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Studies on the Electrode Processes of Oxovanadium (IV). II. Electrolytic Reduction of Vanadyl Acetylacetonate in Acetonitrile Solution at Mercury Electrode

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The electrolytic reduction of vanadyl acetylacetonate in acetonitrile solution was investigated by means of conventional and AC polarography, cyclic voltammetry and controlled-potential electrolysis. A well-defined polarographic cathodic wave was obtained in a solution containing excess acetylacetone. The wave-form was outwardly a single step with two-electron transfer. However, logarithmic analysis revealed that it consists of two steps. The first step is slightly irreversible, being accompanied by V–O bond breaking, and the second one is controlled by the rate of coupled chemical reactions. The reaction mechanism is discussed in detail. The reversible half-wave potentials of the species [VO(acac)$_2$] and [V(acac)$_3$] were determined to be -1.93 and -1.78 V *vs.* Ag/0.1 M AgClO$_4$, respectively, from the logarithmic analysis.

Invesigations on the electrolytic reduction of vanadyl ion and its complexes have been made by many authors. Lingane,[1] reporting on the polarographic behavior in aqueous media, found an irreversible cathodic process with two-electron transfer. Later, Lingane and Meites[2] reported that the reduction wave is accompanied by a pre-wave in an unbuffered solution, assumed to be caused by the rate-controlled reduction of VOOH$^+$ formed by the hydrolysis of VO^{2+}. They found that the pre-wave is no longer observed in an oxalate solution, the main-wave being excessively large. They attributed this to a catalytic reduction of hydrogen oxalate ion. Pecsok and Juvet[3] studied the polarographic reduction of vanadyl-versene complex. They attributed the pre-wave to the reduction of $+4$ to $+3$ vanadium, and the main-wave to the reduction of $+3$ to $+2$ vanadium. The pre-wave in both studies was observed in a limited pH range, and in a strongly acidic or alkaline solution it was completely eradicated. Meites and Moros[4] reported on the electrolytic reduction in an acidic solution, and found that the process consumes a much larger quantity of electricity than expected. This so-called induced current was extensively studied by Israel and Meites,[5] who found that the reduction proceeds in two consecutive steps. They analysed the rate-controlled process and induced current, and pointed out the oligomer formation and deprotonation of the reduced species.

In a previous paper[6] the polarographic cathodic process of vanadyl ion in M potassium oxalate was described. It was pointed out that the irreversible cathodic wave with two-electron transfer shows a trend to split into two waves when the vanadyl ion concentration exceeds 4 mM. The linearity of the wave-height *versus* concentration plot was recognized only up to 2 mM, the dependence of the wave-height on the head of mercury showing a characteristic of diffusion control. In order to clarify the above-mentioned anomalous behavior the present authors investigated the electrolytic reduction of vanadyl acetylacetonate in acetonitrile solution. The results obtained by means of conventional and AC polarography, cyclic voltammetry and controlled-potential electrolysis are presented in this paper.

Experimental

The polarographic current-potential curve was recorded on a Shimadzu Model RP-50 polarograph with an ohmic drop compensator. An AC attachment, Model BF-50 was used for AC polarography. Controlled-potential electrolysis was carried out with a Shimadzu Model PS-2 potentiostat and cyclic voltammetry with a Yanaco Electronic Scanner and Hokuto Denko Model HA-104 potentiostat.

The working electrodes used were a dropping mercury electrode(DME) for the polarography, a hanging mercury drop for the cyclic voltammetry and a mercury pool for the controlled-potential electrolysis. The characteristics of DME are as follows; mercury head$=$49 cm, rate of mercury flow$=$0.71 mg/s, life time$=$7.2 s in open circuit. A platinum cylinder with a surface area of 1 cm^2 was used as an auxiliary electrode. The reference electrode was Ag/AgClO$_4$ (0.1 M in acetonitrile).

