Synthesis of Phosphorus-based Polyoxometalates and Their Corrosion Inhibition Performance

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Abstract. Polyoxometalates corrosion inhibitors used in experiments were prepared based on literatures, the synthesized products were characterized by infrared spectra and ultraviolet spectra. The test results showed that the synthesized polyoxometalates are of Keggin type. The corrosion inhibition performance was determined using A3 carbon steel specimen by static weight-loss technique in this paper. The corrosion inhibition performance of $Na_3[PMo_{12}O_{40}]$, $Na_3[PW_{12}O_{40}]$, $Na_4[PW_{11}VO_{40}]$ and $Na_5[PMo_{10}V_2O_{40}]$ was compared under certain conditions of temperature, corrosion inhibitor concentrations and pH values, and the effects of polyoxometalate concentration and temperature on the corrosion inhibition performance were studied. The experimental results show that all of the synthesized polyoxometalates have a good corrosion resistance, and that the corrosion inhibition efficiency of $Na_4[PW_{11}VO_{40}]$ is the best of all, and it increase with the inhibitors concentration and with the temperature.

1. Introduction

Since the 21st century, the development and application of corrosion inhibitor have been confronted with new challenges because of the deepening of the thought of sustainable development and the increasing awareness of environmental protection. The development of non-toxic harmless, green inhibitors which do not damage the environment will become the focus of the research and development of corrosion inhibitor [1-3]. Polyoxometalates are a type of metal oxide cluster, formed through inorganic metal-oxygen cluster anions, with a variety of structures, compositions, and functionalities [4]. The phosphorus based polyoxometalates is a kind of good corrosion and scale-inhibiting water treatment agent [5].

The aim of the present work is to synthesize the four phosphorus based heteropoly compounds and compare their corrosion inhibition properties in 3.5% sodium chloride solutions.

2. Experimental

2.1. Instruments and reagents

$Na_2WO_4 \cdot 2H_2O$, $Na_2MoO_4 \cdot 2H_2O$, $Na_3PO_4 \cdot 12H_2O$, Na_2HPO_4, $NH_4VO_3 \cdot 2H_2O$, H_2SO_4, $HClO_4$, HCl, NaOH, NaCl and diethyl ether were commercially bought, and the deionized water made in our lab. All reagents except deionized water are of analytical grade.

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DF-101S type heat-collecting constant temperature heating magnetic stirrer, SC-DC-220AB type electronic balance, PHS-3E type pH meter were commercially bought in China.

2.2. *Synthesis* and *structural* characterization of phosphorus-based polyoxometalates

2.2.1. Synthesis of phosphorus-based polyoxometalates. The four hybrid type of heteropoly acids of H_3 $[PMo_{12}O_{40}]$, $H_3[PW_{12}O_{40}]$, $H_4[PW_{11}VO_{40}]$ and $H_4[PMo_{10}V_2O_{40}]$ were synthesized by literature [6,7], respectively.

2.2.2. IR Spectra of Synthesized products. The IR spectra of several compounds were measured by a WQF-510 FT-IR spectrophotometer as KBr disks by a 769YP-15A powder pressing machine at ambient temperature.

2.2.3. UV spectra of Synthesized products. The ultraviolet spectra of several compounds were detected by a TU-1901 type double beam ultraviolet visible spectrophotometer.

2.3. Corrosion inhibition performance of synthesized polyoxometalates

To test for corrosion inhibition of synthetic heteropoly acids, the methods described in literatures [8] are used. A3 steel pieces (50mm×25mm×2mm) were mechanically polished with 4/0 emergy papers. The surface of the steel specimens was washed with hydrochloric acid, deionized water and anhydrous ethanol and finally with anhydrous alcohol. Then the steel specimens were stored in a dryer to dry.

