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ARTICLE

Thermodynamic Analysis of Phosphorus-Sulfur-Vanadium-Water Acidic System for the Extraction of Vanadium

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Abstract: To extract vanadium efficiently from the acidic leachate of vanadium slag, a thermodynamic analysis of phosphorus-sulfur-vanadium-water acidic systems was established at 298 K. Results show that in the P(V)-V(V)-H_2O acidic system, VO_2^+ is first converted to phosphovanadic heteropolyacid ions when pH=1~4 and then converted to vanadium isopolyacid ions when pH=4~7. In the S(VI)-V(V)-H_2O acidic system, VO_2^+ and $VO_2SO_4^-$ are the main existing chemical forms when pH=0~1 and gradually converted to vanadium isopolyacid ions when pH=2~6. In the P(V)-S(VI)-V(V)-H_2O acidic system, when pH=1~3, VO_2^+ and $VO_2SO_4^-$ are gradually converted to phosphovanadic heteropolyacid ions. The optimum molar fraction of ΣPV_{14} (total sum of phosphovanadic heteropolyacid ions) reaches 88.55% at pH=2. As the pH value increases to 4~6, phosphovanadic heteropolyacid ion gradually disappears and is converted to vanadium isopolyacid anions, and the optimum molar fraction of ΣV_{10} (total sum of vanadium isopolyacid ions containing ten vanadium) is 100.00% at pH=5.

Key words: vanadium; thermodynamic; isopolyacid; heteropolyacid; compexation

As an important strategic metal, vanadium has many excellent physical and chemical properties, such as specific physiological functions, fatigue resistance, hardness, and tensile strength [1]. Although vanadium is widely distributed in the nature, it is still difficult to find vanadium in elemental form. Most vanadium coexists with other elements. Currently, vanadium-bearing converter slag and stone coal are the main raw materials for vanadium extraction worldwide, especially in China. As an intermediate product of the vanadium-titanium magnetite smelting process, vanadium-bearing converter slag is the most important raw and processed materials for vanadium extraction, and it has received increasing attention and research [2]. Many methods have been applied for the extraction of vanadium. Among those methods, sodium salt roasting (NaCl, Na_2CO_3, and Na_2SO_4) and water leaching were once the most widely used methods. As a pyro-hydrometallurgical process, Cl_2, HCl, SO_2, or SO_3 can be produced in the sodium salt roasting process, which can contaminate the environment and corrode equipment[3-7]. Therefore, this method has been eliminated based on the strict requirements for environmental protection in China.

Presently, processes involving direct acidic leaching and calcified roasting with the acidic leaching of converter slag have been studied and widely adopted due to the high recovery rate of vanadium and low generation of pollution[8-17]. In China, the majority of vanadium is extracted by the H_2SO_4 leaching process. To improve the extraction ratio of vanadium, high concentrations of H_2SO_4 are commonly used in the acidic leaching process. Accordingly, numerous impurities in converter slag are also dissolved into the leachate, which results in a complex vanadium-bearing leaching solution with a high concentration of impurities at a low pH value. Therefore, it is particularly important to separate and extract vanadium from strong acid leachates containing many impurities [18].

In the H_2SO_4 leachate of vanadium-bearing converter slag, phosphorus (P) and sulfur (S) have an important effect on the existing form and the effective extraction of vanadium. First,

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phosphorus in the vanadium-bearing converter slag originates from the conversion process of molten iron containing vanadium, which is also leached into the acidic leaching solution. In general, phosphorus mainly exists in the forms of H_3PO_4, $H_2PO_4^-$ and HPO_4^{2-} in the acidic solution. However, phosphorus can form phosphovanadic heteropolyacid ions with transition metal vanadium in the actual acidic leachate. Second, sulfur existing in the acidic solution is mainly SO_4^{2-}. Due to the existence of vanadium in the acidic leachate, V-S complex ions can be formed through the complexation action between VO_2^+ and SO_4^{2-}. Phosphovanadic heteropolyacid ions and V-S complex ions can greatly impact vanadium extraction in acidic leaching solutions and subsequent precipitation procedures[19-24].

Therefore, this work studied the thermodynamic analysis of P(V)-S(VI)-V(V)-H_2O systems for vanadium extraction from an actual acidic leachate. Moreover, the existence of vanadium and the variation tendency of the ions (vanadium, phosphorus, and sulfur) at different pH values and different concentrations (phosphorus and sulfur) were investigated.

