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Mathematical model and reaction mechanism of molybdenum and tungsten extraction with TRPO from peroxide solution

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Abstract: To understand the behavior of molybdenum and tungsten extracted by tri-alkyl phosphine oxide (TRPO) from peroxide solution, the extraction mechanism was studied by slope method and Raman and FTIR spectroscopy. The empirical formulas of molybdenum and tungsten extraction distribution ratio (D_{Mo} and D_W) as functions of equilibrium pH, TRPO concentration and temperature were obtained by establishing mathematical models. Furthermore, the reliability of the empirical formula was verified in the H^+−W−Mo−H_2O_2 solution. The results indicate that the calculated values of D_{Mo} or D_W were consistent with the experimental values. The apparent extraction equilibrium constants of molybdenum and tungsten were $K_{Mo}^{app}=8.51\times10^3$ ($0.74\leq pH_e\leq1.7$), $K_{Mo}^{app}=99.89\times10^3$ ($1.7<pH_e\leq4.62$) and $K_W^{app}=2.65\times10^3$ ($0.92<pH_e<2.16$) at 20 °C, respectively. The main extraction complex of molybdenum or tungsten was $[H_2(Mo\text{ or }W)_2O_3(O_2)_4(H_2O)_2]\cdot2TRPO$. These empirical formulas can be used to analyze and estimate the extraction and separation of Mo and W from low molybdenum and tungsten concentration solutions.

Key words: tungsten; molybdenum; solvent extraction; tri-alkyl phosphine oxide (TRPO); hydrogen peroxide (H_2O_2)

1 Introduction

Tungsten (W) and molybdenum (Mo) are important strategic rare metals [1−4]. Due to the effect of lanthanide contraction, W and Mo are similar in nature, associated with each other in tungsten resource, and difficult to separate [5]. With the continuous consumption of high-grade tungsten resources, the Mo content in the available resources has become higher and higher in recent years [6,7]. Therefore, a feasible process for the separation of Mo from tungstate solutions with high Mo content was explored urgently [8−11].

Presently, the methods which have been widely used in industry are based on the property differences between thiomolybdate (MoS_4^{2-}) and tungstate [12−16]. These methods exhibit many advantages of low cost, easy operation and complete removal of Mo when the mass ratio of Mo/WO_3 is low (<2%). However, the sulfurizing reagents used for Mo conversion are malodorous, poisonous and costly, and their consumption increased greatly with the increase of Mo content in tungstate solution [14,17−19]. Thus, these methods are not applicable for Mo removal from tungstate solutions with a high Mo/WO_3 mass ratio. Compared with the thiomolybdate method, the hydrogen peroxide complexation aided extraction method based on the property difference between

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peroxomolybdate and peroxotungstate shows great industrial value due to the advantages of low cost and cleanliness [20−24]. However, this method poses some problems such as high W extraction, high volatility and water solubility of methyl-isobutyl ketone (MIBK), leading to serious organic phase loss [25]. Thus, it has not yet been applied in industry.

Recently, a novel extraction process for separation of Mo from peroxotungstate solution containing high Mo content with tri-alkyl phosphine oxide−tributyl phosphate (TRPO−TBP) mixed extractant was proposed [26,27]. This process has successfully scaled-up to semi-industrialized tests, and achieved good separation effects of W and Mo. However, some problems, such as poor feed solution stability, narrow pH operating window, third phase formation and multiple extraction stages for deep Mo removal, have exposed in the industrialization test [28]. Due to the complex species distribution and conversion in the W−Mo−H_2O_2 system [22,23,29−31], there are few basic studies on the extraction and separation of this system, resulting in the inability to effectively solve the above problems. Therefore, to improve the separation efficiency of the practical process, it is necessary to study the chemical behavior of Mo and W extracted by TRPO and TBP from peroxide solutions.

Previous research results show that the unit saturated Mo capacity of TRPO is much higher than that of TBP in hydrogen peroxide system [21,26], which means that the chemical behavior of Mo and W extracted by TRPO is dominant in the separation of the both. LI and ZHANG [21] determined the extraction reaction of Mo and W with TRPO from peroxide system by using saturation, slope method and IR spectroscopy, indicating that this process is a neutral complexation. However, the effects of different factors on extraction of Mo and W by TRPO were not involved.

The purpose of the present work is to understand the chemical behavior of Mo and W with TRPO from hydrogen peroxide solution. The pure Mo−H_2O_2 or pure W−H_2O_2 system was used as aqueous phase to study reaction mechanism of Mo or W. The effects of different parameters such as pH value, TRPO concentration and temperature on the extraction of Mo and W were investigated. The mathematical models of extraction were established and the empirical formula between logarithm of distribution ratio and these above factors were obtained. The apparent thermodynamic data of extraction process were calculated and the structure of extraction complex was determined by Raman and FTIR spectroscopy. Finally, the reliability of the empirical formulas was verified by comparing the experimental and calculated data of the separation of tungsten and molybdenum from the W−Mo−H_2O_2 system by TRPO.

2 Experimental

2.1 Reagents

Sodium tungstate dihydrate ($Na_2WO_4·2H_2O$, 99.5%), sodium molybdate ($Na_2MoO_4·2H_2O$, 99.0%) and hydrogen peroxide (H_2O_2, mass fraction of 30%) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Other chemical reagents including sulfuric acid (H_2SO_4), sodium sulfate (Na_2SO_4) and sodium hydroxide (NaOH) etc are of analytical reagent grade.

The organic extractant tri-alkyl phosphine oxide (TRPO, purity ≥93%) purchased from Shanghai Rare-Earth Chemical Co., Ltd. (Shanghai, China) was employed for extraction without purification. The commercial sulfonated kerosene (aromatics content is less than 10%) or *n*-heptane (purity ≥97%) was employed as diluent, which were purchased from Wenyi Petrochemical Co., Ltd. (Suzhou, China) and Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China), respectively.

2.2 Aqueous and organic phase preparation

The acid peroxomolybdate solution (or acid peroxotungstate solution, mixed peroxo-molybdate and peroxo-tungstate solution) was prepared by adding sulfuric acid and hydrogen peroxide into sodium molybdate solution (or sodium tungstate solution, mixed sodium molybdate and tungstate solution). To avoid the decomposition of H_2O_2, all solutions must be acidified with sulfuric acid before adding H_2O_2 [32]. The dosage of H_2O_2 was calculated by molar ratio of H_2O_2 to metal (abbreviate to, H_2O_2/Me, where Me is Mo or W). The pH values of solutions were adjusted by adding H_2SO_4 and NaOH solution. The concentration of sulfate was kept at 0.3 mol/L by adding Na_2SO_4 solution. Organic phase was prepared by mixing TRPO with kerosene or *n*-heptane in a certain volume ratio.

2.3 Experimental equipment and method

All solvent extraction experiments were performed by mixing equal volumes (20 mL) of two phases in separatory funnel. A certain reaction temperature and vibration intensity were maintained during the extraction process. After shaking, two phases were separated by standing.

