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Effects of acidity, temperature and surfactants on electrochemical behavior of V^{5+} ion in sulfuric acid solutions①

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Abstract: The effects of sulfuric acid concentration, reaction temperature, potential-scanning rate and surfactants on electrochemical behavior of V^{5+} ion on platinum electrodes were investigated. In voltammetric curves of V^{5+} ion there are two reduction peaks corresponding to reductions of V^{5+} to V^{4+} (R2) and V^{5+} to V^{3+} (R1), which are irreversible and quasi-reversible processes respectively. Oxidation peak of V^{3+} to V^{5+} is intensively affected by pH values on the electrode surface and scanning-potential rates. Only stronger acidity on the electrode surface and faster scanning-potential rates can lead to appearance of this oxidation peak. The neutral surfactant(PCBE) and cationic surfactant(CTAB) retard the V^{5+} electroreduction. The anionic surfactant(SDS), even at a very low concentration, increases the currents of both the reduction peaks R1 and R2, and the oxidation peak involves with the oxidation of H_2 to H^+.

Key words: V^{5+}; redox couple; voltammetry; electrochemistry;
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1 INTRODUCTION

Several redox couples including Ce^{4+}/Ce^{3+}, Mn^{3+}/Mn^{2+}, Co^{3+}/Co^{2+} and V^{5+}/V^{4+} etc have attracted much attention in indirect electrosynthesis of some organic compounds and in mediated electrochemical oxidation of benzene, aniline, phenol and chlorinated organics etc[1-7]. Electrochemical behavior of the redox couple Ce^{4+}/Ce^{3+} has been studied[8, 9]. Being strong and selective oxidizing agents, vanadium salts, compared with copper salts, were more efficient to catalyze the oxidation of toluene to benzaldehyde via electrochemically generated hydrogen peroxide[10]. Electrochemical behavior of some vanadium salts was investigated by many researchers[11-22]. In general, electrode reactions, such as V^{5+}/V^{4+} and V^{3+}/V^{2+}, were irreversible[11, 15-21]. Davis [13] studied electrochemical behavior of V^{5+}/V^{4+} in 1 mol/L HCl solution and determined the exchange rate constant k^0 of the V^{5+}/V^{4+} system. Miller et al[15] investigated the electrode reaction of the couple V^{5+}/V^{4+} in 1 mol/L H_2SO_4 solution and 1 mol/L H_3PO_4 solution. In addition, Voicu[23] reported polarographic kinetic study of the system UO^{2+} + VO^{2+} in sulfuric acid medium. Voltammetric study of vanadium (Ⅴ) in H_2SO_4 solution using a platinum rotating disk electrode was made and certain kinetic and energy parameters were calculated by Nikolaeva et al[24]. Bouchet et al[25] studied the various oxidation states of Ti and V capable of existing in water-H_2SO_4-fuming H_2SO_4 solution using electrochemical analytical methods. In this paper, we reported the electrochemical behavior of vanadium (Ⅴ) salt under the condition of different H_2SO_4 concentrations, reaction temperatures and surfactants in order to further discuss some factors affecting the electrochemical reaction mechanism of V^{5+} ion. Although V^{5+} ion in acidic aqueous solutions was presented as a form of VO_2^+ ion even in a stronger acidic solution because of intensive hydrolysis of V^{5+} ion in aqueous solutions, V^{5+} ion was a habitual expression of VO_2^+ ion and was usually used in literatures or texts.

2 EXPERIMENTAL

All electrochemical experiments were carried out in stationary solutions, with a three-electrode and two-compartment glass cell. The working electrode and counter electrode were always Pt sheets (geometric area 0.12 cm^2) and they were in the same compartment. The saturated calomel reference electrode (SCE) was in the second compartment separated from the working electrode by a Luggin capillary. Potentials reported in this paper were referred to

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SCE. Before each experiment, the Pt electrodes were steeped in concentrated H_2SO_4 solution for several minutes, then washed with distilled water and acetone one by one. Finally, the electrodes were dried at ambient temperature. The instrumentation employed was a computer-based electrochemical analyzer LK98B Ⅱ. Experimental data were collected and analyzed with the software supplied by the same company which offered the above analyzer, and all electrodes used in the experiments were also from that company. It should be especially indicated that, in this paper, oxidation current was negative and reduction current was positive in voltammetric curves.