Vanadyl acetylacetonate (bis(2,4-pentanediono)oxovanadium (IV)), [VO(acac)$_2$], was prepared by the method given by Rowe and Jones,[7] and was recrystallized from a chloroform solution. Acetonitrile (AN) used as a solvent was purified by distillation with phosphorus pentoxide in nitrogen atmosphere.

In order to prevent aerial oxidation, all the solutions of supporting electrolyte and vanadyl acetylacetonate were sufficiently bubbled with purified nitrogen prior to mixing. The prepared solution contained 1 mM vanadyl acetylacetonate, 20 mM acetylacetone (Hacac) and 0.1 M tetraethylammonium perchlorate (TEAP). Purified nitrogen was passed over the solution during the course of electrolysis. The temperature was kept at 20 °C with a water jacket attached to the cell.

Results and Discussion

Polarographic Current-Potential and Current-Time Curves. Vanadyl acetylacetonate usually gives an ill-defined polarographic cathodic wave in an AN solution containing 0.1 M TEAP. When excess Hacac was added to the solution, the wave-form was modified as shown in Fig. 1. A well-defined wave was obtained at least outwardly by adding 20 mM Hacac to 1 mM vanadyl acetylacetonate. Subsequent experiment were carried out under these conditions.

The apparent half-wave potential of the cathodic wave was -2.00 V, the overall electrons transferred per molecule being two. The logarithmic analysis of

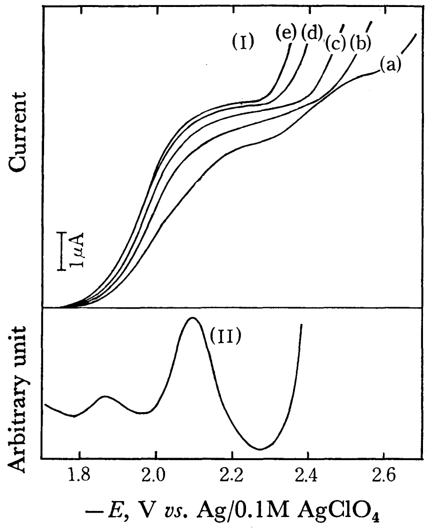

Fig. 1. (I) DC polarograms of 1 mM [$VO(acac)_2$] in AN solution containing 0.1 M TEAP at different concentrations of excess Hacac.
(a) 0, (b) 1 mM, (c) 5 mM, (d) 20 mM, (e) 40 mM Hacac
(II) AC polarogram of the same solution as (I) with 20 mM Hacac (applied sinusoidal voltage=10 mV).

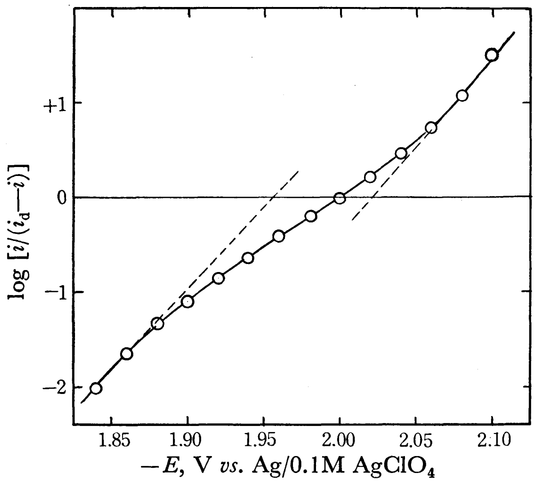

Fig. 2. Logarithmic plot of overall cathodic processes of [$VO(acac)_2$].

the current-potential curve gave a nonlinear plot as shown in Fig. 2. The distorted plot can be divided into three portions, *i.e.*, first and last linear portions and a middle curvilinear portion. The slopes of the first and last portions are 58 and 53 mV, respectively. Both values are approximately equal to the theoretical value of 58 mV for a reversible one-electron transfer process.

