

Notes

An Evaluation of the Rate Constant for the Chemical Step in an ECE Type Reduction of VO^{2+} -Diethylenetriamine pentaacetate

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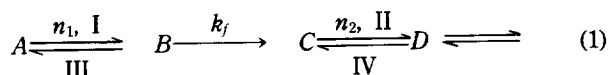
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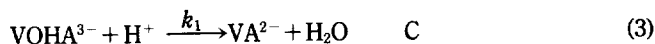
Received November 22, 1990

As is well known, a class of reactions in which a single chemical reaction is coupled between two charge transfers like Eq. (1),

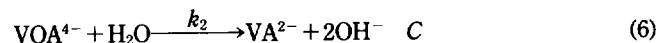


where n_1 and n_2 are the number of electrons involved in the reductions and k_f is first order rate constant, is referred to an ECE mechanism.¹ In Eq. (1), I, II, III and IV represent the respective redox peaks. In light of the reversibility of two charge transfers and ΔE ($=E_2^\circ - E_1^\circ$) where E_1° and E_2° are equilibrium potentials for the first and second charge transfers, respectively, Nicholson and Shain¹ exhibited current functions χ and ϕ for redox peaks I through IV for different values of k_f/a ($a=nFv/RT$) and ΔE . Further, they presented diagnostic criteria to discriminate among the variations in the ECE mechanism.

Recently, we have studied electrode reactions of VO^{2+} -diethylenetriaminepentaacetic acid (H_5DTPA or H_5A) complex.^{2,3} We have proposed an ECE mechanism for the electrode reaction at $3.2 < \text{pH} < 5.9$ as



and at $7.2 < \text{pH} < 10.5$ as



Here $|\Delta E_p$ ($E_{p2} - E_{p1}$) is the largest, being more than 200 mV at $\text{pH}=5.9$. E_p for (5) becomes more negative as pH

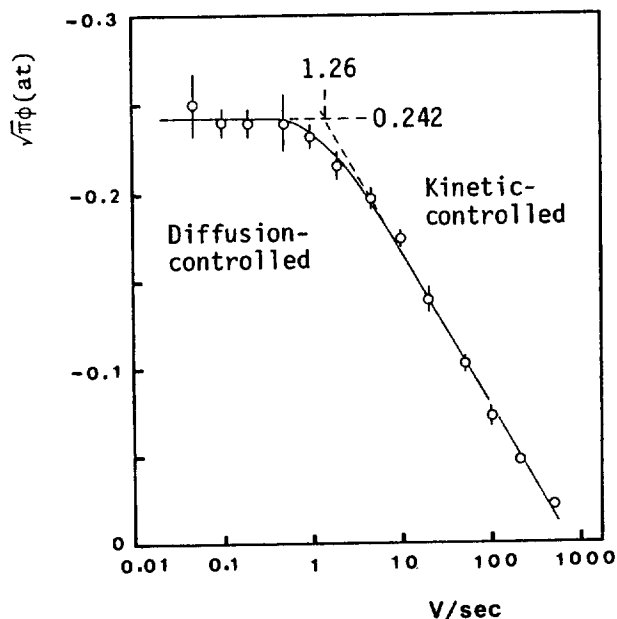


Figure 1. The plot of current function vs. scan rate for peak II ($\text{V}^{3+} + e^- \rightarrow \text{V}^{2+}$) of VO^{2+} -DAPA system from cyclic voltammetry. $[\text{VO}^{2+}] = 2 \text{ mM}$; $[\text{DTPA}] = 0.05 \text{ M}$; $\mu = 0.5 \text{ M NaClO}_4$; $\text{pH} = 6.00$; Electrode area = 1.39 mm^2 ; Temperature = 25°C .

goes higher, resulting in a merge of two voltammetric peaks for (5) and (7).

If reduction product B in reaction (1) is further reduced at more negative potential than the reduction of A , as in the above cases (2) to (4) and (5) to (6), interposed chemical reaction rate can be a ruling factor for the appearance of second peak. That is, if we scan faster, we can not see peak II whereas in slower scans peak II can appear because larger amount of C attributing to peak II is formed. In this respect, an attempt is made in this paper to evaluate rate constant of the interposed chemical reaction in an ECE type reduction of VO^{2+} -DTPA system.

