CHARACTERIZATION OF THE REDOX REACTION OF V(V) IN AMMONIA BUFFERS WITH SQUARE-WAVE VOLTAMMETRY

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ABSTRACT

The redox reaction of V(V) in ammonia buffer solution of pH = 8.60 was studied by means of square-wave (SWV) and cyclic (CV) voltammetry. The redox reaction studied exhibits properties of a surface redox process in which both reactant and product of the redox reaction are immobilized to the electrode surface. A mathematical model for the electrode mechanism proposed was developed under conditions of square-wave voltammetry. In agreement with the theoretical findings, the phenomena of "split SW peaks" and "quasi-reversible maximum" are demonstrated experimentally. These unique features of the SWV response of a surface redox reaction are utilized for characterization of the redox process of V(V) in ammonia buffer. The following values of the kinetic parameters of the investigated redox reaction were estimated: standard rate constant k_s = 120 ± 10 s^{-1} and electron transfer coefficient α = 0.4 ± 0.05. The formal potential of the redox couple V(V)/V(IV) in ammonia buffer with pH = 8.6 is E^{0} = -0.56 V vs. Ag/AgCl (sat. KCl).

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INTRODUCTION

The adsorptive stripping voltammetry has been widely recognized as a sensitive technique for quantitative determination of various electroactive species capable to adsorb onto the working electrode surface. Among the diverse parameters, the sensitivity of particular adsorptive stripping voltammetric method depends principally on the shape of the potential signal applied in the course of the stripping step. It is well known that pulse techniques provide higher sensitivity than linear potential scan voltammetry. Moreover, the inherent ability of the pulse techniques to decouple the Faradaic from the non-Faradaic current is exceptionally important for systems involving reactant and/or product adsorption. In the family of pulse techniques, square-wave voltammetry (SWV) plays a unique role since it offers advantages regarding the speed and sensitivity [1]. These features appear as consequences of the high signal frequency, the large pulse amplitude, and the specific approach in the current-sampling procedure. On the other hand, it was recently demonstrated that SWV response of a surface confined redox reaction depends strongly on the reversibility of the redox reaction [2, 3]. Interestingly, the quasi-reversible redox reaction produces a few times higher response in comparison with the reversible or totally irreversible redox reaction. Therefore, for a developing of an adsorptive stripping SW voltammetric method, the knowledge of kinetic parameters of redox reaction studied is of intrinsic importance.

In this work, the redox reaction of V(V) in ammonia buffers was studied applying SWV and CV. The adsorptive stripping voltammetric behaviour of various V(V) complexes is well documented in the literature [4-12]. A large number of adsorptive stripping voltammetric methods have been reported for determination of vanadium in a form complex created with solochrome violet RS [4], catechol [5,6], 2,5-dichloro-1,4-dihydroxy-3,6-benzoquinone (chloroanilic acid) [7], 2-(5-thiozalolylazo)-p-cresol [8], pyrogallol [9], 8-hydroxyquinoline [10], antipyrylazo III [11] and cupferron [12]. In this paper we demonstrated that the redox reaction of V(V) in ammonia buffer of pH = 8.6 exhibits properties of a surface redox reaction. This process is both experimentally and theoretically studied aiming to elucidate the kinetic parameters of the redox reaction.

EXPERIMENTAL

All the chemicals used were of analytical-reagent grade. The stock solution of V(V) was prepared by dissolving of an appropriate amount of NH_4VO_3 (obtained from MERCK) in twice distilled water. Ammonia buffers were used as supporting electrolytes. The square-wave and the cyclic voltammetric experiments were performed using polarographic analyzer PAR 384B and a three-electrode configuration (static mercury drop electrode PAR 303A) with a hanging mercury drop electrode with surface area of 0.0149 cm^2 as a working electrode, Ag/AgCl (saturated KCl) as a reference and Pt wire as a counter electrode. The solutions were deoxigenyzed with pure nitrogen for 8 minutes prior each measurement. All experiments were performed at room temperature.

RESULTS AND DISCUSSION

Generally speaking, vanadium exhibits complex voltammetric behaviour due to its numerous oxidation states and hence various redox transformations are possible. In a non-complexing medium the reduction of V(V) occurs at a rather positive potentials and its voltammetric response could be masked by the oxidation current of mercury, if the latter was used as a working electrode. In a complexing medium, this process is displaced towards more negative potentials. The potential shift in negative direction depends mainly on the type and the stability constant of the formed complex.