For testing the corrosion behaviour of steel, specimens were immersed in 200 mL water containing 3.5% sodium chloride solutions, different heteropoly acids were added in the testing solutions respectively. After the finishing of the tests which lasted 70 h, the specimens were taken out of the testing solution and corrosion products were cleaned as following. a) The specimens were washed with tap water and then the metallic surface rust was scratched with knife. b) The specimens were washed with 10% hydrochloric acid and 0.5% hexamethylenamine. c) The specimens were washed with tap water, then washed twice with deionized water, finally washed twice with anhydrous alcohol.

The specimens were dried with a blower and weighed. The corrosion rate determined by the rate of loss of the steel owing to corrosion products removal is calculated as the equation

$$v = (m_1 - m_2) / t \cdot A. \qquad (1)$$

Where v is the metallic corrosions rate ($g \cdot m^{-2} \cdot h^{-1}$), m_1 is the metallic gravity before experiment (g), m_2 is the metallic gravity after experiment (g), t is the immersion time (h), A is surface area of sample(m^2).

The corrosion inhibition efficiency of the inhibitor E was calculated from the following equation

$$E = (v_1 - v_2) / v_1 \times 100\%. \qquad (2)$$

Where E corrosion inhibition efficiency, v_1 metallic corrosion rate without its inhibitor, v_2 metallic corrosion rate with its inhibitor.

3. Results and discussion

3.1. IR Spectra of Synthesized products

The synthesized products are detected by a WQF-510 FT-IR spectrophotometer, and the results are shown in Figure 1.

As shown in Figure 1, there are four characteristic absorption peaks of Keggin structure from 700 cm^{-1} to $1100cm^{-1}$ for the four kinds of synthesized heteropoly acids: the peak at from $1050cm^{-1}$ to

1100 cm^{-1} is attributed to the asymmetric stretching vibration of P-O bond, the peak at from 900 cm^{-1} to1000 cm^{-1} is attributed to the asymmetric stretching vibration of M-O (M=Mo, W) bonds, and the ones at from 850 cm^{-1} to 900 cm^{-1} and at from 750 cm^{-1} to 800 cm^{-1}, is to the ones of the M-O$_b$-M bridge bond and of the M-O$_c$-M bridge bonds. In addition, the peak near to 1620 cm^{-1} is attributed to the bending vibration of H-O-H bonds in the water molecule, The IR spectra show that the prepared compounds are of Keggin type [9].