The samples used for spectral analysis were the saturated loaded organic phase after solvent volatilization and moisture drying. In the experiments, the composition of organic phase was 5 vol.% TRPO (0.1176 mol/L) + 95 vol. % *n*-heptane, and aqueous phases were peroxomolybdate solution containing Mo content of 5 g/L and H_2O_2/Mo of 6, and peroxotungstate solution containing W content of 5 g/L and H_2O_2/W of 6. The extraction conditions were described above.

The pH value of aqueous phase was measured by pH meter (HI9125, HANNA, ±0.01). The concentration of H_2O_2 in aqueous phase was measured by potassium permanganate titration. The concentrations of Mo and W in aqueous phase were measured by ICP-OES (Icap7400 Radial, Thermo Scientific). The concentrations of Mo and W in the organic phase were determined by material balance calculation. The Raman spectra of sample aqueous solutions and loaded organic phases were recorded on a confocal micro-Raman spectrometer (inVia, Renishaw). The samples were excited by 532 nm laser line with laser power of 50 mW and exposure time of 10 s at room temperature. The cumulative times of Raman spectra of aqueous solution and organic phases were 10 and 4 times, respectively. The IR spectra of organic phases were recorded at 4 cm^{-1} resolution and in the wavenumber range of 400−4000 cm^{-1} by using FTIR spectrometer (Thermo Scientific Nicolet iS5) with KBr optical windows.

2.4 Data processing

The distribution ratio (D) and separation coefficient ($\beta_{Mo/W}$) were defined as follows:

$$D=\frac{c_{Me}^{org}}{c_{Me}^{aq}} \tag{1}$$

$$\beta_{Mo/W}=\frac{D_{Mo}}{D_{W}} \tag{2}$$

where c_{Me}^{org} and c_{Me}^{aq} are the concentrations of Mo or W in loaded organic phase and raffinate, respectively, mol/L.

2.5 Extraction equilibrium

In acid medium with the presence of H_2O_2, the various polymerization, protonation and complexation equilibria reactions for Mo or W species can be written as general form as follows:

$$pMeO_4^{2-}+qH_2O_2+rH^+ \leftrightarrow [H_{(r+2q-2m)}Me_pO_{(4p-m)}(O_2)_q]^{(2p-r)-}+mH_2O \tag{3}$$

According to the previous works, the following Mo species should be considered in the reaction model for the aqueous phase [22,32]: $[HMoO_3(O_2)]^-$ (8.53), $[H_2MoO_3(O_2)]$ (11.22), $[HMoO_2(O_2)_2]^-$ (11.61), $H_2MoO_2(O_2)_2$ (13.77), $[Mo_2O_3(O_2)_4]^{2-}$ (23.77), $[HMo_2O_3(O_2)_4]^-$ (25.9), $[Mo_4O_{12}(O_2)_2]^{4-}$ (26.8), $[HMo_4O_9(O_2)_4]^-$ (48.8), $[H_nMo_7O_{23}(O_2)]^{(6-n)-}$ (n=0−3, 56.48, 60.88, 64.48, 66.28) and $[H_nMo_7O_{22}(O_2)_2]^{(6-n)-}$ (n=0−3, 59.3, 63.7, 67.5, 71.0). The data in parentheses are the formation constants of the species, that is, lg $K_{(p,q,r)}$. And following W species should be considered [23]: $[HWO_2(O_2)_2]^-$, $[HW_2O_3(O_2)_4]^-$, $[W_4O_{12}(O_2)_2]^{4-}$, $[W_7O_{22}(O_2)_2]^{6-}$ and $[W_7O_{23}(O_2)]^{6-}$. Depending on the pH value, H_2O_2 and metals concentration, some of these species exist in negligible quantities under certain conditions.

The extraction reaction can be described as general equation as follows:

$$M_{(aq)}^{n-}+nH_{(aq)}^{+}+k\text{TRPO}_{(org)}=[H_nM\cdot k\text{TRPO}]_{(org)} \tag{4}$$

where M^{n-} represents peroxide compound that can be extracted; n and k are stoichiometric coefficients. Thus, the thermodynamic equilibrium constant of extraction Reaction (4) can be written as

$$K_{ex}=\frac{a_{(H_nM\cdot k\text{TRPO})}}{a_{M^{n-}}a_{H^+}^{n}a_{\text{TRPO}}^{k}}=\frac{c_{(H_nM\cdot k\text{TRPO})}}{c_{M^{n-}}c_{H^+}^{n}c_{\text{TRPO}}^{k}}\cdot\frac{\gamma_{(H_nM\cdot k\text{TRPO})}}{\gamma_{M^{n-}}\gamma_{H^+}^{n}\gamma_{\text{TRPO}}^{k}}=\frac{[H_nM\cdot k\text{TRPO}]}{[M^{n-}][H^+]^n[\text{TRPO}]^k}\cdot Q \tag{5}$$

where a, c and γ represent the activities, molar concentrations and activity coefficients of corresponding species, respectively; Q is the quotient of the activity coefficients. Based on the assumption of the above equilibrium for data processing to determine the extraction compound, an important prerequisite is to assume that the

activity coefficient of each species is a constant value at equilibrium [33], which is theoretically feasible. Considering that the solubilities of aqueous/organic phases in each other are negligible, the distribution factor of species M between two phases can be calculated by determining the concentration of M in each phase:

$$D=\frac{[\mathrm{M}]_{\mathrm{T,org}}}{[\mathrm{M}]_{\mathrm{T,aq}}}=\frac{[\mathrm{H}_n\mathrm{M}\cdot k\mathrm{TRPO}]}{[\mathrm{M}]_{\mathrm{T,aq}}} \tag{6}$$

Taking Mo as an example, its total concentration in aqueous phase is

$$[\mathrm{Mo}]_{\mathrm{T,aq}}=\sum\nolimits_p[\mathrm{MoO}_4^{2-}]^p[\mathrm{H_2O_2}]^q[\mathrm{H}^+]^r K_{(p,q,r)} \tag{7}$$

When choosing the appropriate hydrogen peroxide dosage and acidity, the species in the system can be simplified. Under the conditions of this study, the main species in the aqueous phase is $\mathrm{M}^{n-}=[\mathrm{H}_{(2-n)}\mathrm{Mo_2O_3(O_2)_4}]^{n-}$ (n=0, 1 or 2). Therefore, the total concentration of M species ($[\mathrm{M}]_\mathrm{T}$) is expressed as

$$[\mathrm{M}]_{\mathrm{T,aq}}=[\mathrm{M}^0]+[\mathrm{M}^{1-}]+[\mathrm{M}^{2-}] \tag{8}$$

where

$$[\mathrm{M}^{n-}]=\beta_{(2-n)}[\mathrm{M}^{2-}][\mathrm{H}^+]^{(2-n)}=\frac{\beta_{(2-n)}[\mathrm{M}]_\mathrm{T}[\mathrm{H}^+]^{(2-n)}}{\left(1+\sum_{i=1}^{2}\beta_i[\mathrm{H}^+]^i\right)}=[\mathrm{M}]_\mathrm{T}\cdot\phi \tag{9}$$

where β_i is the ith cumulative protonation constant of M^{2-}; $\phi=\beta_{(2-n)}[\mathrm{H}^+]^{(2-n)}\Big/(1+\sum_{i=1}^{2}\beta_i[\mathrm{H}^+]^i)$. At a given temperature and acidity, ϕ is constant.