1 Thermodynamic Analysis

All ions in the P(V)-S(VI)-V(V)-H_2O systems are VO_4^{3-}, HVO_4^{2-}, $H_2VO_4^-$, $V_2O_7^{4-}$, $HV_2O_7^{3-}$, $H_2V_2O_7^{2-}$, $V_4O_{12}^{4-}$, $V_5O_{15}^{5-}$, $V_{10}O_{28}^{6-}$, $HV_{10}O_{28}^{5-}$, $HV_{10}O_{28}^{5-}$, $H_2V_{10}O_{28}^{4-}$, $H_3V_{10}O_{28}^{3-}$, VO_2^+, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, $H_5PV_{14}O_{42}^{4-}$, $H_4PV_{14}O_{42}^{5-}$, $H_3PV_{14}O_{42}^{6-}$, $VO_2SO_4^-$, VO_2HSO_4, HSO_4^-, and SO_4^{2-} [25-28]. The equilibrium reactions and corresponding equilibrium constants are listed in Table 1.

According to the data listed in Table 1, thermodynamic analysis was conducted. The concentration was used instead of the activity for the calculation. The mathematical relationships of the species can be expressed as follows [29-31]:

$$[PO_4^{3-}][H^+]^2=10^{-17.650}[H_2PO_4^-] \tag{1}$$

$$[HPO_4^{2-}][H^+]=10^{-6.418}[H_2PO_4^-] \tag{2}$$

$$[H_3PO_4]=10^{1.772}[H^+]\,[H_2PO_4^-] \tag{3}$$

$$[HVO_4^{2-}][H^+]=10^{-7.92}[H_2VO_4^-] \tag{4}$$

$$[V_2O_7^{4-}][H^+]^2=10^{-15.17}[H_2VO_4^-]^2 \tag{5}$$

$$[HV_2O_7^{3-}][H^+]=10^{-5.25}[H_2VO_4^-]^2 \tag{6}$$

$$[H_2V_2O_7^{2-}]=10^{2.77}[H_2VO_4^-]^2 \tag{7}$$

$$[V_4O_{12}^{4-}]=10^{10.00}[H_2VO_4^-]^4 \tag{8}$$

$$[V_5O_{15}^{5-}]=10^{12.38}[H_2VO_4^-]^5 \tag{9}$$

$$[V_{10}O_{28}^{6-}]=10^{52.13}[H^+]^4[H_2VO_4^-]^{10} \tag{10}$$

$$[HV_{10}O_{28}^{5-}]=10^{58.13}[H^+]^5[H_2VO_4^-]^{10} \tag{11}$$

$$[H_2V_{10}O_{28}^{4-}]=10^{61.87}[H^+]^6[H_2VO_4^-]^{10} \tag{12}$$

$$[H_3V_{10}O_{28}^{3-}]=10^{63.47}[H^+]^7[H_2VO_4^-]^{10} \tag{13}$$

$$[VO_2^+]=10^{6.96}[H^+]^2[H_2VO_4^-] \tag{14}$$

$$[H_5PV_{14}O_{42}^{4-}]=10^{96.40}[H^+]^{11}[H_2VO_4^-]^{14}[H_2PO_4^-] \tag{15}$$

$$[H_4PV_{14}O_{42}^{5-}]=10^{94.84}[H^+]^{10}[H_2VO_4^-]^{14}[H_2PO_4^-] \tag{16}$$

$$[H_3PV_{14}O_{42}^{6-}]=10^{90.70}[H^+]^9[H_2VO_4^-]^{14}[H_2PO_4^-] \tag{17}$$

$$[SO_4^{2-}][H^+]=10^{1.99}[HSO_4^-] \tag{18}$$

$$[VO_2SO_4^-]=10^{0.97}[VO_2^+][SO_4^{2-}] \tag{19}$$

$$[VO_2HSO_4]=10^{-0.136}[VO_2^+][HSO_4^-] \tag{20}$$

The total concentrations of V, P and S are expressed in Eq. (21~25):

Table 1 Equilibrium reactions and corresponding equilibrium constants of P-V-H_2O (No.1~17), S-V-H_2O (No.4-20) and P-S-V-H_2O (No.1-20) systems at 298 K