All chemicals used in experiments were analytically pure agents. Solutions were prepared with distilled water. All solutions were deoxygenated prior to each experiment using a fast bubbling of N_2 gas. All measurements were made at constant temperature maintained with a water-bath. The aqueous V^{5+} solutions were obtained by solubilizing NH_4VO_3 in H_2SO_4 solutions and the concentration of the V^{5+} was determined by titrating V^{5+} with the standard Fe^{2+} solution.

3 RESULTS AND DISCUSSION

3.1 General sight into voltammetry of aqueous V^{5+} solutions

Real form of V^{5+} ion in aqueous solutions, even in strong acidic solutions, is usually represented by VO_2^+ ion that indicates the hydration of V^{5+} ion with water molecules. In solutions of different pH values hydrated forms of V^{5+} ion are listed in Table 1.

Table 1 Relationship between V^{5+} ion and pH value[26]

pH	Main ion	Color
> 12.6	VO_4^{3-}	Pale yellow(colorless)
12 - 9	$V_2O_6(OH)^{3-}$	↓
9 - 7	$V_3O_9^{3-}$	
7 - 6.5	$V_{10}O_{28}^{6-}$	Red brown
6.5 - 2.2	$(V_2O_5 \cdot xH_2O)$	Orange brown
2.2 - 1	$V_{10}O_{28}^{6-} \leftrightarrow VO_2^+$	
< 1	VO_2^+	Pale yellow

Therefore, the increase of pH value may lower the oxidation degree of VO_2^+ or V^{5+} ion:

$$VO_2^+ + 2H^+ + e \rightarrow VO^{2+} + H_2O \tag{1}$$

Especially, the increase of pH value changes the hydrated form of V^{5+}, resulting in the changing of its electrochemical behavior. Generally, in addition to the reduction peak RH or RH′ of H^+ to H_2, there are two reduction peaks in voltammetric curves of aqueous V^{5+} solutions. And the peak currents change with concentrations of sulfuric acid and V^{5+} ion. A typical voltammetric curve is shown in Fig. 1 where the lower peaks O and O′ are oxidation peaks and the upper R1 and R2 are reduction peaks. The peak O whose potential is about 0 V may be responsible for the oxidation of hydrogen gas H_2 absorbed on the Pt electrode surface to H^+ ion:

$$H_2(g) \rightarrow 2H^+ + 2e \tag{2}$$

Hydrogen gas is produced at a lower starting potential, − 0.50 V. Therefore, H^+ should be reduced to H_2 gas at such a lower potential. The dashed line in Fig. 1 represents the voltammetric curve of a pure H_2SO_4 solution where a similar oxidation peak O′ is caused by reaction(2). This supports the analysis for the oxidation peak O. The potential difference between the peak O and O′ may be caused by the presence of V^{5+} ion absorbed on the electrode surface which hinders the oxidation of H_2 gas.