Then, substituting Eqs. (6) and (9) into Eq. (5) gives

$$K_{\mathrm{ex}}=\frac{D\cdot Q}{\phi[\mathrm{H}^+]^n[\mathrm{TRPO}]^k} \tag{10}$$

Then, Eq. (10) transforms into

$$\lg D=\lg K_{\mathrm{ex}}+\lg\phi+n\lg[\mathrm{H}^+]+k\lg[\mathrm{TRPO}]-\lg Q \tag{11}$$

The relationship among the change in Gibbs' free energy ΔG^Θ (kJ/mol), standard enthalpy change ΔH^Θ (kJ/mol), standard entropy change ΔS^Θ ($\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$), temperature and natural logarithm of the equilibrium constant is given by

$$\Delta G^\Theta=\Delta H^\Theta-T\cdot\Delta S^\Theta=-2.303RT\lg K_{\mathrm{ex}} \tag{12}$$

Then, Eq. (13) can be obtained:

$$\lg D=-\frac{\Delta H^\Theta}{2.303RT}+\frac{\Delta S^\Theta}{2.303R}+\lg\phi+n\lg[\mathrm{H}^+]+k\lg[\mathrm{TRPO}]-\lg Q \tag{13}$$

It also can be written as

$$\lg D=-\frac{\Delta H^{\mathrm{app}}}{2.303RT}+\frac{\Delta S^{\mathrm{app}}}{2.303R}-n\mathrm{pH_e}+k\lg[\mathrm{TRPO}] \tag{14}$$

where ΔH^{app} and ΔS^{app} represent the apparent standard changes of enthalpy and entropy of the extraction reaction (Eq. (4)), respectively. Therefore, a distribution ratio equation (Eq. (14)) of Mo or W extraction by TRPO from hydrogen peroxide system can be determined. Furthermore, the apparent changes in enthalpy and entropy of the extraction reaction can be obtained.

3 Results and discussion

3.1 Selection of experimental conditions

Previous studies show that various factors, such as metal concentration, H_2O_2 dosage, pH value, TRPO concentration and temperature, have significant effects on the extraction of W and Mo [26,28]. However, to simplify experimental process and improve accuracy of the results, the parameters of some factors should be controlled in an appropriate range.

During the mechanism study, the content of metal should be much smaller than that of TRPO, so that the amount of TRPO consumed via extraction was negligible compared with the initial TRPO concentration [34]. In this research, the content of Mo or W was selected as 1 g/L. In this way, the concentration of TRPO can be appropriately reduced. In addition, to avoid the reaction of TRPO with acid to form the third phase, the initial pH of aqueous phase was controlled above 0.7, which is far less than the acidity required to form the third phase [35].

The H_2O_2 concentration affects the existence form of peroxomolybdates, thereby affecting the extraction of Mo. As shown in Fig. 1, the species, $[\mathrm{Mo_7O_{22}(O_2)_2}]^{6-}$, is gradually converted into $[\mathrm{HMo_2O_3(O_2)_4}]^-$, which simplifies the composition of Mo species in the solution as H_2O_2/Mo increases. When H_2O_2/Mo>2, the degree of Mo polymer

species does not exceed dimerization [22]. In addition, based on the intensity change of peak at 318 cm^{-1}, there is bound water in the dimer ion, namely $[HMo_2O_3(O_2)_4(H_2O)_2]^-$ [36]. It is mentioned in the literature that $[H_2MoO_2(O_2)_2]\cdot SO_4^{2-}$ may also be formed [32], but due to its low concentration and the limited resolution of Raman spectroscopy, it is difficult to identify it spectrally. A similar situation applies to peroxotungstate solution [23]. The H_2O_2 dosage has been selected as molar ratio of 1.5−2.0 in previous study [26]. To reasonably reduce the influence of the species composition, the dosage of H_2O_2 was selected as molar ratio of 6 in this experiment.

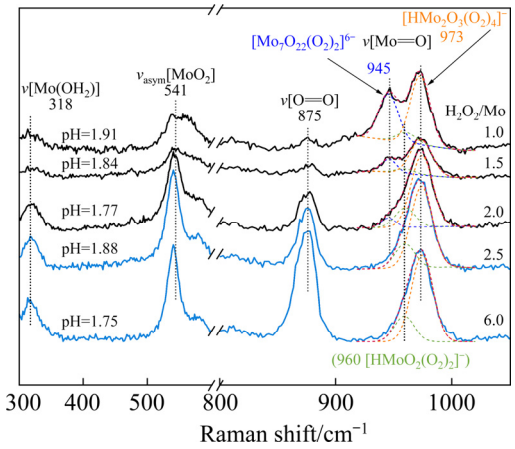

Fig. 1 Raman spectra of peroxomolybdate solution containing 1 g/L Mo at different initial molar ratios of H_2O_2/Mo

3.2 Extraction of Mo by TRPO

3.2.1 Effects of various factors on Mo distribution ratio

The effect of pH on the extraction of Mo with TRPO is mainly reflected by two aspects: composition of Mo species in solution and extraction equilibrium. Figure 2 shows the changes in the pH value of the aqueous solution before and after extraction. When the initial pH (pH_{init}) was in range of 0.74−1.70, the equilibrium pH (pH_e) hardly changed, indicating almost no free H^+ consumption during the extraction process. When the pH_{init} was larger than 1.70, the pH_e changed significantly, higher than the pH_{init} value, which indicates that the extraction process is accompanied by the consumption of a large amount of free H^+. Moreover, an increase of TRPO concentration and decrease of temperature led to a greater increase amplitude in the pH of aqueous phase, indicating that the extraction of molybdenum increased. In the subsequent experiments, the pH_e value was selected as investigating factor.