The reduction of V(V) to V(IV) in ammonia buffer with pH = 8.6, occurs at a potentials of about –0.5 V. Applying cyclic voltammetry (CV), this redox reaction produces a pair of sharp and symmetric peaks, characterized with an equal height. Interestingly, in this medium the redox process studied can be observed only within a narrow pH interval from 8.5 to 8.8. Outside the limits of this pH range, the voltammetric response vanishes completely, indicating decomposition of the formed electroactive complex of V(V). It is also important to noticed here that the voltammetric response of this redox process also vanishes if the ammonia buffer was replaced with some other buffer, e.g. citric, phosphate or Britton-Robbinson's buffers. Obviously, the electroactive specie in the ammonia buffer is an ammin-type complex of V(V) formed only at pH of about 8.6. The formal potential of this redox process is sensitive to the concentration of ammonia buffer, which supports the latest conclusion. In figure 1 is depicted the variation of the formal potential of V(V) measured by

CV, on the logarithm of the ammonia buffer's concentration. The observed dependency is described with a linear function associated with slope of about 59 mV. The latest value is typical for a reversible one-electron redox process of ML type complex.

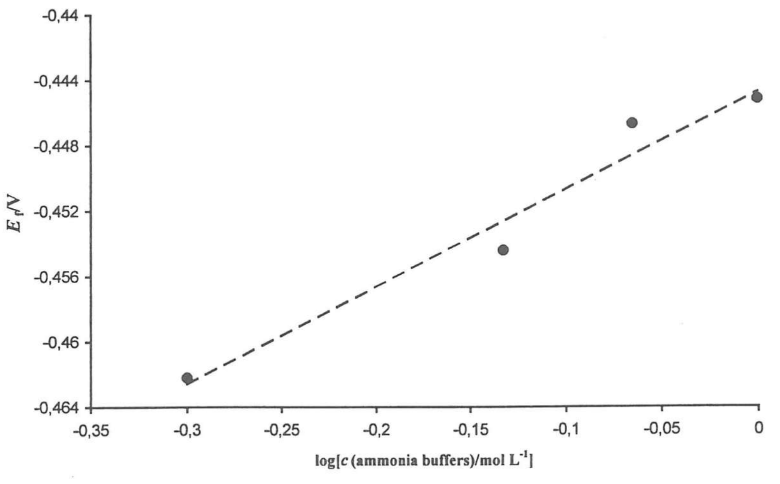


Fig. 1. Dependence of the formal potential of the cyclic voltammograms of 7.5×10^{-5} mol/L V(V) solution on the concentration of the ammonia buffers with pH = 8.60. The scan rate, the accumulation potential and the accumulation time were v = 500 mV/s, $E_{acc.}$ = -0.30 V and $t_{acc.}$ = 15 s, respectively.

Investigating the electrochemical behaviour of V(V) in ammonia buffer solution with pH = 8.6, adsorption phenomena of V(V) complex at a mercury electrode were observed. The adsorption properties of the complex studied are illustrated in the Figure 2. Due to the adsorptive accumulation of the electroactive complex the SWV peak current increases in proportion to the enhancement of the accumulation time. If the accumulation was longer than 225 s, the peak current becomes independent on the accumulation time, which corresponds to the saturation of the electrode surface with the electroactive material. As expected, the entire ΔI_p vs. $t_{acc.}$ relationship possesses a shape of an isotherm.

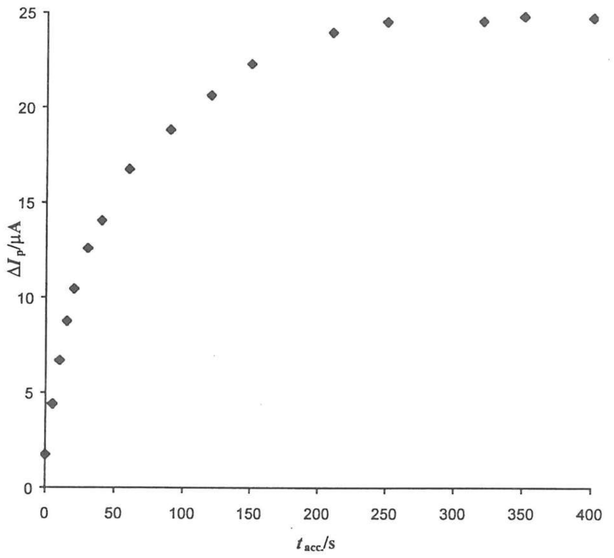


Fig. 2. The dependence of the peak currents of the SW voltammetric response of 7.5×10^{-5} mol/L V(V) solution on the accumulation time. The experimental conditions were: supporting electrolyte was ammonia buffer (c = 1 mol/L) with pH = 8.60, accumulation potential $E_{acc.}$ = -0.35 V, SW frequency f = 120 Hz, SW amplitude E_{sw} = 20 mV and scan increment dE = 4 mV.