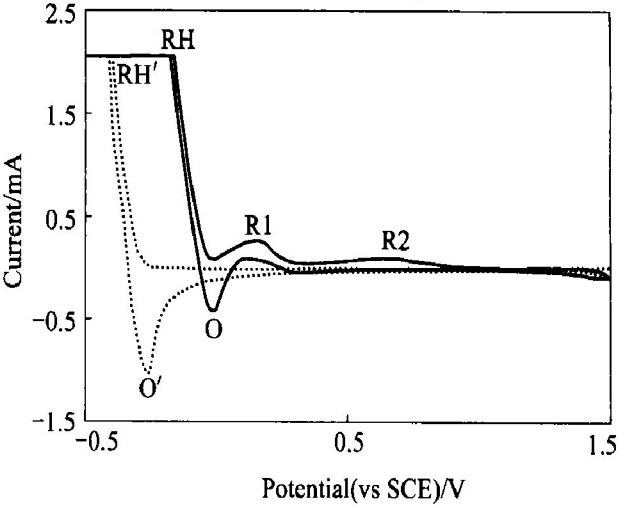

Fig. 1 Typical voltammetry of aqueous V^{5+} ion solution

(T = 298.15 K; v = 200 mV/s; electrolyte for solid line: 0.05 mol/L V^{5+} + 0.50 mol/L H_2SO_4; electrolyte for dashed line: 0.50 mol/L H_2SO_4)

Potentials corresponding to the two reduction peaks are 0.16 V(R1) and 0.68 V(R2), respectively. The two peaks may be related to the reduction of V^{5+} ion to other lower oxidation state ions. Reductions of couples V^{5+}/V^{4+}, V^{5+}/V^{3+} and V^{4+}/V^{3+} and their standard electrode potentials are shown as follows:

$$VO_2^+ + 2H^+ + e \rightarrow VO^{2+} + H_2O \tag{3}$$

$$E^0(\text{vs SHE}) = 1.000\ \text{V}$$

$$VO^{2+} + H^+ + e \rightarrow V(OH)^{2+} \tag{4}$$

$$E^0(\text{vs SHE}) = 0.337\ \text{V}$$

$$VO_2^+ + 3H^+ + 2e \rightarrow V(OH)^{2+} + H_2O \tag{5}$$

$$E^0(\text{vs SHE}) = 0.668\ \text{V}$$

Therefore, if peak R2 is assigned as the reduction of V^{5+} ion to V^{4+} ion, e g. reaction(3), then peak R1 may be related to reaction(4) or (5), or even related to the reductions of V^{5+} to its other lower oxidation state species.

It is seen from Fig. 2 that two reduction peaks in the system V^{5+} + H_2SO_4 are obviously related to the reduction of V^{5+} ion because there is no reduction peak in the potential range of − 0.20~0.80 V in the pure H_2SO_4 solution.

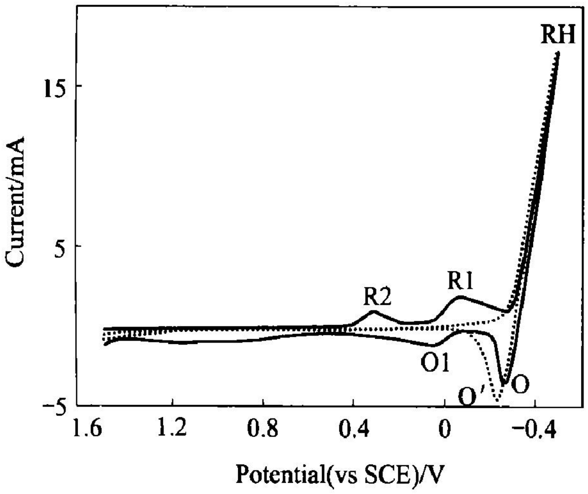

Fig. 2 Voltammetry of aqueous V^{5+} ion solution
(T = 298.15 K; v = 200 mV/s;
electrolyte for solid line: 0.05 mol/L V^{5+} +
0.18 mol/L H_2SO_4; electrolyte for dashed line:
0.18 mol/L H_2SO_4)