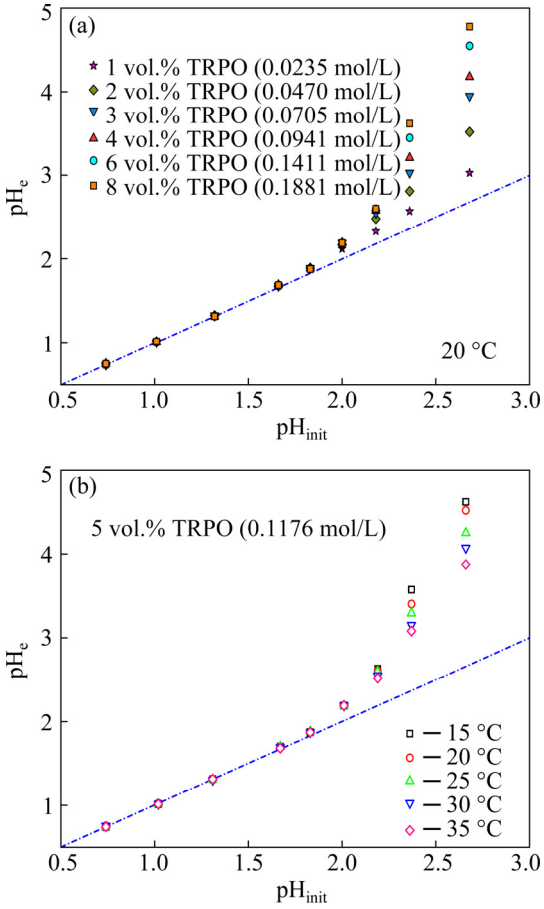

Fig. 2 Changes in pH of aqueous phases before and after Mo extraction at different TRPO contents (a) and temperatures (b)

The effects of pH_e on lg D_{Mo} at different TRPO concentration and temperatures are shown in Figs. 3(a, b), respectively. A decrease of pH_e from 4.62 to 1.70 led to an increase in lg D_{Mo}, while a decrease in pH_e from 1.70 to 0.74 had no effect on Mo extraction by TRPO. The similar linear relation between lg D_{Mo} and pH_e was observed. The average slope factors of two linear relation are zero and −0.62 in the pH_e range of 0.74−1.70 and 1.70−4.62, respectively. However, a decrease of TRPO concentration led to an increase in the slope factor which was −0.329 at 1 vol.% TRPO (0.0235 mol/L). This is mainly because the concentration of free extractant was so low that the effect of pH_e on lg D_{Mo} was no longer the dominant factor. This value was not used in the calculation of above average slope due to the large deviation. To sum up,

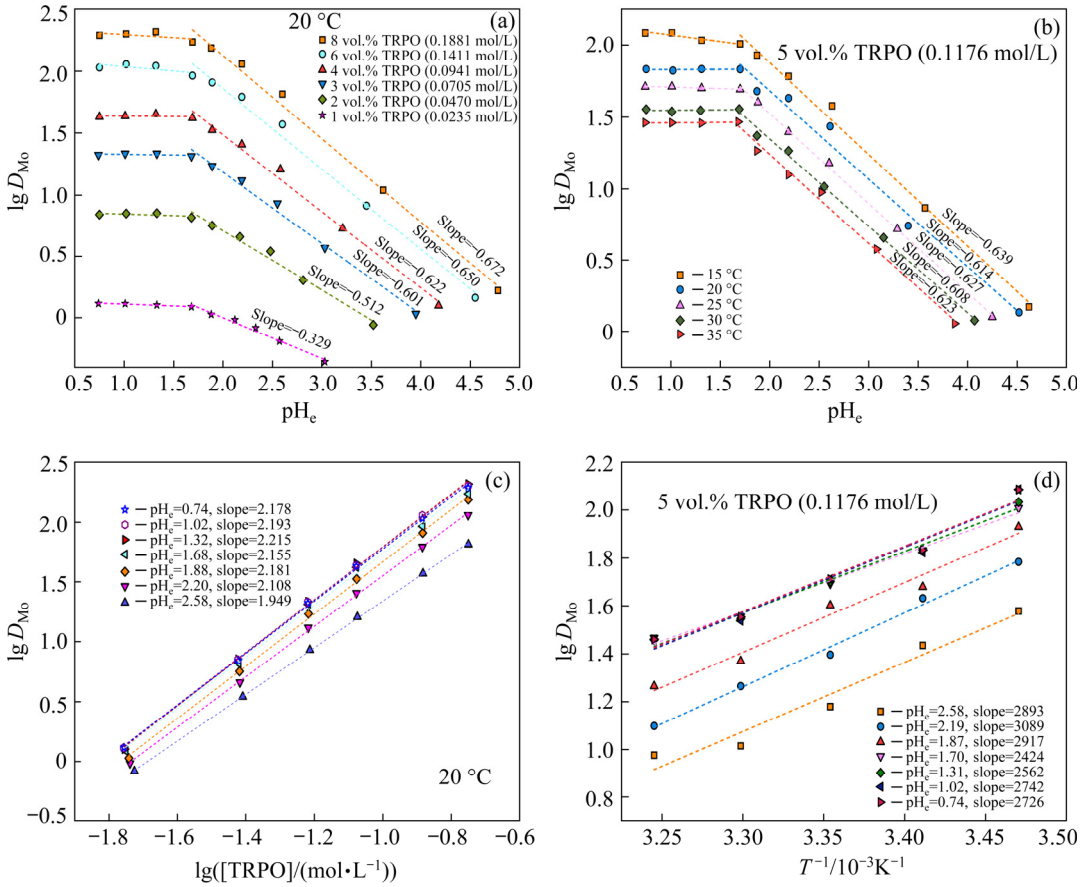

Fig. 3 Logarithm of distribution ratio of Mo as functions of various factors: (a, b) pH_e; (c) lg[TRPO]; (d) Reciprocal of temperature

the extraction reaction has almost no free H^+ consumption at high acidity, while the extraction needs to consume large amount of free H^+ at low acidity.

The effects of lg[TRPO] on $\lg D_{Mo}$ were investigated at different pH_e (0.74−2.58) and at 20 °C (Fig. 3(c)). The values of $\lg D_{Mo}$ increased with an increase in lg[TRPO]. In addition, an excellent linear relation with an average slope of 2.14(±0.12) in the pH_e range of 0.74−2.58 was obtained. Therefore, the coefficient of lg[TRPO] in Eq. (14) for Mo extraction can be determined to be 2.14.

The effect of temperature on distribution ratio of Mo at TRPO volume fraction of 5% (0.1176 mol/L) is shown in Fig. 3(d). The negative correlation between $\lg D_{Mo}$ and temperature was observed, suggesting that lower temperature was beneficial to Mo extraction. An excellent linear relation is shown between $\lg D_{Mo}$ and $1/T$. The average slope factors were calculated in the range $0.74 \le pH_e \le 1.70$ and $1.70 < pH_e \le 4.62$ to be 2614 and 2831, respectively, according to the previous analysis on the effect of pH_e.

3.2.2 Equation model of molybdenum extraction by TRPO

Based on the data in Fig. 3, the distribution ratio equation of Mo during its extraction by TRPO has different expressions in two pH_e windows. The main equation parameters and thermodynamic data for Mo extraction are summarized in Table 1. The negative apparent enthalpy and entropy changes indicate that the process is exothermic and there is reduction in the disorder of the extraction system.