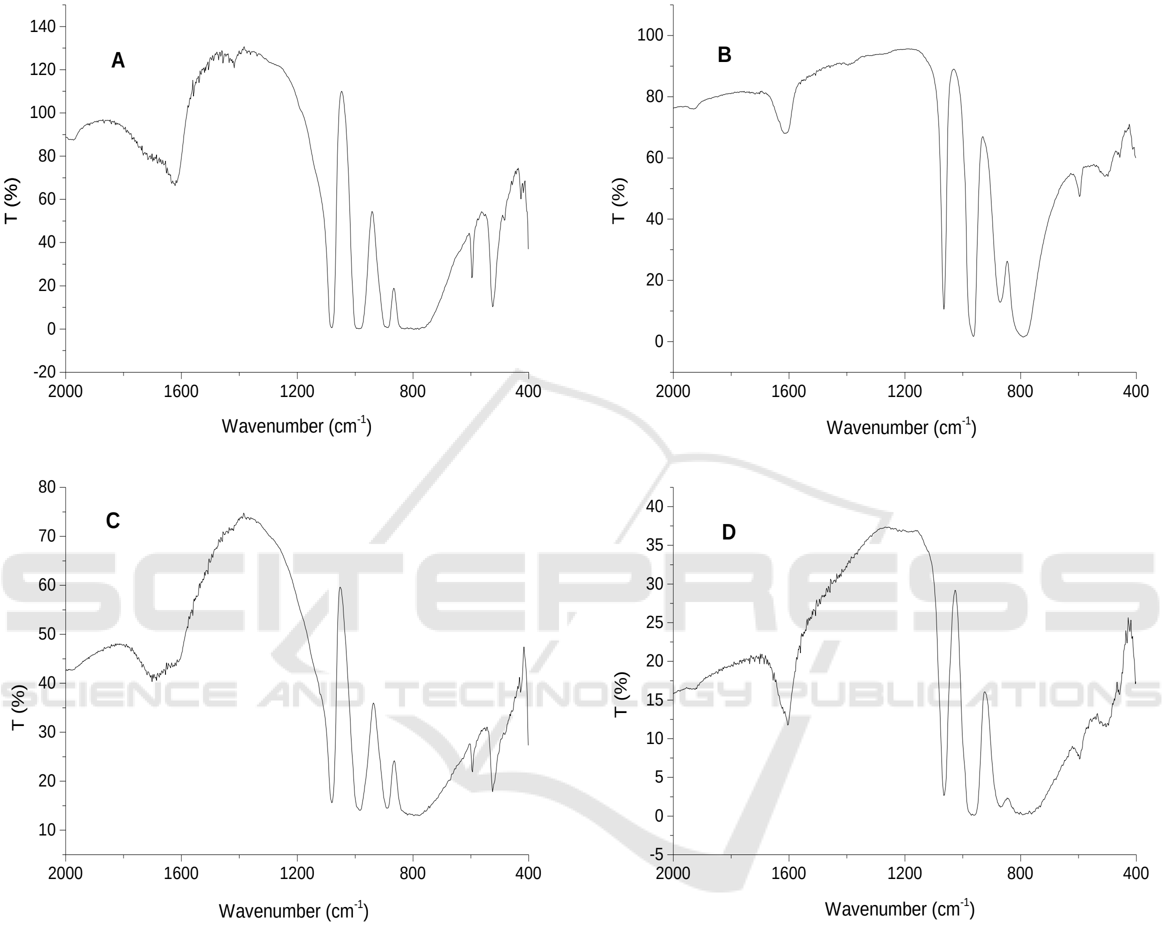

Figure 1. IR spectra of $H_3[PW_{12}O_{40}]$ (A), $H_5[PMo_{10}V_2O_{40}]$ (B), $H_4[PW_{11}VO_{40}]$ (C) and $H_5[PMo_{10}V_2O_{40}]$ (D).

3.2. UV spectra of Synthesized products

The synthesized products are detected by a double beam ultraviolet visible spectrophotometer, and the results are shown in Figure 2.

It is shown in Figure 2 that there are the two characteristic absorption peaks at about 200 nm and at about 260 nm in the four kinds of heteropoly acids. The one at about 200 nm is generated by the charge-transfer of Od→M, and the other at about 260 nm are generated by the charge-transfer of Ob/Oc→M [10]. The ultraviolet spectra further confirmed that the four synthesized heteropoly acids are of Keggin type.