Experiments

The experimental procedure has been detailed elsewhere.^{2,3} Peak currents in cyclic voltammograms were measured from the baseline referenced to blank solution which does not contain VO^{2+} ion.

Results and Discussion

At $\text{pH}=6$ where peaks I and II show the largest separation from each other and the reaction scheme of (2) to (4) holds, current functions of peak II were plotted against scan rates as shown in Figure 1. Figure 1 clearly shows two regions of interest: the one at slow scans is diffusion controlled whereas the other at faster scans is kinetic controlled. Since peak II is well separated from peak I and is satisfactorily reversible, quasi-reversible nature of peak I is not thought

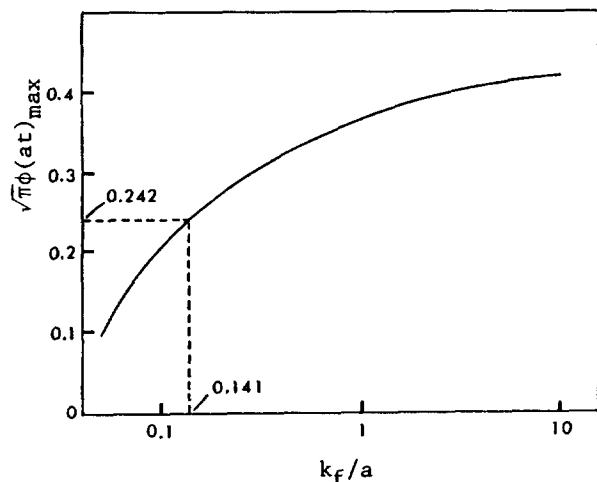


Figure 2. Maximum values of current function ($\sqrt{\pi\phi}$) vs. k_f/a for the second charge transfer (II). Case $R-R$, $n_2/n_1=1$, and $\Delta E^\circ = -180$ mV.

to affect peak II. During the slow scan in the acidic condition, much of VOHA^{3-} is converted to VA^{2-} and the peak corresponding to the reduction of VA^{2-} to VHA^{2-} would be diffusion controlled. On the other hand, during the faster scan, there is little time for VOHA^{3-} to become VA^{2-} and we have a kinetic controlled current.

The intersection (scan rate = 1.26 V/sec and $\sqrt{\pi\phi} = 0.242$) of two regions is a point where the effect of the chemical reaction appears. Said otherwise, the point would correspond to the fastest chemical reaction rate or the intrinsic rate itself. Thus the current function ϕ of the intersection can be an indicator for rate constant:

$$\phi = \frac{i}{nFA\sqrt{\pi Da} C^*} \quad (8)$$

where $a = nFv/RT$ and other symbols have their usual meaning.¹ Nicholson and Shain¹ tabulated values of current functions $\sqrt{\pi\phi}$ for various values of k_f/a and potentials. We obtain a working curve for the case of reversible-reversible ($R-R$) reaction with $n_2/n_1 = 1.0$ and $\Delta E^\circ = -180$ mV to which our data correspond from the table of Nicholson and Shain,¹ as shown in Figure 2 which is a plot of maximum values of the current function vs. k_f/a .

Applying the obtained value of the current function to the working curve, a value of k_f/a is estimated as 0.141. Thus, k_f for reduction of VOHA^{3-} can be calculated as $k_f = 0.141 \times a = 6.91 \text{ sec}^{-1}$, where $a = (nF/RT) \times 1.26 = 49.0$. This is more than ten times faster compared to the rate constant of the chemical step in the reduction reaction of *p*-nitrosophenol which was estimated to be 0.6 sec^{-1} using an empirical equation relating k_f/a and $1/a$ established by Nicholson and Shain.⁴ They revealed that the reduction of *p*-nitrosophenol occurs through an ECE mechanism with E_{p2} more positive than E_{p1} .⁴ However, E_{p1} is more positive than E_{p2} in reduction reaction of VO^{2+} -DTPA. Less reversible nature and negative shift in E_p of reaction (5) with the resultant merge of peaks for (5) and (7) hinders evaluation of k_2 at high pH region.

Reference

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4. R. S. Nicholson and I. Shain, *Anal. Chem.*, **37**, 190 (1965).