Comparing Fig. 2 with Fig. 1, it is found that peak potentials for R1 and R2 in Fig. 1 are different from those in Fig. 2, respectively. This potential shift is mainly caused by the difference of pH values on the working electrode surface. However, when potentials during positive-going scan increase, as shown in Fig. 1, H^+ concentration on the electrode surface increases considerably, due to the oxidation of H_2 gas to H^+ ion on the electrode surface, as expressed in reaction(2). According to reactions(3)~(5), the increase of H^+ concentration will lead to the increase of thermodynamic potentials of the couples V^{5+}/V^{4+}, V^{5+}/V^{3+} and V^{4+}/V^{3+}. This, of course, results in the peak potentials shifting positively (Fig. 1). Other two experimental facts are presented here in order to support this conclusion. Firstly, even if the electrolytes are H_2SO_4 solution and two different scanning-potential manners, as shown in Figs. 1 and 2, are applied, the peak potentials of R1 or R2 are different, indicating that the reduction of H_2 gas on the electrode influences the electrochemical properties of the couples. Secondly, both peak potentials of R1 and R2 always increase with sulfuric acid concentrations at these two different scanning-potential manners. When the scanning potential manner adopted the same as Fig. 1, the results are shown in Table 2.

Table 2 Effect of sulfuric acid concentration on peak potentials of R1 and R2 (V)

Scan rate/ (mV·s^{-1})	Sulfuric acid concentration					
	8 mol/L		4.5 mol/L		2.75 mol/L	
	R1	R2	R1	R2	R1	R2
200	0.158	0.773	0.158	0.760	0.145	0.722
400	0.149	0.739	0.145	0.709	0.141	0.696

3.2 Effect of scan rate on reduction peaks R1 and R2

Currents for peaks R1 and R2 increase and potential for peak R1 shifts to more negative, with the increase of scanning-potential rates. For the electrolyte 0.10 mol/L V^{5+} + 1.0 mol/L H_2SO_4, the peak current of R1, I_p, varies linearly with square root of scan rate, $v^{1/2}$, as shown in Fig. 3. In addition, the peak potentials for peak R1 decreases with the increase of the scanning-potential rates, and the peak current of R1, I_p, is found to increase linearly with concentration of V^{5+} under different scan rates (Fig. 4). Furthermore, the line in Fig. 3 goes through the initial point (0, 0), and a difference between E_p for R1 peak and E_p for O1 peak of 0.103 V is found from Fig. 2. On the basis of these observations it is suggested that the reaction corresponding to the reduction peak R1 is a 2-electron transfer, diffusion controlled and quasi-reversible process. In other words, the peak R1 may be caused by reduction of V^{5+} ion to V^{3+} ion. Reaction(3) is an irreversible process because there is no oxidation peak corresponding to the peak R2.

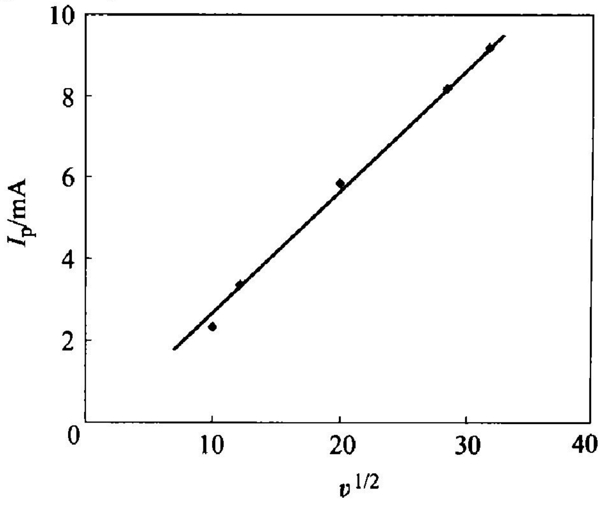

Fig. 3 Dependence of R1 peak current (I_p) on square root of scan rate ($v^{1/2}$)
(Solution composition: 0.10 mol/L V^{5+} +
1.0 mol/L H_2SO_4; T = 298.15 K)