No.	Equilibrium reaction	Equilibrium constants, lg*K*	Ref.
1	$H_2PO_4^-=PO_4^{3-}+2H^+$	−17.650	[20]
2	$H_2PO_4^-=HPO_4^{2-}+H^+$	−6.418	[20]
3	$H^++H_2PO_4^-=H_3PO_4$	1.772	[20]
4	$H_2VO_4^-= HVO_4^{2-}+H^+$	−7.92	[20]
5	$2H_2VO_4^-=V_2O_7^{4-}+2H^++H_2O$	−15.17	[20]
6	$2H_2VO_4^-= HV_2O_7^{3-}+H^++H_2O$	−5.25	[20]
7	$2H_2VO_4^-=H_2V_2O_7^{2-}+H_2O$	2.77	[20]
8	$4H_2VO_4^-= V_4O_{12}^{4-}+4H_2O$	10.00	[20]
9	$5H_2VO_4^-= V_5O_{15}^{5-}+5H_2O$	12.38	[20]
10	$4H^++10H_2VO_4^-=V_{10}O_{28}^{6-}+12H_2O$	52.13	[20]
11	$5H^++10H_2VO_4^-=HV_{10}O_{28}^{5-}+12H_2O$	58.13	[20]
12	$6H^++10H_2VO_4^-=H_2V_{10}O_{28}^{4-}+12H_2O$	61.87	[20]
13	$7H^++10H_2VO_4^-=H_3V_{10}O_{28}^{3-}+12H_2O$	63.47	[20]
14	$2H^++H_2VO_4^-=VO_2^++2H_2O$	6.96	[20]
15	$11H^++14H_2VO_4^-+H_2PO_4^-=H_5PV_{14}O_{42}^{4-}+18H_2O$	96.4	[20]
16	$10H^++14H_2VO_4^-+H_2PO_4^-=H_4PV_{14}O_{42}^{5-}+18H_2O$	94.84	[20]
17	$9H^++14H_2VO_4^-+H_2PO_4^-=H_3PV_{14}O_{42}^{6-}+18H_2O$	90.7	[20]
18	$HSO_4^-= SO_4^{2-}+H^+$	1.99	[28]
19	$VO_2^++SO_4^{2-}= VO_2SO_4^-$	0.97	[28]
20	$VO_2^++HSO_4^-= VO_2HSO_4$	−0.136	[28]

In the P(V)-V(V)-H_2O acidic solution,

$$\begin{aligned}[V]_{T(V\text{-}P\text{-}H_2O)}=&[VO_4^{3-}]+[HVO_4^{2-}]+[H_2VO_4^{-}]+2[V_2O_7^{4-}]+\\&2[HV_2O_7^{3-}]+2[H_2V_2O_7^{2-}]+4[V_4O_{12}^{4-}]+5[V_5O_{15}^{5-}]+\\&10[V_{10}O_{28}^{6-}]+10[HV_{10}O_{28}^{5-}]+10[HV_{10}O_{28}^{5-}]+\\&10[H_2V_{10}O_{28}^{4-}]+10[H_3V_{10}O_{28}^{3-}]+[VO_2^{+}]+\\&14[H_5PV_{14}O_{42}^{4-}]+14[H_4PV_{14}O_{42}^{5-}]+\\&14[H_3PV_{14}O_{42}^{6-}]\end{aligned}\tag{21}$$

$$\begin{aligned}[P]_{T(V\text{-}P\text{-}H_2O)}=&[H_3PO_4]+[H_2PO_4^{-}]+[HPO_4^{2-}]+[PO_4^{3-}]+\\&[H_5PV_{14}O_{42}^{4-}]+[H_4PV_{14}O_{42}^{5-}]+[H_3PV_{14}O_{42}^{6-}]\end{aligned}\tag{22}$$

In the S(VI)-V(V)-H_2O acidic solution,

$$\begin{aligned}[V]_{T(V\text{-}S\text{-}H_2O)}=&[VO_4^{3-}]+[HVO_4^{2-}]+[H_2VO_4^{-}]+2[V_2O_7^{4-}]+\\&2[HV_2O_7^{3-}]+2[H_2V_2O_7^{2-}]+4[V_4O_{12}^{4-}]+5[V_5O_{15}^{5-}]+\\&10[V_{10}O_{28}^{6-}]+10[HV_{10}O_{28}^{5-}]+10[HV_{10}O_{28}^{5-}]+\\&10[H_2V_{10}O_{28}^{4-}]+10[H_3V_{10}O_{28}^{3-}]+[VO_2^{+}]+\\&[VO_2SO_4^{-}]+[VO_2HSO_4]\end{aligned}\tag{23}$$

$$[S]_{T(V\text{-}S\text{-}H_2O)}=[SO_4^{2-}]+[HSO_4^{-}]+[VO_2SO_4^{-}]+[VO_2HSO_4]\tag{24}$$

In the P(V)-S(VI)-V(V)-H_2O acidic solution,

$$\begin{aligned}[V]_{T(V\text{-}P\text{-}H_2O)}=&[VO_4^{3-}]+[HVO_4^{2-}]+[H_2VO_4^{-}]+\\&2[V_2O_7^{4-}]+2[HV_2O_7^{3-}]+2[H_2V_2O_7^{2-}]+\\&4[V_4O_{12}^{4-}]+5[V_5O_{15}^{5-}]+10[V_{10}O_{28}^{6-}]+\\&10[HV_{10}O_{28}^{5-}]+10[HV_{10}O_{28}^{5-}]+10[H_2V_{10}O_{28}^{4-}]+\\&10[H_3V_{10}O_{28}^{3-}]+[VO_2^{+}]+14[H_5PV_{14}O_{42}^{4-}]+\\&14[H_4PV_{14}O_{42}^{5-}]+14[H_3PV_{14}O_{42}^{6-}]+[VO_2SO_4^{-}]\\&+[VO_2HSO_4]\end{aligned}\tag{25}$$