From those data listed in Table 1, the equation for Mo distribution ratio is written as

$$\lg D_{Mo} = \begin{cases} 2614/T - 4.988 + 2.14\lg[\text{TRPO}] \\ \quad (0.74 \le pH_e \le 1.70) \\ 2831/T - 4.659 - 0.62pH_e + \\ \quad 2.14\lg[\text{TRPO}] \quad (1.70 < pH_e \le 4.62) \end{cases} \tag{15}$$

Table 1 Parameters in distribution equation of Mo extracted by TRPO from acidic peroxomolybdate solution

Factor	$0.74 \le pH_e \le 1.70$		$1.70 < pH_e \le 4.62$	
	Value	Standard error	Value	Standard error
Coefficient of $1/T$	2614	65.06	2831	123.35
Coefficient of pH_e	0	–	−0.62	0.01
Coefficient of lg[TRPO]	2.14	0.04	2.14	0.04
Constant	−4.988	0.01	−4.659	0.01
ΔH^{app}/(J·mol^{-1})	−50050.63	–	−54205.56	–
ΔS^{app}/(J·mol^{-1}·K^{-1})	−95.50	0.69	−89.20	1.35
K_e^{app} (20 °C)	8.51×10^3	–	99.89	–

To verify the reliability of the distribution ratio of Eq. (15), subsequently, Mo extraction experiments were conducted at different temperatures, pH_e values and TRPO concentrations with initial H_2O_2/Mo of 6 and Mo content of 1 g/L, and forty experimental data were obtained. A plot of the relationship between experimental and calculated lg D_{Mo} values is displayed in Fig. 4. The line fitted by calculated values almost coincides with the expected value line, indicating that this equation has a good prediction of Mo extraction from peroxomolybdate solution with TRPO.

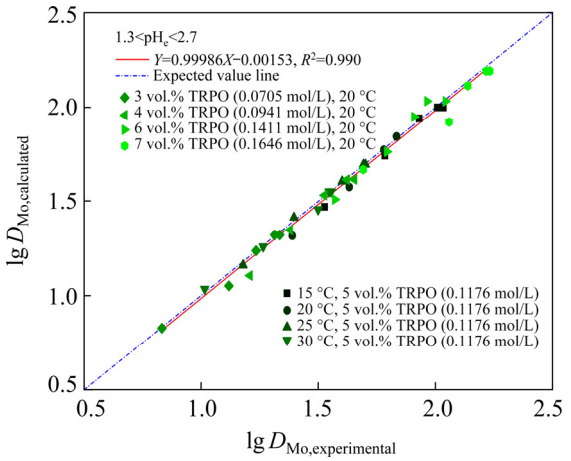

Fig. 4 Comparison of experimental and calculated values for Mo distribution ratio in extraction of peroxomolybdate solution by TRPO at Mo content of 1 g/L and H_2O_2/Mo of 6

3.2.3 Reaction equation of Mo extraction

To further reveal the reaction mechanism of Mo extraction by TRPO in acidic solution containing rich hydrogen peroxide, the change in structure of organic phase before and after extraction was characterized by FTIR and Raman spectroscopy (Fig. 5). No difference was observed

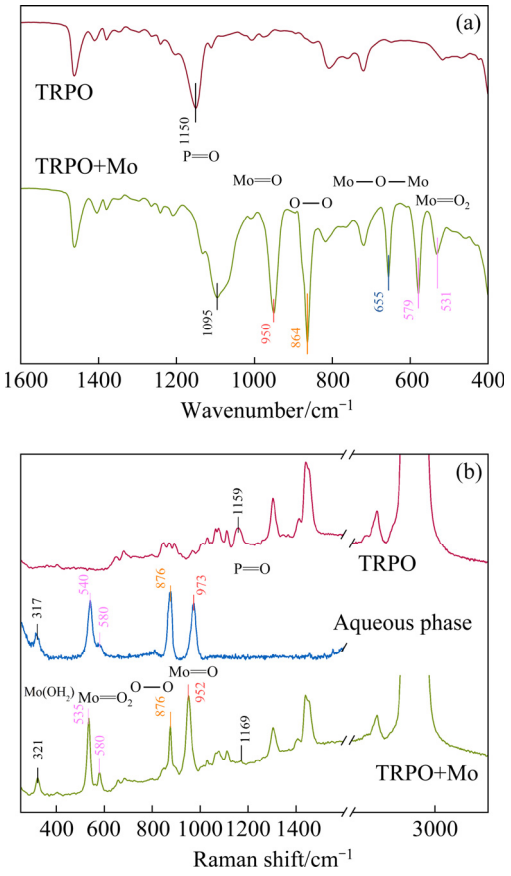

Fig. 5 FTIR (a) and Raman (b) spectra of organic phase before and after Mo extraction at pH_e 1.32 and Raman spectrum of aqueous phase before extraction

in the wavenumber range of 1600−4000 cm^{-1}, and this range is not the fingerprint area of peroxomolybdate, so the spectrum in this range was not shown (Fig. 5(a)). As shown in Fig. 5(a), the observed peaks at 950, 864, 655, 576 and 531 cm^{-1} on FTIR spectrum of loaded organic phase were attributed to ν[Mo═O], ν[O—O], ν_{asym}[Mo_2O], ν_{sym}[MoO_2] and ν_{asym}[MoO_2] [21,37], respectively, which suggested that the Mo species extracted was peroxomolybdate [$H_2Mo_2O_3(O_2)_4$]. Similarly, the characteristic vibration frequencies of

peroxomolybdate also were observed on Raman spectrum of loaded organic phase (Fig. 5(b)). By comparing the Raman spectra of dimeric peroxomolybdate in the aqueous phase, the stretching vibration peak of the Mo═O bond red-shifted from 973 to 952 cm^{-1} after peroxomolybdate was extracted by TRPO. In addition, the peak at 321 cm^{-1} also indicates that the dimer extracted contains bond water, namely $[H_2Mo_2O_3(O_2)_4(H_2O)_2]$ [36]. No characteristic peak of S—O bond (about 980 cm^{-1}) was observed on the Raman spectrum of the loaded organic phase, indicating that the extracted peroxomolybdate did not coordinate with SO_4^{2-}. The peak at 1150 cm^{-1} on FTIR spectra was assigned to the stretching vibration of phosphoryl (P═O) in TRPO [21,38], red-shifting to 1095 cm^{-1} after loading peroxomolybdate. This indicates that the reaction mechanism of peroxomolybdate extraction by TRPO is neutral complexation, that is, the coordination between peroxomolybdate and oxygen atom in phosphoryl.

Since the stoichiometric constants of extraction reaction are all integer numbers, the stoichiometric constant of H^+ in the extraction reaction is 0 ($0.74 \le pH_e \le 1.70$) and 1 ($1.70 < pH_e \le 4.62$), and the constant of TRPO is 2. Therefore, it can be considered that the above two reaction modes occurred simultaneously in the solution with $pH_e > 1.70$, where the apparent slope is about 0.62. The extraction equation of Mo in solution with high molar ratio of H_2O_2/Mo (H_2O_2/Mo>2) can be deduced as follows:

When $0.74 \le pH_e \le 1.70$,

$$H_2Mo_2O_3(O_2)_4(H_2O)_{2(aq)} + 2TRPO_{(org)} = [H_2Mo_2O_3(O_2)_4(H_2O)_2 \cdot 2TRPO]_{(org)} \quad (16)$$

When $1.70 < pH_e \le 4.62$, in addition to Eq. (16), the following reaction also occurs:

$$[HMo_2O_3(O_2)_4(H_2O)_2]^-_{(aq)} + H^+_{(aq)} + 2TRPO_{(org)} = [H_2Mo_2O_3(O_2)_4(H_2O)_2 \cdot 2TRPO]_{(org)} \quad (17)$$

3.3 Extraction of W by TRPO

3.3.1 Effects of various factors on W distribution ratio

The pH change of aqueous phase before and after W extraction with TRPO was not obvious (Fig. 6). After W extraction by TRPO, the pH of aqueous phase also increased, but the increase was much smaller than that caused by the extraction of Mo. When pH_{init} was less than 1.2, there was no change in pH before and after extraction, speculating an extraction reaction of W by TRPO without H^+ consumption at this acidity [21]. However, it is evident from the relationship between lg D_W and pH_e (Figs. 7(a, b)) that an excellent linear relation with an average slope value of (−1.02±0.11) was observed in entire pH_e range from 0.92 to 2.16, indicating that the W extraction process has a constant reaction mode which consumes H^+ even at low pH. This is because the amount of tungsten extracted is small, resulting in a negligible change in the total acidity of the system caused by the consumption of free H^+.