The current-time curves during one drop-growth of the DME were recorded at different potentials along the polarographic wave, and the exponent, γ, in $i=kt^{\gamma}$ (i: the current, k: the constant, t: the time) was estimated. In the estimation the rising portion of the i-t curve was omitted because of distortion by the dilution effect. The result is illustrated in Fig. 3.

Vlček[8] classified the varied values of γ as follows:

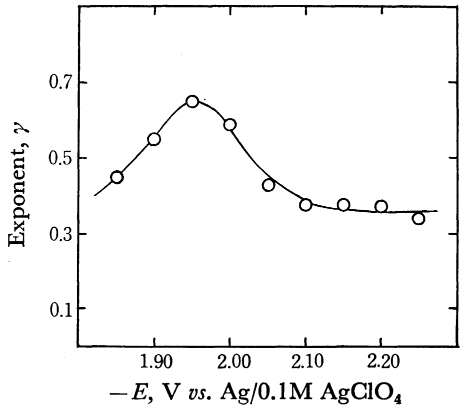

Fig. 3. Variation of exponent, γ, in $i=kt^{\gamma}$ with electrode potential.

(a) $\gamma=0.17-0.2$; diffusion-controlled process
(b) $\gamma=0.67$; reaction-rate control
(c) $\gamma=0.2-0.67$; diffusion and reaction-rate in competition
(d) γ changes with t during a drop-growth from 0.67 to 0.2; irreversible process
(e) γ changes with increasing i/i_l (i_l: the limiting current) or E (E: the applied potential) from $\simeq$0.4 to 0.17 through a maximum; slightly irreversible process

In the present case the value of γ changes with increasing i/i_l from 0.45 at −1.85 V to 0.34 at −2.25 V through a maximum of 0.65 at −1.95 V. In view of the above-mentioned classification the electrode reaction seems to proceed slightly irreversibly in the first step, proceeding thereafter with diffusion and reaction-rate control in competition.

In relation to the irreversible electrode process of VO^{2+} in M HCl solution, Suchomel and Vlček[8] pointed out that the reaction proceeds inherently in two stages as follows:

$$VO^{2+}\,aq \xrightarrow{+e^-} V(H_2O)_6{}^{3+} \xrightarrow{+e^-} V(H_2O)_6{}^{2+}$$

The first step proceeds highly irreversibly and the second one with only a very small overvoltage. No separate waves, corresponding to these two stages, could be observed in the conventional polarogram, but two separate waves appeared (Fig. 1) in the AC polarogram. The first AC peak at −1.85 V is more rounded, showing its irreversible characteristic. The second peak at −2.1 V is rather sharp, reflecting its reversibility. The effect of kinetic currents on an AC polarogram is small compared with the DC polarogram because the reaction time in an AC cycle is small. This supports the fact that the AC polarogram shows distinctly separated peaks.

Controlled-Potential Electrolysis and Cyclic Voltammetry. The controlled-potential electrolysis was carried out in a cell with the anode and cathode compartments separated by a sintered glass disc. By electrolysis at −2.1 V the solution color turned from light-blue (λ_{max} of the optical absorption band=710, 591 and 393 nm) to greenish-yellow. By continuation of electrolysis it turned to dark-green especially in the vicinity of the cathode surface. However, the dark-green color promptly faded to yellow (λ_{max}=275 nm) on being left to stand in nitrogen atmosphere.

A similar trend was observed in the reduction of VO^{2+} with zinc amalgam. In an acidic aqueous solution vanadyl acetylacetonate was reduced easily by zinc amalgam. The color turned from light-blue to purple, showing the formation of V(II) entities. In AN solution, however, the reduction did not proceed markedly, but it proceeded slowly in the presence of excess Hacac. The reduction product was yellow, giving a polarographic cathodic wave at −1.78 V. On being left to stand in the air, no noticeable change was observed in the yellow coloration after a few hours, but the color faded very slowly in a few days.