The influence of the accumulation potential on the adsorption properties of V(V) complex was also investigated. Altering the accumulation potential within the interval from –0.1 to –0.6 V, a non-linear parabolic-type relationship between the peak current and the accumulation potential was observed. The curve is characterized with a maximum located at about -0.35 V indicating that the accumulation of V(V) complex is most effective at this potential. Applying accumulation of 180 s at potential of -0.35 V, a liner function of the SW peak current on the V(V) concentration exists within the interval from 2 to 12×10^{-8} mol/L. The latest results reveal that this medium could be employed for development of a sensitive adsorptive stripping voltammetric method for quantitative determination of V(V).

Additional information about the redox properties of the reaction studied in ammonia buffer with pH = 8.6 were collected by cyclic voltammetry. Cyclic voltammograms of 7.5 x

10^{-5} mol/L V(V) solution recorded within the potential range from -0.3 to -0.7 V have shown an interesting behaviour when mercury electrode was held for a certain time at a starting potential prior the cycling of the potential. The cyclic voltammograms recorded after accumulation of a few seconds were consisted of a pair of sharp peaks, which were symmetrically positioned, in the respect to the potential axes. Prolonged accumulation time caused both CV peaks to increase in proportion to the accumulation time indicating that both the reactant and the product of the redox reaction remain immobilized on the electrode surface (see Fig. 3). When electrode was saturated with the electroactive material (large V(V) concentration or long accumulation time), repetitive cycling of the potential exhibited no influence to the cyclic voltammetric response and a steady-state voltammograms have been obtained. Based on the results presented above it is reasonable to assume that the redox reaction of V(V) in ammonia buffer with pH = 8.6 appears as a surface redox process in which both the reactant and the product of the redox reaction are immobilized on the electrode surface. Hence, the electrode reaction can be described by the following scheme:

$$V(V)_{(ads)} + e^{-} = V(IV)_{(ads)}$$

In order to elucidate the complex voltammetric behaviour of V(V) in ammonia buffer solution with pH = 8.6 under conditions of SWV, as well as to estimate the kinetic parameters of this redox reaction, a theoretical model for surface redox reaction was developed, which is presented in the Appendix of the paper.

According to eq. (7) in the Appendix, the reversibility of a surface redox reaction depends on a single kinetic parameter κ defined as a ratio between the standard rate constant k_s and the frequency f of the applied SW signal $\kappa = k_s/f$. The redox reaction appears quasi-reversible if the kinetic parameter was ranged within the interval $-1.5 \leq \log(\kappa) \leq 1$. The dependence of the dimensionless peak current $\Delta \Psi_p$ on logarithm of the kinetic parameter κ is presented in the Figure 4. As can be seen, the quasi-reversible region is characterized with dramatic enhancement of the dimensionless peak current. Within this region, the dimensionless peak current reaches a maximum value associated with a certain critical value of the kinetic parameter κ_{max}.