According to the aforementioned 25 equations, a thermodynamic analysis of the P(V)-V(V)-H_2O, S(VI)-V(V)-H_2O and P(V)-S(VI)-V(V)-H_2O systems was performed to determine the existing form and variation tendency of ions in the acidic leachate of vanadium-bearing converter slag[32-35].

2 Thermodynamic Discussion

2.1 P(V)-V(V)-H_2O system

2.1.1 Molar fraction of ions containing vanadium in the P(V)-V(V)-H_2O system

The molar fraction of ions containing vanadium in the P(V)-V(V)-H_2O system and varying at different pH values is shown in Fig.1 when $[P^{5+}]$=0.1 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1} (based on the concentration range of vanadium and pho-sphorus in the acid leaching solution of calcification roasting-acid leaching process and direct acid leaching process).

When the pH value is 1, VO_2^+ is first converted to phosphovanadic heteropolyacid ions ($H_5PV_{14}O_{42}^{4-}$, $H_4PV_{14}O_{42}^{5-}$, or $H_3PV_{14}O_{42}^{6-}$). When the pH value increases to 1~4, vanadium is mainly phosphovanadic heteropolyacid ions, and the optimum molar fraction of ΣPV_{14} (total sum of all the phosphovanadic heteropolyacid ions $[\Sigma PV_{14}]=[H_5PV_{14}O_{42}^{4-}]+[H_4PV_{14}O_{42}^{5-}]+[H_3PV_{14}O_{42}^{6-}]$) reaches 97.14% when the pH value is 2.5. When the pH value is 4~7, phosphovanadic heteropolyacid ions are converted to vanadium isopolyacid anions ($V_{10}O_{28}^{6-}$, $HV_{10}O_{28}^{5-}$, or $H_2V_{10}O_{28}^{4-}$), and the optimum molar fraction of ΣV_{10}($[\Sigma V_{10}]=[V_{10}O_{28}^{6-}]+[HV_{10}O_{28}^{5-}]+[H_2V_{10}O_{28}^{4-}]$) reaches 98.77% when the pH value is 5.

In conclusion, VO_2^+ is first converted to phosphovanadic heteropolyacid ions and then converted to vanadium isopolyacid ions (ΣV_{10}) in the P(V)-V(V)-H_2O system when pH=0~7.

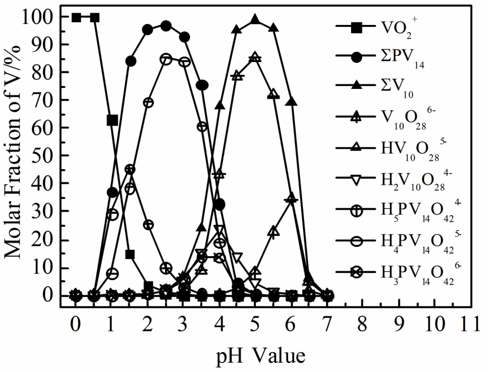

Fig.1 Molar fraction of ions containing vanadium in the P(V)-V(V)-H_2O system at 298 K ($[P^{5+}]$=0.1mol·L^{-1}, $[V^{5+}]$=0.1mol·L^{-1}; $[\Sigma PV_{14}]=[H_5PV_{14}O_{42}^{4-}]+[H_4PV_{14}O_{42}^{5-}]+[H_3PV_{14}O_{42}^{6-}]$, $[\Sigma V_{10}]=[V_{10}O_{28}^{6-}]+[HV_{10}O_{28}^{5-}]+[H_2V_{10}O_{28}^{4-}]$)

A comparison of the molar fraction in the P(V)-V(V)-H_2O system with different concentrations of phosphorus ($[P^{5+}]$=0.1 mol·L^{-1}, $[V^{5+}]$=0.1mol·L^{-1}; $[P^{5+}]$=0.001 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1}) is displayed in Fig.2.