3.3 Effect of reaction temperature on reduction peaks R1 and R2

Reaction temperature has , at the same scan-

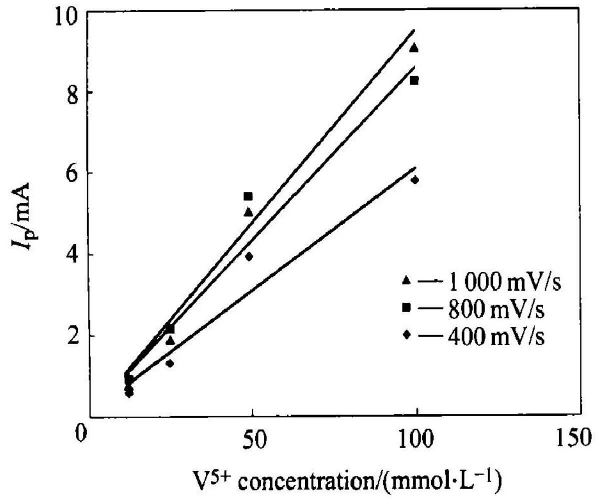

Fig. 4 Dependence of R1 peak current on concentration of V^{5+} in 1.0 mol/L H_2SO_4 solution (T = 298.15 K)

ning-potential rate, little effect on peak potentials of both R1 and R2. However, with the increase of temperature, peak currents of R1 or R2 increase. If the transfer coefficient of electrode reactions be kept constant, the relationship of current and activation energy of an electrode reaction can be expressed as Eqn. (6).

$$I_\eta = B \cdot \exp\left(-\frac{E_\eta}{RT}\right) \qquad (6)$$

where I_η and E_η are current and activation energy of an electrode reaction, respectively, under given values of potential; B is a constant for a given reaction. Under different potentials, linear dependences of logarithmic values of current, $\ln I$, on reciprocals of reaction temperature, T^{-1}, are shown in Fig. 5. According to Eqn. (6) and Fig. 5, the average values of activation energy of the reactions corresponding to peaks R1 and R2 are obtained:

R1 peak E_η = 12.86 kJ/mol;

R2 peak E_η = 47.72 kJ/mol.

3.4 Effect of scanning-potential rate on oxidation peak O1

Fig. 6 indicates the effect of scanning-potential rates on voltammetric curves of V^{5+} ion in 0.5 mol/L H_2SO_4 solution. It is found that both the reduction peak potentials of R1 and R2, and the oxidation peak potential of O1 shift to more negative values with the increase of the scanning-potential rate. However, the value of $|E_p(\text{O1}) - E_p(\text{R1})|$ decreases with the scanning-potential rate and it is higher than 59/n mV. This also shows that the reaction corresponding to the peak R1 is a quasi-reversible process.

The peak O1 disappears at lower scanning-potential rate, e.g. 100 mV/s. With the increase of scanning-potential rate, the ratio $|I_p(\text{O1})/I_p(\text{R1})|$ increased too. For example, $|I_p(\text{O1})/I_p(\text{R1})|$ = 0.116 at 200 mV/s however it is 0.878 at 1 200 mV/s. This indicates that lower scanning-potential rates make H^+ ion on the electrode surface produced

