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Polarographic Investigation of Oxidation Reaction of Vanadium(II) by Nitrate Ion

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The polarographic behavior of V(II) species in various solutions has been investigated by Lingane and Meites.[1,2] Rates of the oxidation of V(II) by nitrate ion in perchlorate, sulfate, and halide solutions have been determined by means of polarography.[3] The polarographic method was applied because it was possible to measure the-rates at low acidities. It was found that sulfate ion increased the rate of oxidation to some extent. The relationship between the half-wave potentials and the rates of homogenous reactions has been suggested.[4] In the present work, the rates in various supporting electrolytes were determined by the polarographic method. It may be concluded that the difference in the rates was mostly related to that in the half-wave potentials of V(II) in the corresponding media. However, for the systems having similar half-wave potentials, the difference in the rates seems to be related to the polarographic reversibilities of the systems. The relationship will be discussed.

Experimental

All the reagents used were of analytical grade. The preparation and analysis of V(II) solution were reported elsewhere.[3] Ionic strength was adjusted to 0.5 by adding sodium perchlorate.

Measuremnet. An appropriate amount of V(II) perchlorate solution was added to the deaerated solution of a supporting electrolyte, and the polarographic measurements were carried out to obtain the half-wave potential and the reversibility of V(II) ion. While the solution was being stirred by passing N_2 gas, sodium nitrate was added to the solution, and the time dependence of the diffusion current was then recorded at a constant potential. Measurements were performed at 25°C.

Results and Discussion

Calculation of Rate Constants. The overall oxidation of V(II) by nitrate ion was proposed as follows:[3]

$$8\mathrm{V(II)} + 2\mathrm{NO_3^-} + 10\mathrm{H^+} \rightarrow 8\mathrm{V(III)} + \mathrm{N_2O} + 5\mathrm{H_2O}$$

The reaction between V(II) and nitric oxide was involved in the oxidation paths, but its rate was considerably slow.[3] When excess nitrate ions in relation to V(II) ions are present, the amount of V(II) oxidized by nitrate ions is almost three times as large as that of nitrate ions consumed. Thus, the apparent second-order rate constant, k, corresponding to the decrease in V(II) ions can be calculated from the time dependence of the diffusion current using equation

$$kt = \frac{3}{3[\mathrm{NO_3^-}]_i - [\mathrm{V(II)}]_i} \times \ln\left\{\left(\frac{[\mathrm{V(II)}]_i}{[\mathrm{NO_3^-}]_i}\right)\frac{[\mathrm{NO_3^-}]_i - \mathrm{X}}{[\mathrm{V(II)}]_i - \mathrm{X}/3}\right\} \tag{1}$$

where X is the increment of reaction at any time, and i denotes the initial concentration. When the rate of oxidation is considerably small, a large excess of nitrate ions over V(II) ions is added to the solution in order to obtain feasible rates. In this case, the rate constant is also calculated from the half time assuming that the rate is pseudo first-order with respect to V(II).

Polarographic Behavior of V(II). The half-wave potentials and the polarographic reversibility as defined by Senda and Tachi[5] are shown in Table 1. From the half-wave potentials, it was concluded that the complex formation of V(II) ions took place in almost all the solutions, except for perchlorate, thiocyanate, and ammonium chloride solutions. In the thiocyanate solution, the concentration of thiocyanate ions was adjusted to 0.05 M in order to prevent the dissolution of mercury of the electrode, but at this concentration

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[1] J. J. Lingane and L. Meites, *J. Amer. Chem. Soc.*, **69**, 1021 (1947).

[2] J. J. Lingane and L. Meites, *ibid.*, **73**, 2165 (1951).

[3] K. Tanaka, This Bulletin, **43**, 2030 (1970).

[4] A. A. Vlček, "Advances in the Chemistry of the Coordination Compound" Macmillan, New York (1961), p. 590.

[5] M. Senda and I. Tachi, *J. Electrochem. Soc. Jap.*, **27**, 83 (1957).