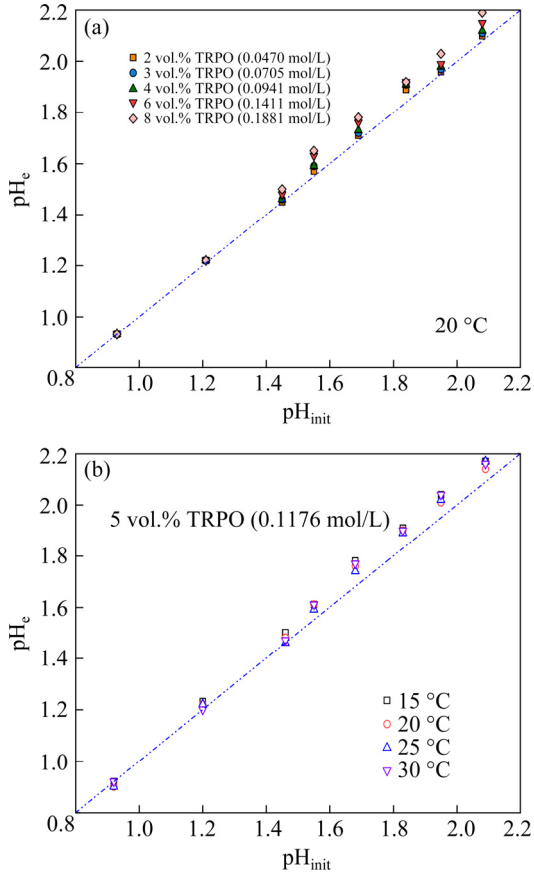

Fig. 6 Changes in pH of aqueous phase before and after W extraction at different TRPO concentration (a) and temperatures (b)

Figure 7(c) shows the effect of lg[φ(TRPO)] on lg D_W at different pH_e (0.93−1.98) and at 20 °C. Increasing TRPO concentration led to an increase in the extraction of W. An excellent linear relation with an average slope of (1.83±0.18) in the pH_e range of 0.93−1.98 was obtained. Therefore, the coefficient of lg[TRPO] in Eq. (14) for W extraction can be determined to be 1.83.

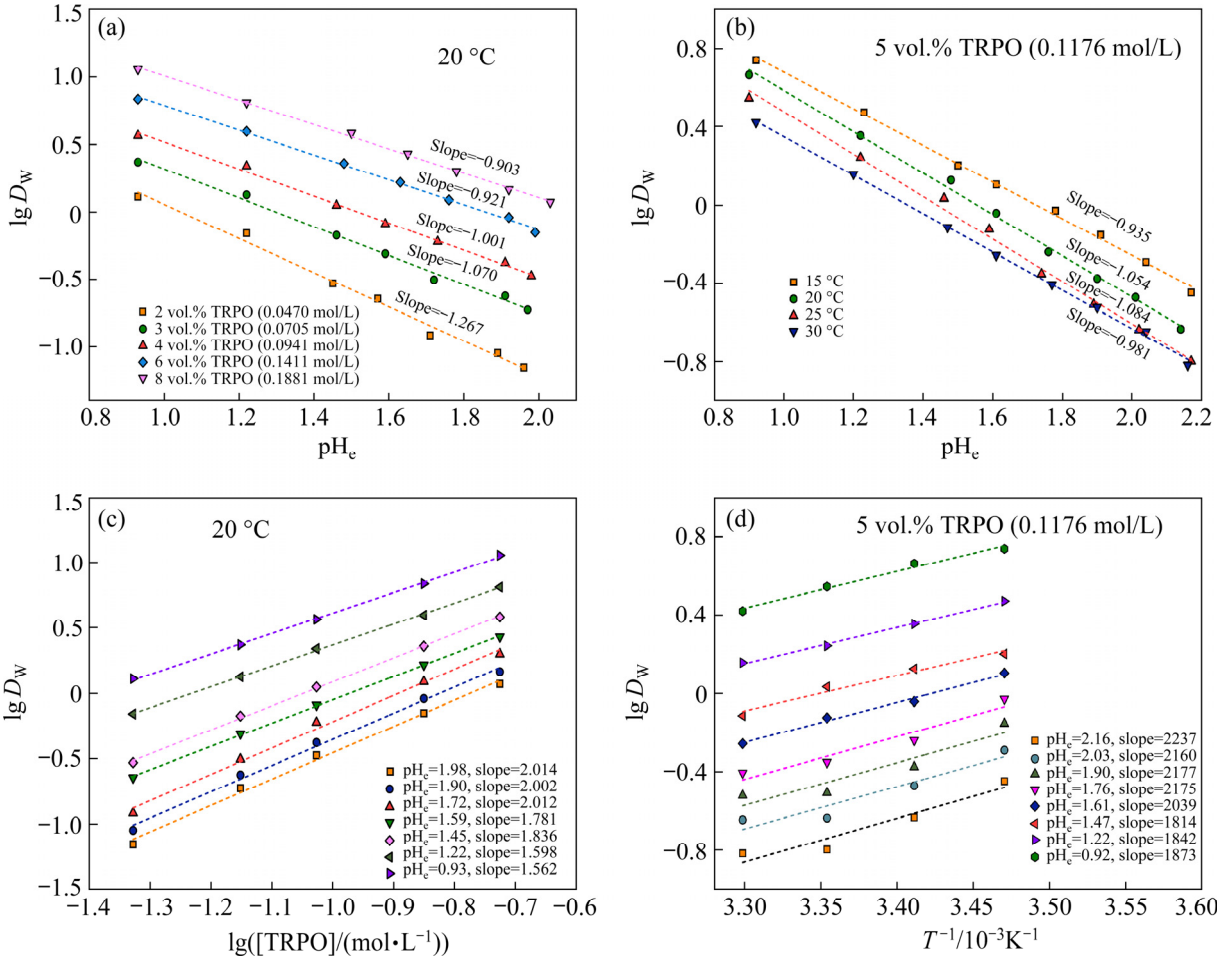

Fig. 7 Logarithm of distribution ratio of W as functions of various factors: (a, b) pH_e; (c) lg[TRPO]; (d) Reciprocal of temperature

Figure 7(d) shows the effect of temperature on distribution ratio of W at TRPO volume fraction of 5% (0.1176 mol/L). The negative correlation between lg D_W and temperature was also observed, which is the same as the case of Mo extraction. An excellent linear relation was shown between lg D_W and $1/T$, and the average slope value was 2040.