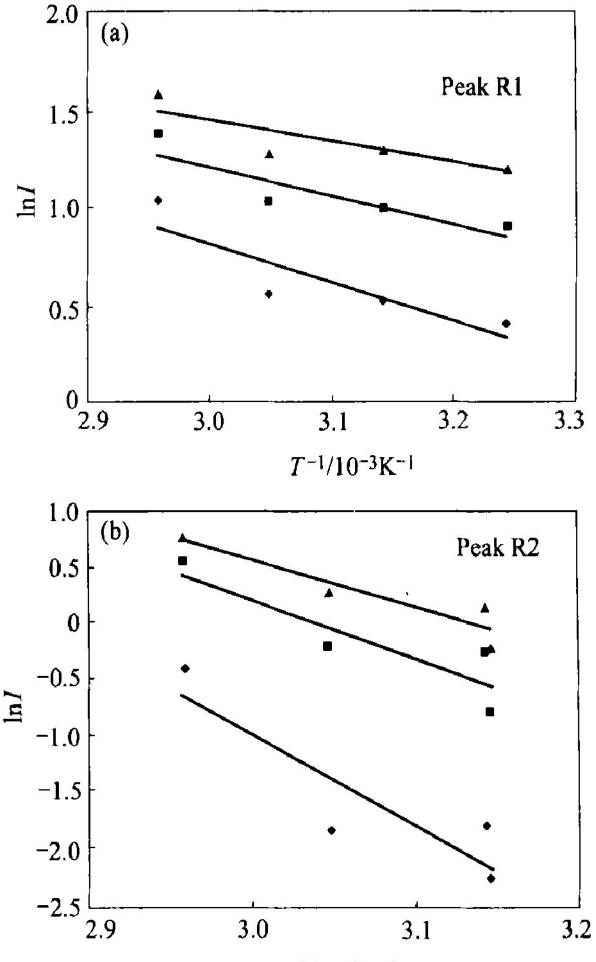

Fig. 5 Dependences of logarithmic current($\ln I$) on reciprocals of reaction temperature(T^{-1}) for reactions corresponding peaks R1(a) and R2(b)
(Scan rate = 200 mV/s; electrolyte: 0.05 mol/L V^{5+} + 0.5 mol/L H_2SO_4)

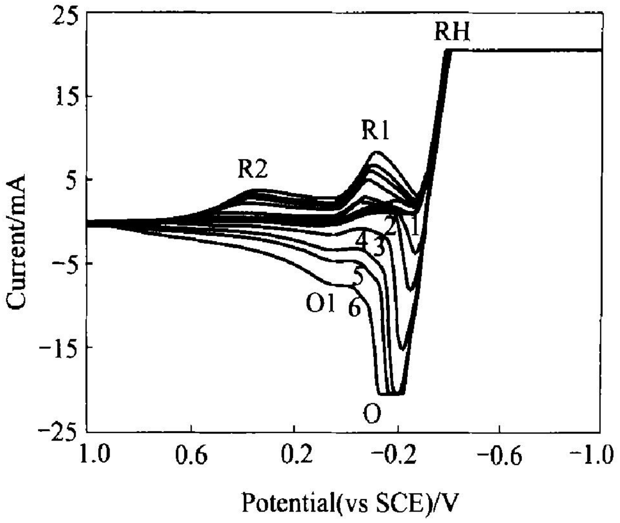

Fig. 6 Effect of scan rates on voltammetry of 0.05 mol/L V^{5+} ion in 0.5 mol/L sulfuric acid solution at 298.15 K
1—100 mV/s; 2—200 mV/s; 3—400 mV/s;
4—600 mV/s; 5—800 mV/s; 6—1 200 mV/s

during formation of the reduction peak RH have enough time to leave the surface for bulk solution, resulting in pH on the surface increasing and hydrated forms of V^{5+} and other vanadium ions changing. Therefore, peak O1 disappears during negative-going scan at lower scanning-potential rates.

Further illustration can be obtained from Fig. 7 where maximum positive-going scan potential is limited to − 0. 25 V and there is no oxidation peak O1 at any scanning-potential rate. In other words, during the positive-going scan H_2 gas does not evolved out on the electrode surface, the reaction(2) does not occur on the surface during negative-going scan, and hence, pH value on the surface increases due to the consumption of H^+ ion by reactions(3) and (5) corresponding to the peaks R1 and R2. The increase of pH value changes the hydrated forms of vanadium ions and influences their electrochemical behavior.

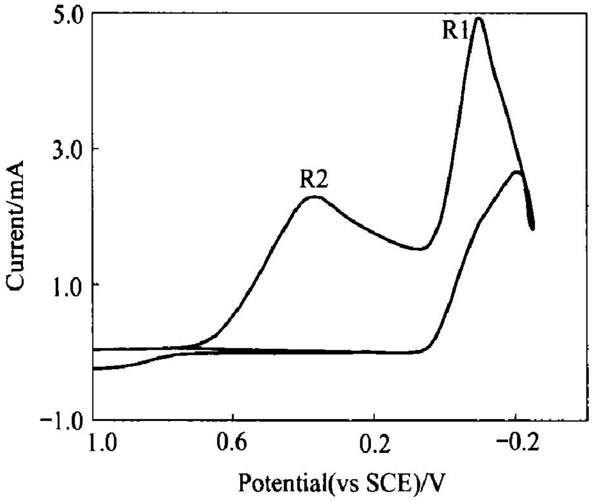

Fig. 7 Voltammetry of 0. 05 mol/ L V^{5+} ion in 0. 5 mol/ L sulfuric acid solution at 298. 15 K
(Scan rate 400 mV/ s; cathodic scan limit − 0. 25 V)