Table 1. Half-wave potentials, reversibility, and rates of oxidation of vanadium (II) at 25°C

Group	Supporting electrolytes	pH	$-E_{1/2}$ V *vs.* SCE	$i_p/i_d\sqrt{\tau}$ $\mho\cdot\mathrm{A}^{-1}\cdot\mathrm{sec}^{-1}$	k $l\cdot\mathrm{mol}^{-1}\cdot\mathrm{sec}^{-1}$	Color of solution Reactant	Color of solution Product
I	0.05 M EDTA	3.79	$\sim$1.26	59.6	$\sim 2\times10^2$	yellow brown	brown
	0.25 M potassium oxalate	7.21	1.13	5.3	1.3×10^2	black purple	pale blue
	0.10 M sodium oxalate	7.73	1.00	4.4	1.2×10^2	black purple	pale blue
II	0.10 M sodium citrate	7.08	1.12	2.6	3.8×10	pale brown	colorless
	0.10 M sodium fluoride	6.75	0.67	3.5	2.5×10	colorless	white ppt*
	0.10 M sodium succinate	6.72	0.88	$\sim$0	2.2×10	colorless	pale green
	0.10 M sodium tartrate	5.72	0.76	3.5	2.0×10	colorless	blue
III	0.10 M sodium salicylate	4.70	0.69	13.1	7.2	colorless	yellow green
	0.10 M sodium fumarate	6.08	0.72	4.4	3.8	red brown	yellow green ppt*
IV	0.50 M sodium perchlorate	4.38	0.50	8.1	1.4×10^{-1}	colorless	pale green
	0.05 M sodium thiocyanate	4.52	0.53	46.5	1.3×10^{-1}	pink	colorless
	0.25 M ammonium chloride	4.38	0.52	15.8	1.0×10^{-1}	colorless	pale green

* ppt = precipitation

V(II) ions might form a thiocyanato-complex as reported by Biermann and Wong.[6] In this solution, a polarographic minimum was observed at ~ -0.05 V *vs.* SCE. From the fact that the half-wave potential shifted to more negative side with increasing oxalate concentration, V(II) ion seems to be able to form a mono-oxalato complex in the range of 0.1—0.25 M oxalate ions as suggested by Lingane and Meites.[2] The polarographic behavior of V(II) ion in fumarate, and succinate solutions were first investigated in this work. In these solutions, two polarographic waves were obtained, the more negative half-wave potentials being listed in Table 1. The a.c. polarographic measurement in fumarate solution indicated that the reversibility of the second wave (more positive) was almost twice as high as that of the first one, and the a.c. polarogram of the first wave was split into two peaks. The same phenomenon was found in a citrate solution.

Rates of Oxidation. A considerable variation in the rate constants was observed for this oxidation reaction. From their magnitudes the results may be divided into four groups as shown in Table 1. It was suggested by Vlček that the more negative the half-wave potential, the faster the rate of oxidation.[4] This relationship may hold among the groups in Table 1, but not always within each group. The difference in the rates between fluoride and succinate solutions, and salicylate and fumarate solutions, could not be related to their half-wave potentials, but probably to their reversibility. It is supposed qualitatively that the difference in the rates of the oxidation is related to the rates of the electrode reaction of V(II) species. For example, the difference in the rates between oxalate and citrate solutions, in which almost the same half-wave potentials were obtained, is considered to be related to their polarographic reversibility. The fastest rate of oxidation and the highest reversibility were obtained in EDTA solution. However, the relationship does not always hold, because the reversibility is easily changed by: (1) polarographic kinetics, and (2) adsorption of supporting electrolytes or depolarizer on mercury electrode. As shown in group IV, the rates in thiocyanate, and ammonium chloride solutions were slow, but their reversibility were higher than that in perchlorate solution. This is thought to be caused by the adsorption of each anion. It has been found that the rate of the oxidation decreased with increasing chloride ion concentration.[3]

No influence of sulfate ion on the rates could be observed in fumarate, and tartrate solutions. However, when 0.05 M sodium sulfate was present in thiocyanate solution, the rate increased about 10%, and after completion of oxidation the solution became pale yellow, indicating that a single two-electron oxidation step might be involved.[3]

As shown in Table 1, the rates of oxidation decreased as: oxalate > citrate > tartrate > thiocyanate. This decreasing order in the rates is in good agreement with the results obtained for the oxidation of Ti(III) by chlorate ion.[7]

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6) W. J. Biermann and W-K. Wong, *Can. J. Chem.*, **41**, 2510 (1963).

7) K. Tanaka, K. Morinaga and K. Nakano, *Nippon Kagaku Zasshi*, **90**, 478 (1969).