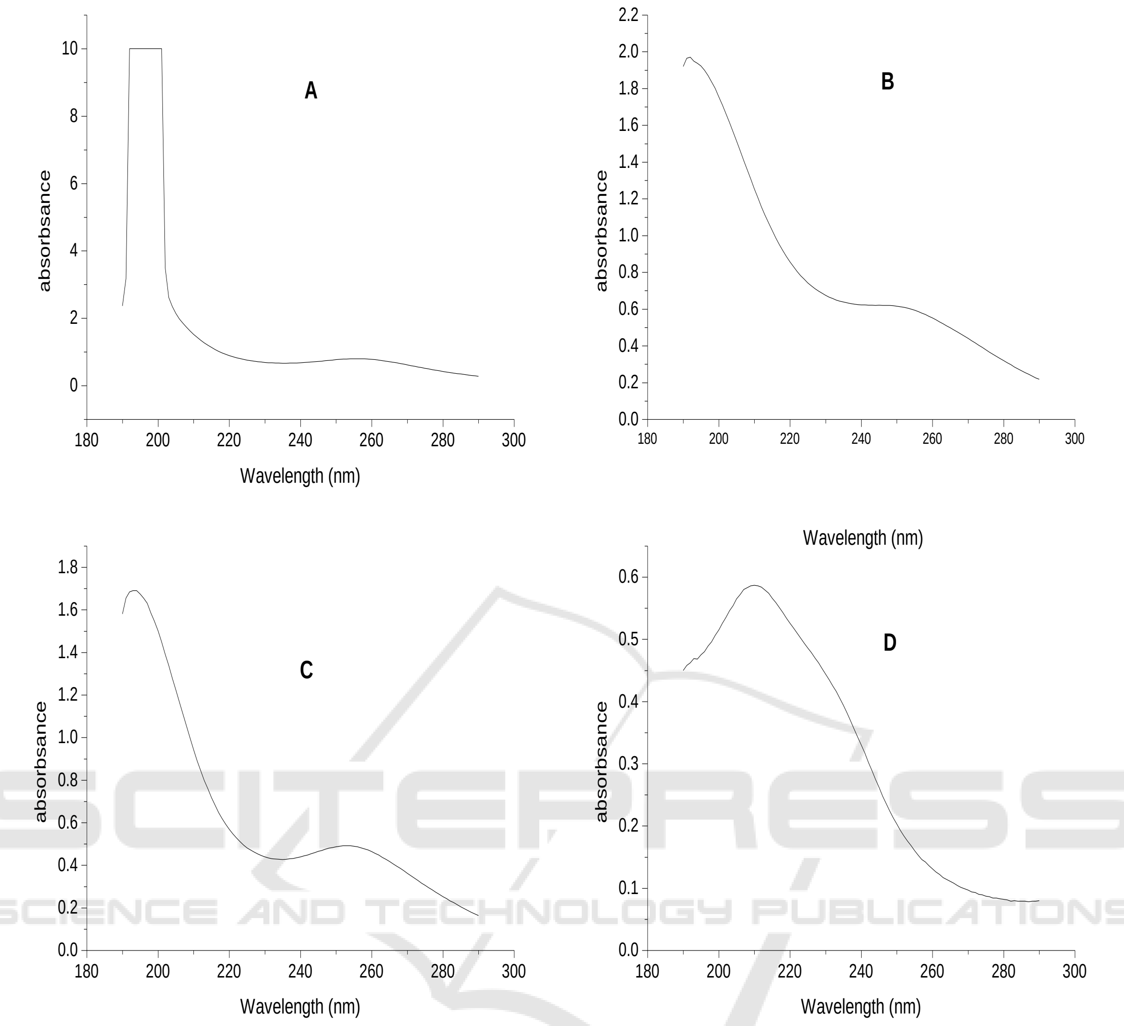

Figure 2. UV spectra of $H_3[PW_{12}O_{40}]$ (A), $H_5[PMo_{10}V_2O_{40}]$ (B), $H_4[PW_{11}VO_{40}]$ (C) and $H_5[PMo_{10}V_2O_{40}]$ (D).

3.3. Analysis on corrosion inhibition performance of synthesized products

The test results for corrosion resistance of synthesized products are shown in Table 1, Table 2 and Table 3.

Table 1. The corrosion rate and corrosion inhibition efficiency in different solutions[a].

inhibitor	pH value	Weight loss (g)	corrosion rate ($g\ m^{-2}\ h^{-1}$)	corrosion inhibition efficiency (%)
without inhibitor	8.13	0.148	0.7551	_
$Na_3[PMo_{12}O_{40}]$	8.09	0.058	0.2951	60.92
$Na_3[PW_{12}O_{40}]$	8.11	0.051	0.2602	65.54
$Na_4[PW_{11}VO_{40}]$	8.12	0.040	0.2041	72.97
$Na_5[PMo_{10}V_2O_{40}]$	8.11	0.042	0.2143	71.62

[a] Under the condition of the temperature of 20 ℃, the solution of 500 mg l^{-1}, and the immersing time of 70h.

Table 2. The corrosion rate and corrosion inhibition efficiency in different concentration of solutions[a].

inhibitor	Concentration (mg l^{-1})	Weight loss (g)	corrosion rate (g m^{-2} h^{-1})	corrosion inhibition efficiency (%)
without inhibitor		0.148	0.7551	_
Na4[PW11VO40]	300	0.063	0.3214	57.44
Na4[PW11VO40]	800	0.025	0.1276	83.10
Na5[PMo10V2O40]	300	0.065	0.3316	56.09
Na5[PMo10V2O40]	800	0.026	0.1327	82.43

[a] Under the condition of the temperature of 20 ℃, the pH of 8.0, and the immersing time of 70h.