3. 5 Effect of surfactants on voltammograms

Surfactants that can change interfacial properties of electrode/ solution because of their special molecular structures have been applied in some electrochemical processes. Gyenge et al[27] reported the effect of anionic, neutral and cationic surfactants on cathodic reduction of oxygen gas. Anodic current density for electrochemical oxidation of aqueous S^{2-} solution at graphite electrodes increased obviously in the presence of a cationic surfactant[28, 29]. In this paper, we report the effect of anionic (sodium dodecyl sulfate, SDS) , cationic (cetanetrimethylammonium bromide, CTAB) and neutral (polyethyleneglycolcaprybenzol ether, PCBE) surfactants on voltammograms of V^{5+} ion. The results are shown in Fig. 8.

An interesting phenomenon in Fig. 8 is that both the reduction peaks R1 and R2 disappeared in the presence of CTAB or PCBE . This may be caused by the specific adsorption of the surfactants on the electrode surface, as shown in Fig. 9.

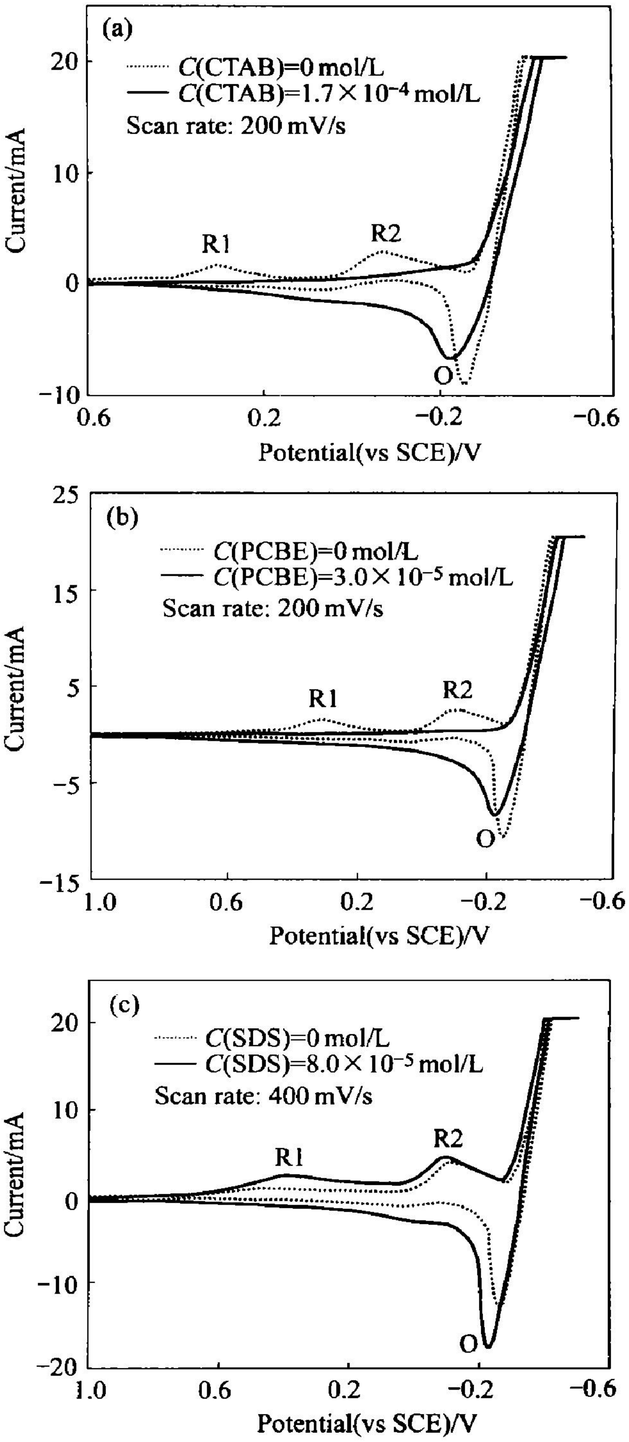

Fig. 8 Effect of surfactants on voltammograms of 0. 05 mol/ L V^{5+} in 0. 5 mol/ L H_2SO_4 at 298. 15 K
(a) —Cationic; (b) —Neutral; (c) —Anionic

Fig. 9 indicates that the specific adsorption of CTAB or PCBE hindered the electron-transfer process of V^{5+} on the electrode surface, resulting in the disappearance of peaks R1 and R2. This is presumably due to the "blocking effect" of these surfactants[27] . It is hypothesized that the hydrocarbon chain of these surfactants is facing the electrode surface, as displayed in Fig. 9. In addition, it is found from Fig. 8(a) and 8(b) that oxidation peak currents of H_2 during negative - going scan de -

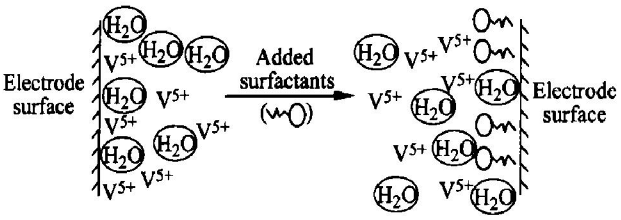

Fig. 9 Adsorption schematic diagram of surfactant CTAB or PCBE on electrode surface