3.3.2 Equation model of W extraction by TRPO

The coefficients in distribution ratio equation and thermodynamic data for W extraction are summarized in Table 2. The negative apparent enthalpy changes indicate that the extraction process of W is also exothermic. By comparing the apparent extraction equilibrium constant between W and Mo, the degree of Mo extraction by TRPO is much larger than that of W, which provides a theoretical explanation for the separation of Mo from tungstate solution with TRPO and hydrogen peroxide.

The distribution ratio function of W is expressed as

Table 2 Parameters in distribution equation of W extracted by TRPO from acidic peroxotungstate solution

Factor	Value	Standard error
Coefficient of $1/T$	2040	57.06
Coefficient of pH_e	−1.02	0.04
Coefficient of lg[TRPO]	1.83	0.07
Constant	−3.537	0.01
ΔH^{app}/(J·mol^{-1})	−39060.170	–
ΔS^{app}/(J·mol^{-1}·K^{-1})	−67.72	0.53
K_e^{app} (20°C)	2.65×10^3	–

$$\lg D_W = 2040/T - 3.537 - 1.02pH_e + 1.83\lg[\text{TRPO}] \quad (18)$$

More than sixty experimental data were compared with the values calculated under same conditions (Fig. 8). The calculated values distributed with no tendencies around the expected value line, which shows an excellent prediction for the extraction of W.

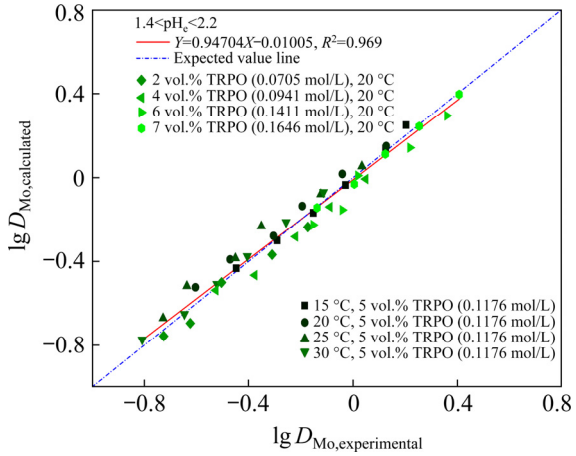

Fig. 8 Comparison of experimental and calculated values for W distribution ratio in extraction of peroxotungstate solution by TRPO at W content of 1 g/L and H_2O_2/W of 6

3.3.3 Reaction equation of W extraction

To further reveal the reaction mechanism of W extraction by TRPO in acidic solution system with hydrogen peroxide, the FTIR and Raman spectra of organic phases were collected (Fig. 9). The observed peaks at 954, 833, 647 and 539 cm^{-1} on FTIR spectrum were attributed to ν[W═O], ν[O—O], ν_{sym}[WO_2] and ν_{asym}[WO_2], respectively [21,37], which are the characteristic peaks of peroxotungstate [$H_2W_2O_3(O_2)_4$]. In the Raman spectra, only one peak attributed to stretching vibration of the W═O appeared at 954 cm^{-1} on spectrum of loaded organic phase, indicating the uniqueness of the peroxotungstate extracted. Other peaks centered at 319, 554, 580 and 850 cm^{-1} were attributed to ν[$W(OH_2)$], ν_{asym}[WO_2], ν_{sym}[WO_2] and ν[O — O] in peroxotungstate [36], respectively. Similar to Mo extraction compound, the stretching vibration peak of W═O bond on Raman spectra red-shifted from 962 to 954 cm^{-1} after peroxotungstate was extracted by TRPO. In addition, the dimer peroxotungstate $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ is the dominant species in tungstate solution containing high ratio of H_2O_2/W [23,36], as shown on the spectrum of peroxotungstate solution (Fig. 9(b)). Similar to the molybdenum extraction, the presence of sulfate was not observed on the Raman spectrum of loaded organic phase. Therefore, the W species extracted by TRPO is [$H_2W_2O_3(O_2)_4(H_2O)_2$] at high H_2O_2/W molar ratio.

The changes in the stretching vibration frequency of phosphoryl in extraction compound containing W were similar to those in the extraction compound containing Mo, which indicates that the extraction mode of W by TRPO is also neutral complexation.

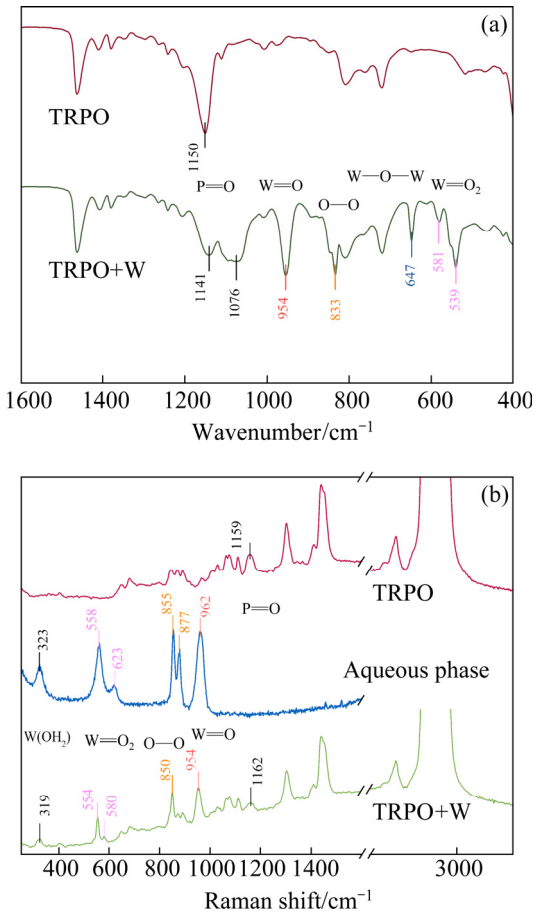

Fig. 9 FTIR (a) and Raman (b) spectra of organic phase (solvent volatilized) before and after W extraction at pH_e 1.32 and Raman spectrum of aqueous phase before extraction

According to Eq. (18), the stoichiometric constants of H^+ and TRPO in extraction reaction are 1 and 2, respectively. The extraction equation of W by TRPO from peroxotungstate solution at H_2O_2/W of 6 can be deduced as follows:

$$[HW_2O_3(O_2)_4(H_2O)_2]^-_{(aq)}+H^+_{(aq)}+2TRPO_{(org)}=[H_2W_2O_3(O_2)_4(H_2O)_2\cdot 2TRPO]_{(org)} \quad (19)$$