The current-potential curve obtained *in situ* in the electrolysis cell is shown in Fig. 4. The greenish-yellow solution gave a cathodic wave at −1.78 V and an anodic wave at about −0.45 V. In addition to these waves the dark-green solution gave an unstable anodic wave at −1.70 V, but it could no longer be observed on being left to stand, the coloration of the solution turning to yellow. The yellow solution obtained finally gave a cathodic wave at −1.78 V and an anodic wave at −0.45 V (A similar anodic wave was observed in 20 mM Hacac solution containing 0.1 M TEAP after controlled-potential electrolysis at −2.3 V. For the cathodic process of Hacac in aqueous solution refer to 9).).

The slope of the logarithmic plot of the cathodic wave developed in the yellow solution was about 65 mV, the initial value being 55 mV (Fig. 6). The exponent, γ, of the current-time relationship varies with increase of i/i_l from 0.32 at −1.80 V to 0.34 at −1.85 V, 0.35 at −1.90 V and 0.34 at −2.00 and −2.10 V. These results indicate that the cathodic process is a slightly irreversible one-electron transfer one, coupled with a reaction-rate controlled process.

The cyclic voltammogram of vanadyl acetylacetonate in AN solution is shown in Fig. 5. A sharp cathodic peak and a rounded anodic peak appear in the first cycle of the applied triangular voltage. The cathodic peak potential, E_p^c, was −2.02 V, and the anodic peak potential, E_p^a, was −1.80 V. The difference between E_p^a and E_p^c is noticeable as compared with the theoretical value of $E_p^a - E_p^c = 0.058/n$ V[10,11] for a reversible process at 20 °C. However, in the second and the following cycles a new cathodic peak appeared at −1.85 V, its peak-height gradually increasing in the consecutive cycles of the applied sweep. The new peak corresponds to the anodic peak at −1.80 V. When the scan-rate of the triangular voltage decreased from 50 mV/s to 20 and 10 mV/s, the ratio of the anodic and cathodic peak-heights decreased noticeably, the anodic peak disappearing completely under the scan-rate of 5 mV/s. It seems that the entity, which gives an anodic peak at −1.80 V, is unstable in solution, corresponding to the unstable anodic wave developed by the dark-green solution at −1.70 V. It is concluded that the cathodic peaks at −2.02 and −1.85 V and anodic peak at −1.80 V can be assigned to the cathodic waves at −2.00 and −1.78 V and the anodic wave at −1.70 V, respectively, in the conventional polarography.

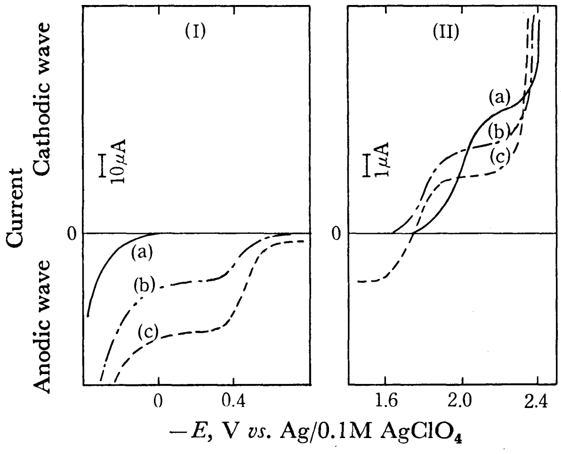

Fig. 4. Polarograms recorded *in situ* in course of controlled-potential electrolysis of [VO(acac)$_2$] in AN solution containing 0.1 M TEAP and 20 mM Hacac at −2.1 V.

(I) Anodic wave, (II) Cathodic wave; (a) 0 hr, (b) 1 hr, (c) 3 hr electrolysis.