When the pH value is 1~4, the molar fraction of ΣPV_{14} when $[P^{5+}]$=0.001 mol·L^{-1} is always lower than that when $[P^{5+}]$=0.1 mol·L^{-1}, and its optimum molar fraction is only 13.79% when the pH value is 2. As the pH value is increased, phosphovanadic heteropolyacid ions are converted to vanadium isopolyacid ions, and the molar fraction of ΣV_{10} when $[P^{5+}]$=0.001 mol·L^{-1} is higher than that when $[P^{5+}]$=0.1 mol·L^{-1} at pH=1~5. Moreover, the optimum molar fraction of ΣV_{10} when $[P^{5+}]$=0.001 mol·L^{-1} can reach 100.00% when the pH value is 4~5.

It can be concluded that a decrease in the phosphorus concentration (from 0.1 mol·L^{-1} to 0.001 mol·L^{-1}) can significantly decrease the molar fraction of ΣPV_{14} and increase

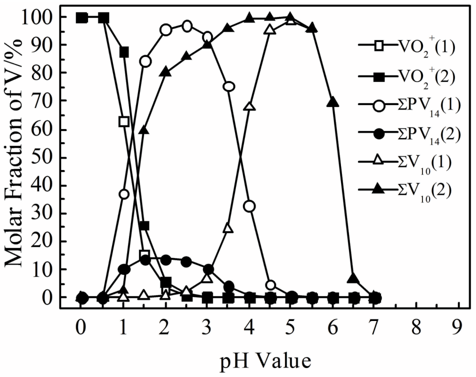

Fig.2 Comparison of molar fraction (ions containing vanadium) in the P(V)-V(V)-H_2O system at 298 K ((1): $[P^{5+}]$=0.1 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1}; (2): $[P^{5+}]$=0.001 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1})

the existing range of ΣV_{10} in the P(V)-V(V)-H_2O system.

2.1.2 Molar fraction of ions containing phosphorus in the P(V)-V(V)-H_2O system

The molar fraction of ions containing phosphorus in the P(V)-V(V)-H_2O system and varying at different pH values is shown in Fig.3 when $[P^{5+}]$=0.1 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1}.

As shown in Fig. 3, the existing forms of phosphorus are mainly H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} in the acidic P(V)-V(V)-H_2O system (pH=0~7). However, phosphovanadic heteropolyacid anions can be formed when 1<pH<4 in the P(V)-V(V)-H_2O system. When the pH value is increased, H_3PO_4 is first converted to ΣPV_{14} and $H_2PO_4^-$, and then $H_2PO_4^-$ is converted to HPO_4^{2-}. The optimum molar fraction of H_3PO_4 is 98.34% when the pH value is 0; the optimum molar fraction of ΣPV_{14} is 6.94% when the pH value is 2.5; the optimum molar fraction of $H_2PO_4^-$ is 98.28% when the pH value is 4.5; and the optimum molar fraction of HPO_4^{2-} is 79.25% when the pH value is 7.

The molar fractions of ions containing phosphorus at different concentrations ($[P^{5+}]$=0.1 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1}; and $[P^{5+}]$=0.001 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1}) are displayed in Fig.4.

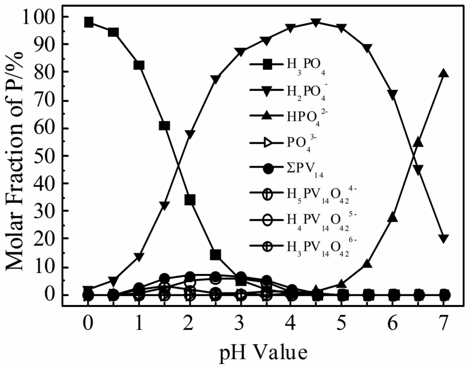

Fig.3 Molar fraction of ions containing phosphorus in the P(V)-V(V)-H_2O system at 298 K ($[P^{5+}]$=0.1 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1})

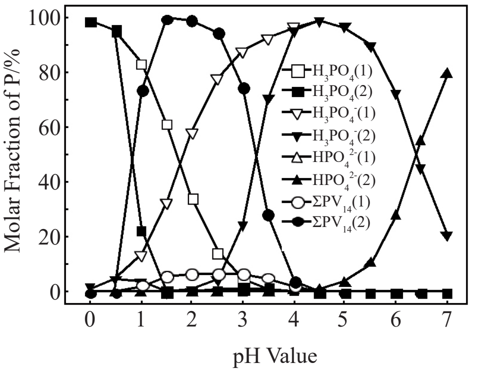

Fig.4 Comparison of molar fraction (ions containing phosphorus) in the P(V)-V(V)-H_2O system at 298 K ((1): $[P^{5+}]$=0.1 mol·L^{-1}, $V^{5+}]$=0.1 mol·L^{-1}; (2): $[P^{5+}]$=0.001 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1})

As shown in Fig.4, ions containing phosphorus in the P(V)-V(V)-H_2O system are still mainly in the forms of H_3PO_4, ΣPV_{14}, $H_2PO_4^-$, and HPO_4^{2-} when the phosphorus concentration is decreased from 0.1 mol·L^{-1} to 0.001 mol·L^{-1}. The reason for this difference is that the molar fraction of ΣPV_{14} when $[P^{5+}]$= 0.001 mol·L^{-1} is much bigger than that when $[P^{5+}]$=0.1 mol·L^{-1}, and it can be considerably increased to 73.59%~99.20% when pH=1~3.