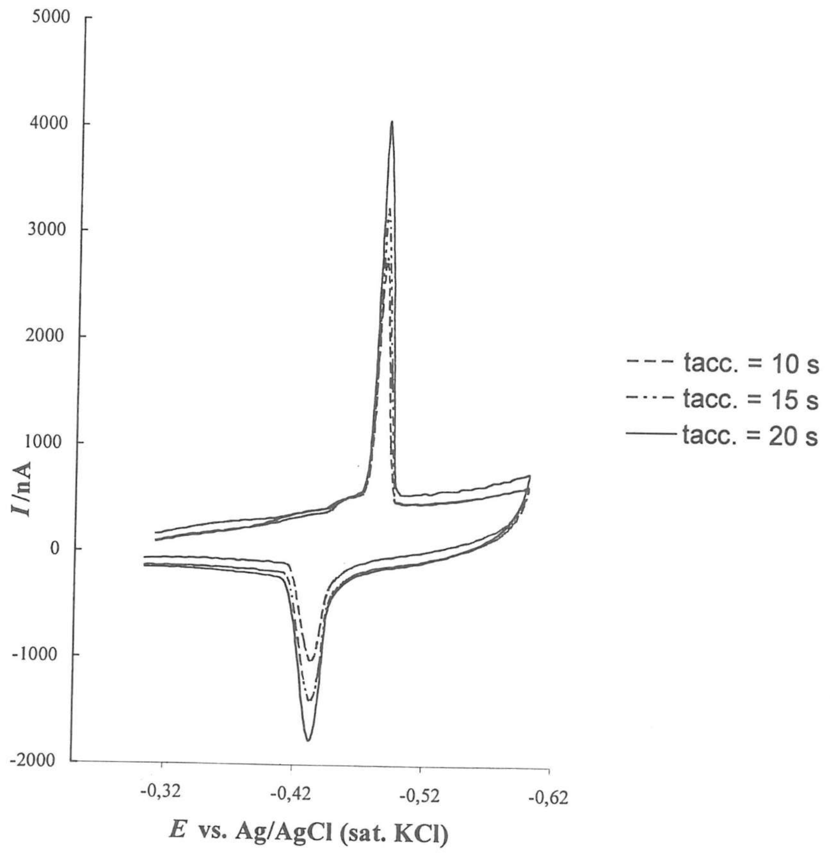


Fig. 3. Cyclic voltammograms of V(V) solution recorded after accumulation for 10, 15 and 20 s at accumulation potential of $E_{acc.}$ = -0.3 V. The scan rate was v = 500 mV/s. All other conditions were the same as in the caption of the Fig. 2.

This phenomenon, known as a "quasi-reversible maximum", appears to be an essential property of a whole class of redox reactions in which either one or both species of the redox couple are immobilized on the working electrode surface [2, 3]. The quasi-reversible maximum is pronounced exceptionally in the case of a surface reaction in which both species of the redox couple are strongly adsorbed on the electrode surface. This phenomenon arises as a consequence of the current sampling procedure used in the SW voltammetry. When the frequency of the signal is synchronized to the charge transfer rate, a multiple and exhaustive reuse of the surface confined material occurs, and thus the SW voltammetry induces a maximum response. Therefore, it is evident that the knowledge of the standard rate constant of the surface confined redox reaction is of particular importance. Knowing the standard rate constant of the investigated redox reaction, one could select the frequency of the signal which produces the highest response, which is of particular significance from an analytical point of view. Moreover, around quasi-reversible maximum, the forward and the backward component of the SWV response are symmetrically located with respect to the potential axes, yielding both the narrowest and the highest net SW peak. Thus, the ratio between the peak current and the half-peak width reaches a maximum value, which is also of particular analytical importance.

The "quasi-reversible maximum" is also important peculiarity from a kinetic point of view, inasmuch as it can be utilized for estimation of the standard rate constant of a surface redox reaction [3, 12]. As it was mentioned previously, the position of the maximum is associated with a certain critical value of the kinetic parameter $\kappa_{\max}$. The latter parameter, depends primarily on the amplitude of the SW excitation signal E_{sw} as well as the transfer coefficient α. If the values of the critical parameter $\kappa_{\max} = k_s/f_{\max}$ were calculated theoretically and the critical frequency $f_{\max}$ determined experimentally, than the standard rate constant cold be calculated trough the following simple equation: $k_s = \kappa_{\max} f_{\max}$.

The reversibility of a single redox reaction can be varied experimentally adjusting the frequency of the signal. Plotting the ratio of the real peak current and the corresponding frequency of the SW signal, versus the logarithm of the inverse frequency, one can obtain a corresponding dependence as that presented in the Fig. 4. This procedure was applied in the case of V(V) in ammonia buffer with pH = 8.6 and the quasi-reversible maximum was experimentally approved (see Fig. 5). The critical frequency at which the maximum was achieved is $f_{\max} = 100$ Hz.

If the simulation was carried out under corresponding conditions as those used in the experimental measurements of the quasi-reversible maximum, the critical value of the kinetic parameter reads $\kappa_{\max} = 1.25 \pm 0.06$, which is valid for transfer coefficient $0.3 \le \alpha \le 0.7$. Therefore, calculating the standard rate constant trough the relation $k_s = \kappa_{\max} f_{\max}$, one obtains $k_s = 125 \pm 6$ s^{-1}.