crease with the addition of CTAB or PCBE. However, when anionic surfactant SDS is added to the anolyte, the peak currents for both the reduction peak R1 or R2 and oxidation peak O are increased. It is proposed that the anionic surfactant SDS may adsorb on the electrode surface in the form of highly-ordered aggregates with head-down facing the surface, hence it is favorable for the electro-active species V^{5+} ion to migrate toward the surface where reduction of V^{5+} ion takes place. A common characteristic in Fig. 8 is the positive shifting of the potential of the oxidation peak O in the presence of surfactants. Furthermore, it is found that the peak currents for R1, R2 and O at 8.0×10^{-5} mol/L SDS are almost the same as those at other concentrations of SDS, such as 1.1×10^{-3} mol/L SDS.

4 CONCLUSIONS

1) There are two reduction peaks R2 and R1 corresponding to the reductions of V^{5+} ion to V^{4+} and V^{5+} ion to V^{3+} ions, respectively. The reduction of V^{5+} to V^{4+} is irreversible but that of V^{5+} to V^{3+} is a quasi-reversible process.

2) Electrochemical behavior of V^{5+} ion is affected by pH value on the electrode surface, scanning-potential rate and reaction temperature, etc. Hydration of V^{5+} ion in the solution is strong and is intensively influenced by acidity of the solution. Oxidation of H_2 gas during negative-going scan makes H^+ concentration on the electrode surface increase, and this compensates the consumption of H^+ ion because of the reduction of V^{5+} (VO_2^+) ion during positive-going scan.

3) With the increase of scanning-potential rate peak current for oxidation of V^{3+} to V^{5+} increases. However, lower scanning-potential rates lead to the disappearing of this oxidation peak.

4) Activation energy of the reaction involved with the peak R2 is larger than that with the peak R1, indicating that the reaction of V^{5+} to V^{3+} is faster than that of V^{5+} to V^{4+}.

5) Cationic surfactant (CTAB) and neutral surfactant (PCBE) suppress the electrochemical reduction of V^{5+}, hence their presence in the anolyte leads to the disappearing of reduction peaks R1 and R2. Anionic surfactant (SDS), even at a very low concentration, increases the currents of the peaks R1, R2 and O.

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