This result is mainly because when $[V^{5+}]$=0.1 mol·L^{-1} and $[P^{5+}]$=0.001 mol·L^{-1}, the molar ratio of phosphorus to vanadium is 1:100, which is much less than the ratio of 1:14 in ΣPV_{14}. Therefore, most of the 0.001 mol/L phosphorus is converted to ΣPV_{14} by combining with vanadium. However, when $[V^{5+}]$=0.1 mol·L^{-1} and $[P^{5+}]$=0.1 mol·L^{-1}, the molar ratio of phosphorus to vanadium is 1:1, which is bigger than the ratio of 1:14 in ΣPV_{14}. Therefore, only a small part of the 0.1 mol·L^{-1} phosphorus is converted to ΣPV_{14} by combining with vanadium. Therefore, the molar ratio of ΣPV_{14}/total P when $[P^{5+}]$=0.001 mol·L^{-1} is far bigger than that when $[P^{5+}]$=0.1 mol·L^{-1} and pH=1~3.5 in the P(V)-V(V)-H_2O system.

2.2 S(VI)-V(V)-H_2O system

2.2.1 Molar fraction of ions containing vanadium in the S(VI)- V(V)-H_2O system

The molar fraction of ions containing vanadium in the S(VI)-V(V)-H_2O system and varying at different pH values is shown in Fig.5 when $[S^{6+}]$=0.05 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1}.

When pH=0~1, vanadium is mainly in the forms of VO_2^+ and $VO_2SO_4^-$, and the proportion is 79% and 21%, respectively. With continuously increasing the pH value, VO_2^+ and $VO_2SO_4^-$ are gradually converted to ΣV_{10} and almost all vanadium exists in the form of ΣV_{10} when pH value is 2~6. With continuously increasing the pH value to 6~7, vanadium exists mainly in the forms of $V_4O_{12}^{4-}$ and $V_5O_{15}^{5-}$.

A comparison of the molar fraction in the S(VI)-V(V)-H_2O system with different sulfur concentrations ($[S^{6+}]$=0.05 mol·L^{-1}, $[V^{5+}]$=0.1mol·L^{-1}; $[S^{6+}]$=0.5 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1}) is illustrated in Fig.6.

When the pH value is 0~1, the molar fraction of VO_2^+

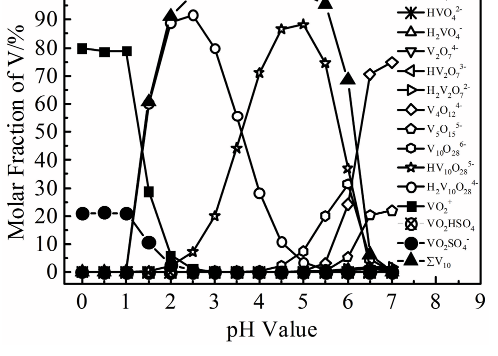

Fig.5 Molar fraction of ions containing vanadium in the S(VI)-V(V)-H_2O system at 298 K ($[S^{6+}]$=0.05 mol/L, $[V^{5+}]$=0.1 mol/L)

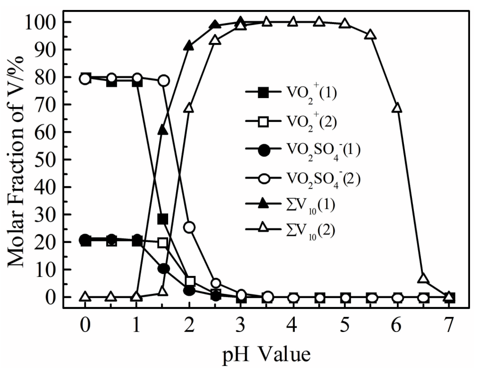

Fig.6 Comparison of molar fraction (ions containing vanadium) in the V(V)-S(VI)-H_2O system at 298 K ((1): $[S^{6+}]$=0.05 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1}; (2): $[S^{6+}]$=0.5 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1})

decreases from 79% to 20%, and the molar fraction of $VO_2SO_4^-$ increases from 21% to 79% when the sulfur concentration is increased from 0.05 mol·L^{-1} to 0.5 mol·L^{-1}. In addition, the pH value of forming ΣV_{10} increases from 1.0 to 1.5, and the molar fraction of ΣV_{10} when $[S^{6+}]$=0.05 mol·L^{-1} is always larger than that when $[S^{6+}]$=0.5 mol·L^{-1} at pH=1.5~2.5. Moreover, the molar fractions of ΣV_{10} is almost the same when the pH value is 3~7 and close to 100% when the pH value is 3.0~5.5.