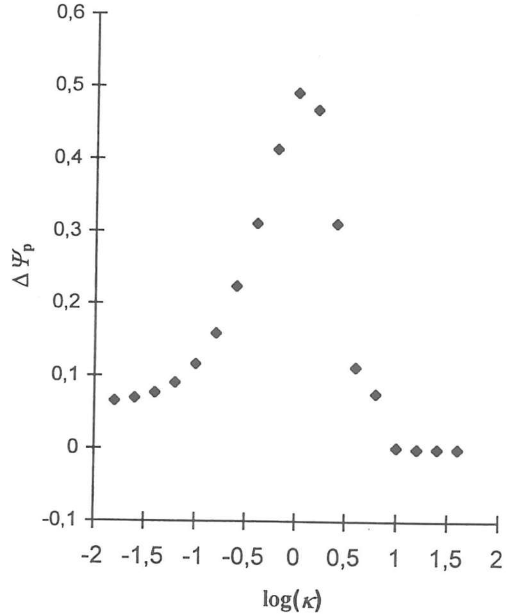


Fig. 4. Theoretical dependence of the dimensionless peak currents on the logarithm of the kinetic parameter κ. The conditions of the simulations were: electron transfer coefficient α = 0.5, square-wave amplitude E_{sw} = 25 mV, and potential scan increment dE = 10 mV.

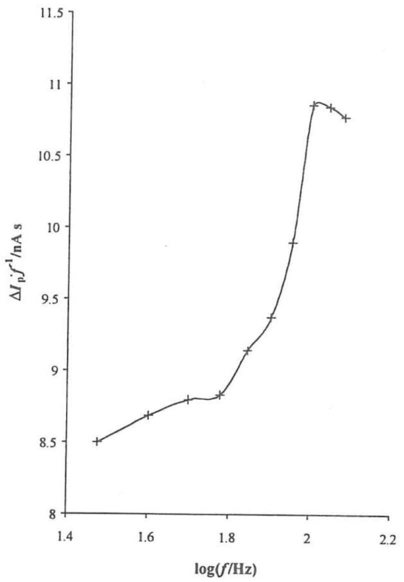


Fig. 5. Quasi-reversible maximum of 1.75×10^{-5} mol/L V(V) solution recorded in 1 mol/L ammonia buffer with pH = 8.6. The other experimental conditions were: accumulation time $t_{acc.}$ = 5 s, accumulation potential $E_{acc.}$ = -0.35 V, SW amplitude E_{sw} = 20 mV, and scan increment dE = 4 mV.

Further theoretical analysis of the proposed electrode mechanism revealed that the SWV response strongly depends on the amplitude of the applied SW signal. If the amplitude of the signal was increased over a certain critical value, the single SWV response splits in two symmetric peaks [12, 13] (see Fig. 6). This is another essential property of the SWV response of a surface redox reaction. This phenomena is an unique feature of the SW voltammetric response of the reaction of immobilized redox couple and it can be utilized for qualitative distinction as well as for kinetics characterization of this mechanism. The splitting of the SWV response appears only if the redox reaction is fast and chemically reversible. Under certain experimental conditions, the cathodic and anodic branch of the SW response are widely separated and the net-voltammetric response is consisted of two peaks. The theory predicts that the potential separation between these branches ΔE_p is proportional to the SW amplitude. Figure 7 shows that the relationship between ΔE_p and the SW amplitude is linear and the intercept of the lines depends on the kinetic parameter κ. The higher the reversibility of the surface redox reaction, the larger the value of the potential separation ΔE_p between split peaks. Moreover, the theoretical calculations have revealed that the potential separation depends linearly on the logarithm of the kinetic parameter κ, as shown in the Fig. 8. The latest results indicate that the splitting of the SW peak is an identifiable feature for estimation of the standard rate constant k_s via kinetic parameter $\kappa = k_s/f$.

The splitting of the SW peak of V(V) in ammonia buffers was observed if the amplitude was increased over 40 mV (see Figure 9), which confirms that the studied electrode mechanism is a surface redox reaction of an immobilized redox couple. The separation between the split peaks increases in proportion with the amplitude of the SW signal, which is in agreement with the theoretical prediction. Figure 10 shows a comparison between the experimentally measured potential separation of the split SW peaks and the theoretically calculated values under corresponding conditions. The best fitting between the experimental and theoretical values for standard rate constant of $k_s = 120 \pm 10$ s^{-1} has been achieved. The correlation between the experimentally measured and theoretically calculated values for the potential separation ΔE_p is characterized with a correlation coefficient of R = 0.999, which could be regarded as a quantitative indicator for the precision of the applied method. The standard rate constant estimated on the base of split SW peaks is in well agreement with the value obtained utilizing the property of quasi-reversible maximum.