Table 3. The corrosion rate and corrosion inhibition efficiency at 40 ℃ [a].

inhibitor	Concentration (mg l^{-1})	Weight loss (g)	corrosion rate (g m^{-2} h^{-1})	corrosion inhibition efficiency (%)
blank	800	0.187	0.9541	_
$Na_3[PMo_{12}O_{40}]$	800	0.031	0.1582	83.42
$Na_3[PW_{12}O_{40}]$	800	0.024	0.1224	87.17
$Na_4[PW_{11}VO_{40}]$	800	0.023	0.1173	87.71
$Na_5[PMo_{10}V_2O_{40}]$	800	0.025	0.1276	86.63

[a] Under the condition of the pH of 8.0, and the immersing time of 70h.

Table 1 shows the corrosion behaviour of steel without and with 500 mg·l^{-1} heteropoly compounds solutions containing 3.5% sodium chloride for 70 h at 20℃. It is observed that all of heteropoly compounds have some inhibition, and that the corrosion inhibition efficiency of heteropoly compounds containing vanadium are better than of the others, but the corrosion inhibition efficiency of $Na_4[PW_{11}VO_{40}]$ is the highest of all, that is, 72.97%. On the one hand, the corrosion resistance of multicomponent polyoxometalates is higher than that of bicomponent polyoxometalates. On the other hand, the oxidation of tungsten (VI) is weaker than that of molybdenum (VI), so that the tungstophosphoric polyoxometalates and the molybdophosphorates have different effects on metal materials. The tungstophosphoric polyoxometalates is less corrosive to metallic materials and easy to form a protective film on the surface of metal material to protect metallic materials from corrosion [11]. However, molybdophosphoric polyoxometalates has strong oxidizing effect, it can form a passivation film on the surface of metal material, and it will produce deeper corrosion to metal material. So, the corrosion inhibition efficiency of $Na_4[PW_{11}VO_{40}]$ is higher than that of $H_5[PMo_{10}V_2O_{40}]$.

Table 2 summarizes the results of steel corrosion with the change of concentration of $Na_4[PW_{11}VO_{40}]$ and $Na_5[PMo_{10}V_2O_{40}]$ in 3.5% sodium chloride solutions for 70h at 40℃. It is evident that the increase in concentration of $Na_4[PW_{11}VO_{40}]$ or $Na_5[PMo_{10}V_2O_{40}]$ has considerably reduced (up to about 10%) the corrosion rate. This is interpreted that the increase in concentration of heteropoly compounds favor the formation of a protective film on the surface of metal material to protect the surface of metallic materials from corrosion.

Table 3 lists the corrosion rate and the corrosion inhibition efficiency without and with 800 $mg \cdot l^{-1}$ heteropoly compounds solutions containing 3.5% sodium chloride for 70h at 40℃. It is easily to known that the corrosion inhibition properties of each of heteropoly compounds is almost equal when the solution contains 800 $mg \cdot l^{-1}$. This can be explained that the rate of the formation of a protective film on the surface of metal material from corrosion in all kinds of polyoxometalates solution is only related to the concentration of various ions, but not to the oxidation properties of ions.

4. Conclusions

(1) The synthesized polyoxometalates of $Na_3[PMo_{12}O_{40}]$, $Na_3[PW_{12}O_{40}]$, $Na_4[PW_{11}VO_{40}]$ and $Na_5[PMo_{10}V_2O_{40}]$ have good corrosion inhibition. When the concentration is low, the corrosion inhibition efficiency of $Na_4[PW_{11}VO_{40}]$ is the highest of all.

(2) The inhibition property of each of polyoxometalate increases with the increase of its concentration, and the corrosion inhibition of various polyoxometalates was close to a certain concentration.

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