Based on these thermodynamic results, it can be concluded that increasing the sulfur concentration (from 0.05 mol·L^{-1} to 0.5 mol·L^{-1}) in the S(VI)-V(V)-H_2O solution can improve the molar fraction of $VO_2SO_4^-$ and reduce the existing range of vanadium isopolyacid ions (ΣV_{10}).

2.2.2 Molar fraction of ions containing sulfur in the S(VI)-V(V)-H_2O system

The molar fraction of ions containing sulfur in the S(VI)-V(V)-H_2O system and varying at different pH values is shown in Fig.7 when $[S^{6+}]$=0.05 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1}.

As observed, the anion $VO_2SO_4^-$ is formed due to the complexation of SO_4^{2-} and VO_2^+ when pH=0~1 in the acidic S(VI)-V(V)-H_2O system, and its molar fraction reaches 42%. The remaining 56% of sulfur is in the form of SO_4^{2-}. As the pH value continues to increase, the anion $VO_2SO_4^-$ gradually disappears. When pH=2.5~7, almost 100% of sulfur in the solution is SO_4^{2-}. Moreover, HSO_4^{2-} and VO_2HSO_4 hardly exist in the whole pH range of 0~7.

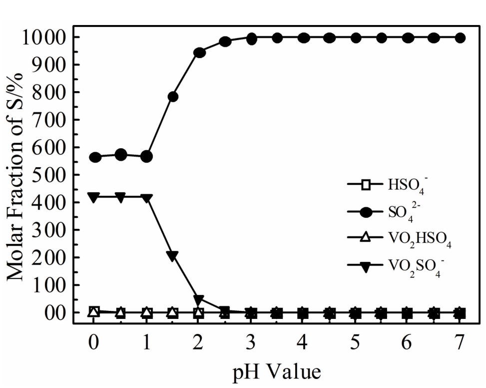

Fig.7 Molar fraction of ions containing sulfur in the S(VI)-V(V)-H_2O system at 298 K ($[S^{6+}]$=0.05 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1})

The molar fraction of ions containing sulfur at different sulfur concentrations ($[S^{6+}]$=0.05 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1}; $[S^{6+}]$=0.5 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1};) is shown in Fig.8.

In Fig. 8, ions containing sulfur in the S(VI)-V(V)-H_2O system are mainly SO_4^{2-} and $VO_2SO_4^-$. When the sulfur concentration is increased from 0.05 mol·L^{-1} to 0.50 mol·L^{-1}, the molar fraction of SO_4^{2-} increases from 57% to 84% and the corresponding molar fraction of $VO_2SO_4^-$ decreases from 42% to 16% when pH=0~1. Moreover, $VO_2SO_4^-$ is gradually converted to SO_4^{2-}, and almost all sulfur is SO_4^{2-} when the pH value is 3~7 in the acidic S(VI)-V(V)-H_2O system.

2.3 P(V)-S(VI)-V(V)-H_2O system

The molar fraction of ions containing vanadium in the P(V)-S(VI)-V(V)-H_2O system and varying at different pH values is shown in Fig.9 when $[P^{5+}]$=0.01 mol·L^{-1}, $[S^{6+}]$=0.05 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1}.

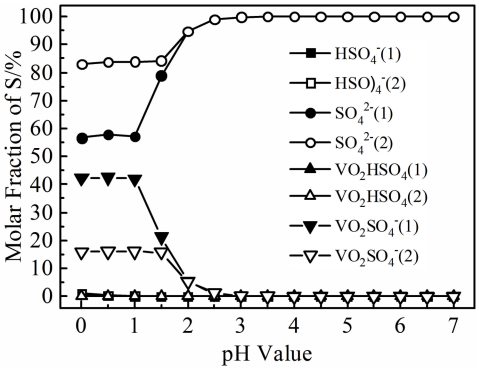

Fig.8 Comparison of molar fraction (ions containing sulfur) in the S(VI)-V(V)-H_2O system at 298 K ((1): $[S^{6+}]$=0.05 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1}; (2): $[S^{6+}]$=0.5 mol·L^{-1} and $[V^{5+}]$=0.1 mol·L^{-1})