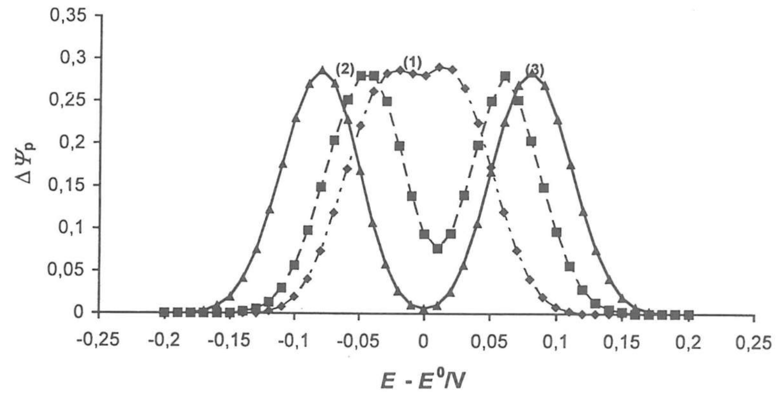


Fig. 6. The splitting of the theoretical SW response under influence of the signal amplitude. The conditions of the simulations are: kinetic parameter $\kappa = 2.5$, transfer coefficient $\alpha = 0.5$, scan increment dE = 4 mV, and SW amplitude E_{sw} = 50 (1), 75 (2) and 100 mV (3).

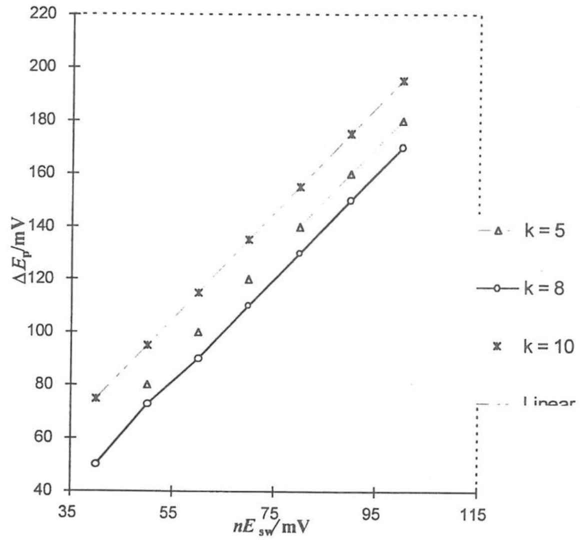


Fig. 7. Theoretical dependence of the potential separation between the split peaks ΔE_p on the amplitude of the SW signal for different reversibility of the redox reaction. The conditions of the simulations are: scan increment dE = 5 mV, electron transfer coefficient α = 0,5 and kinetic parameter κ = 4 (1), 5 (2), 8 (3), and 10 (4).

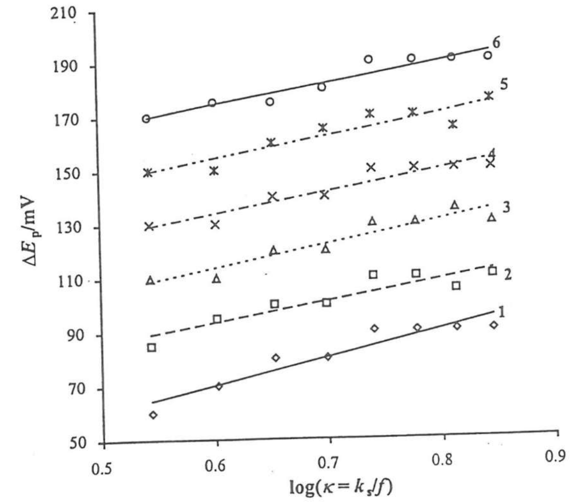
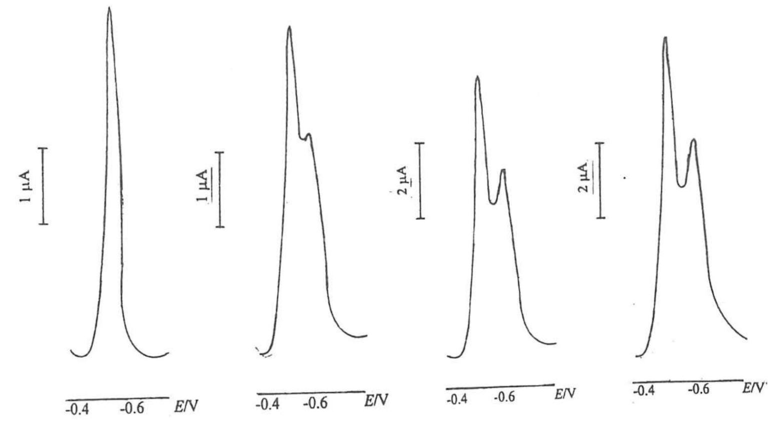


Fig. 8. Theoretical dependence of the potential separation between the split peaks ΔE_p on the kinetic parameter κ for different amplitude of the SW signal. The conditions of the simulations are: scan increment dE = 5 mV, electron transfer coefficient $\alpha = 0.5$ and SW amplitude $E_{sw} = 50$ (1), 60 (2), 70 (3), 80 (4), 90 (5) and 100 mV (6).



