disintegration in these electrochemical reactions, while in anhydrous environment POM without proton can behave differently and the POM structure retains stable. For these matters, $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$ can undergo one-step reversible electrochemical reactions at certain conditions that merely cause the vanadium in the POM anion reduced.

60 Conclusion

In this paper, we have reported the synthesis, the thermal properties and the electrochemical properties of a series of reversible phase transformation ionic-liquid-type gels based on sulfo-group grafted ammonium and Dawson structure POM anions, $[\text{TEAPS}]_7\text{P}_2\text{W}_{17}\text{VO}_{62}$ and $[\text{TEAPS}]_9\text{P}_2\text{W}_{15}\text{V}_3\text{O}_{62}$. These compounds can process phase transmission from a crystal phase to an isotropic phase, and during this period they show liquid crystal state, so they are promising candidates for the phase-transmission material in the application of fuel cell. What's more, these compounds can occur reversible electrochemical reaction in DMF at certain conditions, which is the vanadium in polyoxoanions can process electrochemical reactions that is unlikely to happen in water solution, which means they can be used in anhydrous environment as suitable oxidant.

75 Acknowledgments

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