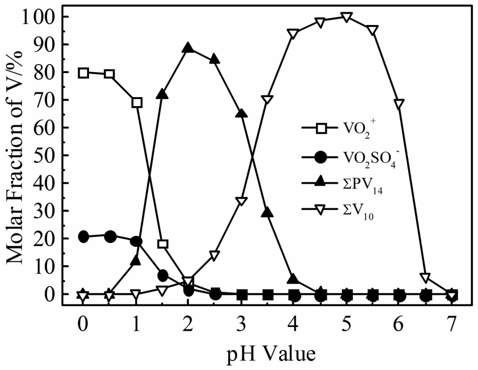

Fig.9 Molar fraction of ions containing vanadium in the P(V)-S(VI)-V(V)-H_2O system at 298 K ($[P^{5+}]$=0.01 mol·L^{-1}, $[S^{6+}]$=0.05 mol·L^{-1}, $[V^{5+}]$=0.1 mol·L^{-1})

When pH=0~1, vanadium is mainly VO_2^+ and $VO_2SO_4^-$. In addition, the molar fraction of VO_2^+ ranges from 79.84% to 69.26%, and the molar fraction of $VO_2SO_4^-$ ranges from 21.10% to 19.37%. As the pH value continuously increases to 1~3, VO_2^+ and $VO_2SO_4^-$ gradually disappear and are converted to phosphovanadic heteropolyacid ions, and the optimum molar fraction of ΣPV_{14} is 88.55% when the pH value is 2. As the pH value continuously increases to 4~6, ΣPV_{14} gradually disappears and is converted to vanadium isopolyacid ions, and the optimum molar fraction of ΣV_{10} reaches 100.00% when the pH value is 5.

3 Conclusions

1) In the P(V) -V(V) -H_2O acidic system, VO_2^+ is first converted to phosphovanadic heteropolyacid ions when pH= 1~4, and the optimum molar fraction of ΣPV_{14} (total sum of phosphovanadic heteropolyacid ions) is 97.14% when the pH value is 2.5. As the pH value increases to 4~7, the phosphovanadic heteropolyacid ions are converted to vanadium isopolyacid ions, and the optimum molar fraction of ΣV_{10} (total sum of vanadium isopolyacid ions containing ten vanadium) is 98.77% when the pH value is 5.

2) In the S(VI) -V(V) -H_2O acidic solution, when the pH value is 0~1, the molar fractions of VO_2^+ and $VO_2SO_4^-$ are 79% and 21%, respectively. As the pH value continuously increases, VO_2^+ and $VO_2SO_4^-$ are gradually converted to vanadium isopolyacid ions ΣV_{10}, and almost 100% of the vanadium exists in the form of ΣV_{10} when the pH value is 2~6.

3) In the P(V)-S(VI)-V(V)-H_2O acidic system, when the pH value is 0~1, the molar fraction of VO_2^+ ranges from 79.84% to 69.26%, and the molar fraction of $VO_2SO_4^-$ ranges from 21.10% to 19.37%. As the pH value continuously increases to 1~3, VO_2^+ and $VO_2SO_4^-$ gradually disappear and are converted to phosphovanadic heteropolyacid ions ΣPV_{14}, and the optimum molar fraction of ΣPV_{14} reaches 88.55% when the pH value is 2. As the pH value continuously increases to 4~6, ΣPV_{14} gradually disappears and is converted to vanadium isopolyacid anion ΣV_{10}, and the optimum molar fraction of ΣV_{10} is 100.00% when the pH value is 5.

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磷-硫-钒-水体系酸性溶液中钒的提取热力学分析

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摘　要： 针对含钒酸浸液中钒的有效提取问题，研究了298 K时磷-硫-钒-水溶液酸性体系中钒的提取热力学分析过程。结果表明，在P(V)-V(V)-H_2O酸性溶液体系中，pH=1~4时VO_2^+首先转变为磷钒杂多酸阴离子，pH=4~7时磷钒杂多酸阴离子转变为同多酸阴离子；在S(VI)-V(V)-H_2O酸性溶液体系中，pH=0~1时钒主要以VO_2^+和$VO_2SO_4^-$形式存在，pH=2~6时钒逐渐转变为同多酸阴离子；在P(V)-S(VI)-V(V)-H_2O酸性溶液体系中，pH=1~3时VO_2^+和$VO_2SO_4^-$逐渐转变为磷钒杂多酸阴离子，当pH=2时ΣPV_{14}（所有磷钒杂多酸阴离子之和）的摩尔分数最大为88.55%；pH=4~6时，磷钒杂多酸阴离子消失并逐渐转变为同多酸阴离子，当pH=5时ΣV_{10}（所有同多酸阴离子之和）的摩尔分数最大为100.00%。

关键词： 钒；热力学；同多酸；杂多酸；络合

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