(a) (b) (c) (d)

Fig. 9. The splitting of the SWV response of 5×10^{-5} mol/L solution of V(V) under increasing signal amplitude. The experimental conditions were: accumulation time $t_{acc.} = 10$ s, accumulation potential $E_{acc.} = -0.35$ V, SW frequency $f = 90$ Hz, scan increment dE = 2 mV and SW amplitude $E_{sw} = 20$ (a), 40 (b), 50 (c) and 60 mV (d). All other conditions are the same as in the caption of the Fig. 2.

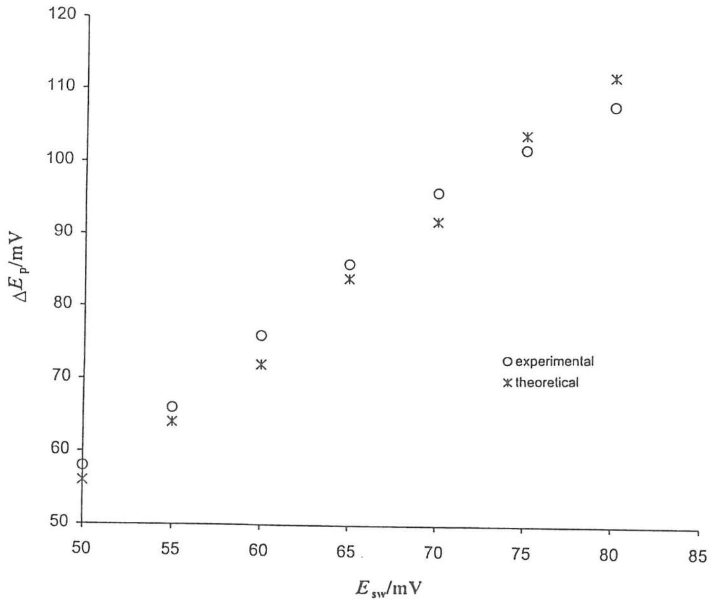


Fig. 10. A comparison between the theoretically calculated and experimentally measured values of the potential separation ΔE_p between the split SW peaks. The theoretical values are calculated for standard rate constant of $k_s = 120$ s^{-1} and electron transfer coefficient of $\alpha = 0.4$. The experimental conditions are the same as in the Fig. 9.

On the other hand, theoretical considerations have shown that the potential separation between split peaks is independent on the transfer coefficient α of the investigated redox reaction. However, the transfer coefficient influences markedly the shape of the SW response and the heights of the split peaks. The relationship between the ratio of peak currents of split peaks $\Psi_{p,c}/\Psi_{p,a}$ and the electron transfer coefficient reads: $\alpha = [1.73 - \ln(\Psi_{p,c}/\Psi_{p,a})]/3.4606$. The average value of the ratio between the split SW peaks of V(V) $I_{p,c}/I_{p,a}$ is 1.4. Therefore, the electron transfer coefficient of the studied redox reaction is $\alpha = 0.4 \pm 0.05$.

Finally it should be pointed out that the split peaks are symmetrically located around the value of the formal redox potential of the investigated redox system. Thus, estimation of this important thermodynamic parameter is strength forward. Therefore, the formal redox potential of the redox system V(V)/V(IV) in ammonia buffers with pH = 8.6 is –0.56 V vs. Ag/AgCl (sat. KCl).

CONCLUSION

In ammonia buffers with pH = 8.60, V(V) exists as an ammonia-type complex with pronounced adsorption properties on the mercury electrode surface. The redox reaction of this electroactive form exhibits properties of a surface confined redox process in which both the reactant and the product of the redox reaction are immobilized on the electrode surface. The findings from the theoretical analysis of the proposed electrode mechanism are in well agreement with the experimental results obtained under conditions of the square-wave voltammetry. The phenomena of "split SW peaks" and "quasi-reversible maximum" are both experimentally and theoretically demonstrated. These unique features of the SWV response of a surface immobilized redox reaction are utilized for entire characterization of the studied redox reaction. The kinetic parameters of the redox reaction of V(V) in ammonia buffer with pH = 8.6 are as follows: standard rate constant k_s = 120 ± 10 s^{-1} and electron transfer coefficient α = 0.4 ± 0.05. The formal potential of the redox couple V(V)/V(IV) in this medium is E^0 = -0.56 V vs. Ag/AgCl (sat. KCl).