3.4 Extraction separation of Mo and W by TRPO

To illustrate the credibility and application of the equations obtained above, the experiments of Mo and W extraction by TRPO from mixed solution of peroxomolybdate and peroxotungstate were conducted under the following conditions: pH_e

1.05−2.70, 2−6 vol.% TRPO (0.0470−0.1411 mol/L), 1 g/L Mo, 1 g/L W, H_2O_2/(W+Mo) 6 and 20 °C. The calculated (-Cal) and experimental (-Obs) values of distribution ratio of Mo and W extraction and separation coefficient under corresponding conditions are shown in Fig. 10. The affecting laws of pH_e and TRPO concentration on the distribution ratio of Mo and W were consistent with those determined previously, and the distribution ratio of Mo and W was almost the same as calculated value. Although decreasing pH improved the extraction of Mo, it also increased the extraction of W, which was not conducive to the separation. The separation coefficient increased with an increase in pH_e, which should be expected because the decrease rate in D_W with pH_e is greater than that of D_{Mo} by comparing the gradient of $\lg D_W$ and $\lg D_{Mo}$ versus pH_e. Increasing TRPO concentration was good for W and Mo extraction, and can increase the separation coefficient appropriately (Fig. 10(b)). At pH_e 2.27, an increase in TRPO volume fraction from 2% to 3% led to a decrease of separation coefficient from

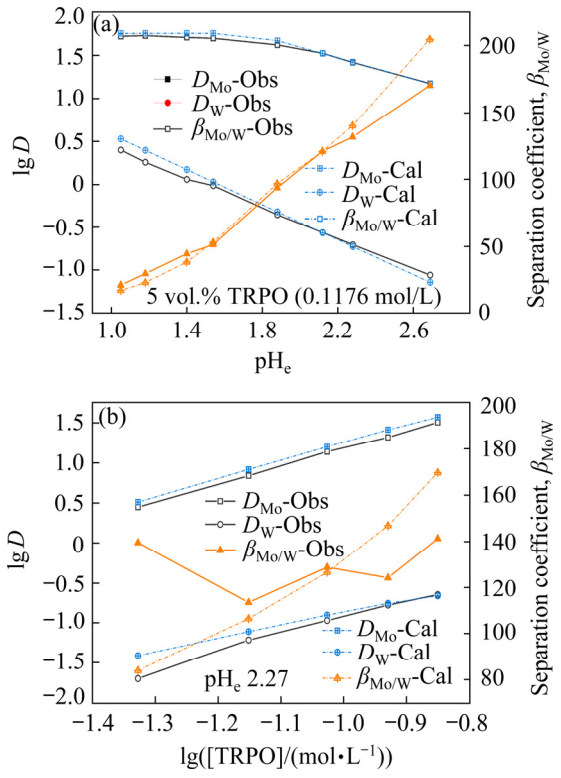

Fig. 10 Comparison of observed and calculated values in $\lg D_{Mo}$, $\lg D_W$ and separation coefficients ($\beta_{Mo/W}$) as functions of pH_e (a), and TPRO concentration (b) during extraction process by TRPO from mixed solution of W and Mo (Other parameters are as follows: H_2O_2/(Mo+W) 6, 20 °C, 1 g/L Mo,1 g/L W)

140 to 113, which is different from the prediction. This is because the competitive extraction of Mo in the mixed solution results in less W extraction. This effect is obviously greater at low TRPO concentration, thereby resulting in a larger separation factor. In the TRPO volume fraction range of 3%−6% (0.0705−0.1411 mol/L), the experimental and calculated values of the separation coefficient have the same changing law, but the experimental value is slightly smaller than the calculated value. To sum up, the extraction effect of Mo and W by TRPO from mixed solution is worse than that from simple solution due to the competitive relationship between the two metals. Even so, the distribution ratio equations obtained from simple solutions can still provide a good prediction and analysis for the extraction and separation effect of Mo and W in a mixed solution with low metal content.

4 Conclusions

(1) A series of univariate experiments of two extraction systems Na_2MoO_4−H_2O_2/TRPO−kerosene and Na_2WO_4−H_2O_2/TRPO−kerosene indicate that increasing the concentration of H^+ and TRPO or decreasing temperature led to an increase in W and Mo extraction. Continuous decrease of pH would further increase the extraction of W, but it had no effect on the extraction of Mo when pH was less than 1.70.

(2) By establishing extraction models, the mathematical empirical formulas of extraction distribution ratio of molybdenum and tungsten were obtained, which reflects the relationship between extraction distribution ratio and equilibrium pH, TRPO concentration and temperature. The empirical formulas and spectral results show that molybdenum was extracted as $[H_2Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2$TRPO via two reaction modes with and without H^+ consumption, while tungsten was extracted as $[H_2W_2O_3(O_2)_4(H_2O)_2]\cdot 2$TRPO via only one reaction mode with H^+ consumption. The extraction reactions of W and Mo with TRPO were all exothermic reactions, and the apparent extraction equilibrium constant at 20 °C were $K_W^{app}=2.65\times10^3$ ($0.92<pH_e<2.16$), $K_{Mo}^{app}=8.51\times10^3$ ($0.74\leq pH_e\leq1.70$) and $K_{Mo}^{app}=99.89\times10^3$ ($1.70<pH_e\leq 4.62$), respectively.

(3) These empirical formulas can be used not

only to predict the extraction of tungsten and molybdenum from $W-H_2O_2$ and $Mo-H_2O_2$ with low metal ion concentration, respectively, but also to predict the extraction behavior and separation effect of Mo and W from peroxy complexation solutions with low W−Mo content.

Acknowledgments

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采用 TRPO 从过氧化氢溶液中萃取钼和钨的数学模型和反应机理

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摘 要：为了解利用三烷基氧化膦(TRPO)从过氧化氢溶液中萃取钼和钨的化学行为，采用斜率法、拉曼和红外光谱 研究钼和钨的萃取反应机理。通过建立数学模型，获得钼或钨的萃取分配比(D_{Mo} 或 D_W)关于平衡 pH 值、TRPO 浓度和温度等变量的经验公式，并进一步在 H^+−W−Mo−H_2O_2 溶液中验证经验公式的可靠性。结果表明：经验公式计算的 D_{Mo} 或 D_W 和实验值吻合度良好。实验条件下，20 °C 时钼和钨的萃取平衡常数分别为 $K_{Mo}^{app}=8.51\times10^3$ ($0.74\le pH_e\le1.70$)、$K_{Mo}^{app}=99.89\times10^3$ ($1.7<pH_e\le4.62$)和 $K_W^{app}=2.65\times10^3$ ($0.92<pH_e<2.16$)。钼和钨的主要萃合物结构为$[H_2Me_2O_3(O_2)_4(H_2O)_2]\cdot2$TRPO (Me=Mo 或 W)。获得的经验公式可以用于估算和分析低浓度钼和钨混合溶液中钼和钨的萃取和分离。

关键词：钨；钼；溶剂萃取；三烷基氯化磷(TRPO)；过氧化氢(H_2O_2)

(Edited by Bing YANG)