APPENDIX

A reaction of two chemically stable compounds, which are strongly adsorbed to the surface of the working electrode, is investigated:

$$(\mathrm{Ox})_{\mathrm{ads}} + ne^- = (\mathrm{Red})_{\mathrm{ads}} \qquad (\mathrm{I})$$

It is assumed that the reaction is controlled by the charge transfer kinetics, that the adsorption of both reactant and product is totally irreversible, that there is no interactions between the adsorbed molecules in the case of submonolayer surface coverage and that the additional adsorption and the redox reaction of the dissolved molecules can be neglected. Under these conditions, the system (I) is described by the following differential equations:

$$\mathrm{d}\,\Gamma_{\mathrm{Ox}}/\mathrm{d}t = -I/(nFS) \qquad (1)$$

$$\mathrm{d}\,\Gamma_{\mathrm{Red}}/\mathrm{d}t = I/(nFS) \qquad (2)$$

which should be solved under the following starting and boundary conditions:

$$t = 0:\ \Gamma_{\mathrm{Ox}} = \Gamma_0,\ \Gamma_{\mathrm{Red}} = 0 \qquad (a)$$

$$t > 0:\ \Gamma_{\mathrm{Ox}} + \Gamma_{\mathrm{Red}} = \Gamma_0 \qquad (b)$$

On the electrode surface, the followindg conditions is valid:

$$I/(nFS) = k_s \exp(-\alpha\phi)\,[\Gamma_{\mathrm{Ox}} - \exp(\phi)\,\Gamma_{\mathrm{Red}}] \qquad (3)$$

were: $\phi = nF(E - E_{\Gamma\mathrm{Ox}/\Gamma\mathrm{Red}})/RT$ is dimensionless potential, Γ_{Ox} and Γ_{Red} are surface concentrations of Ox and Red, respectively, Γ_0 is the initial surface concentration of the reactant Ox, k_s is the standard redox reaction rate constant expresed in unit s^{-1}, α is the cathodic electron transfer coefficient, I is the current, E is the working electrode potential, $E_{\Gamma\mathrm{Ox}/\Gamma\mathrm{Red}}$ is the standard potential, S is electrode surface, while n, F, R, T and t have their usual meanings.

The solutions of the differential equations (1) and (2) were obtained with the aid of Laplace transformations and they read:

$$\Gamma_{Ox} = \Gamma_0 - \int_0^t \frac{I(\tau)}{n\cdot F\cdot S}\,d\tau \qquad (4)$$

$$\Gamma_{Red} = \int_0^t \frac{I(\tau)}{n \cdot F \cdot S} d\tau \qquad (5)$$

Substituting the equations (4) and (5) into the kinetic equation (3), an integral equation is obtained which can be regarded as a mathematical representation of the electrode mechanism (I) under voltammetric conditions:

$$\frac{I}{n \cdot F \cdot S} = k_s \cdot e^{-\alpha \cdot \phi} \cdot \left(\Gamma - \int_0^t \frac{I(\tau)}{n \cdot F \cdot S} d\tau - e^{\phi} \cdot \int_0^t \frac{I(\tau)}{n \cdot F \cdot S} d\tau \right) \qquad (6)$$

The latest equation was numerically solved according to the method of Nicholson and Olmstead [14]. The numerical solution under conditions of square-wave voltammetry reads:

$$\Psi_m = \frac{\kappa \cdot e^{-\alpha \cdot \phi_m} - \kappa \cdot e^{-\alpha \cdot \phi_m} \cdot \left(\frac{1 + e^{\phi_m}}{50} \right) \cdot \sum_{j=1}^{m-1} \Psi_j}{1 + \kappa \cdot e^{-\alpha \cdot \phi \cdot m} \cdot \left(\frac{1 + e^{\phi_m}}{50} \right)} \qquad (7)$$

where: $\Psi = I/nFSf\Gamma_0$ is a dimensionless current, $\kappa = k_s/f$ is a dimensionless kinetic parameter, and f is a SW frequency.

The square-wave signal is a train of cathodic and anodic pulses, which are superimposed to a staircase potential ramp. The highs of each cathodic and anodic pulses are equal and designated as square-wave amplitude E_{sw}. Additionally, the SW signal is characterized by the staircase potential increment dE and frequency f of the pulses.

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