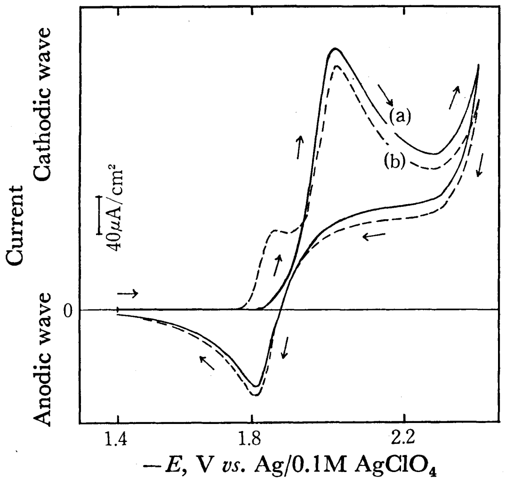

Fig. 5. Cyclic voltammograms of 1 mM [VO(acac)$_2$] in AN solution containing 0.1 M TEAP and 20 mM Hacac.

(a) First cycle of triangular sweep, (b) Second cycle of triangular sweep; scan-rate=50 mV/s.

Reaction Mechanism of Electrode Processes. Vanadyl acetylacetonate is stable and soluble in a large number of solvents without exchange of ligands. Dodge, Templeton and Zalkin[12] reported the composition and structure of anhydrous vanadyl acetylacetonates as five-coordinated complex with VO^{2+} perpendicular to the oxygen base of a square pyramid. The complex presumably retains its VO^{2+} identity in solution forming a distorted octahedral array. The vanadyl oxygen is expected to dominate the electrostatic interactions between the central ion and the ligand by virtue of its close approach to vanadium. The sixth ligand, *trans* to the vanadyl oxygen, is open and can be coordinated by solvent molecules as pointed out by Bernal and Rieger.[13] Ballhausen and Gray[14] investigated the complex by the MO theory, and pointed out the significance of the π-bonding in VO^{2+}. It seems that at least two factors have to be considered in relation to the irreversible electrode process. The predominant factor is the extreme stability of the V–O bond. Since all the orbitals are occupied and the lowest vacant orbitals in a σ-antibonding orbital are of relatively high energy, the strong V–O bond has to be broken and the low-lying orbital must be vacated for the electron transfer. The second minor factor is a structural change of ligands, *i.e.*, a breaking of the V–O bond accompanies the rearrangement of bidentate ligands, (acac$^-$).

Since the kinetic current is reduced to minimum at the plateau potential of the cathodic wave, the diffusion-controlled current for the first electron transfer can be approximated by one half of the overall limiting current. By using this value a logarithmic plot for the first electron transfer process is obtained as shown in Fig. 6. The reversible half-wave potential of the first electron transfer is estimated to be -1.93 V. The reductant by the first electron transfer would necessitate a ligand rearrangement. Accordingly, the middle portion of the cathodic wave is affected by this rearrangement reaction. Once the reaction is over, the following electron transfer would proceed with a close resemblance to the atomic configuration in the environment. However, the internuclear distance should change due to the ionic valency change of the central atom. The cathodic process developed by the yellow solution seems to correspond to this case. The reversible half-wave potential is estimated to be -1.78 V by logarithmic analysis (Fig. 6). It is noteworthy that this process proceeds at a less negative potential by 0.15 V than the first electron transfer. The discrepancy seems to be attributed mainly to the V–O bond strength. Newton and Baker[15] studied the second-order rate law of the reduction of V(IV) species by V(II) species in an aqueous solution. This reaction seems to play the role of the kinetic current in the present case, causing deformation in the middle portion of the cathodic wave. At the plateau of the polarogram the formation of V(II) species dominates, and the V(IV) entity diffusing toward the electrode from the solution bulk will be depleted in the reaction layer by the reaction of V(II) with V(IV). Thus, the last portion of the polarogram is hardly affected at all by the rate-controlled process. Another possible coupled chemical reaction is the oligomer formation of the reduced species as pointed out by Israel and Meites.[5] No convincing evidence for this process, however, was found in the present investigation.

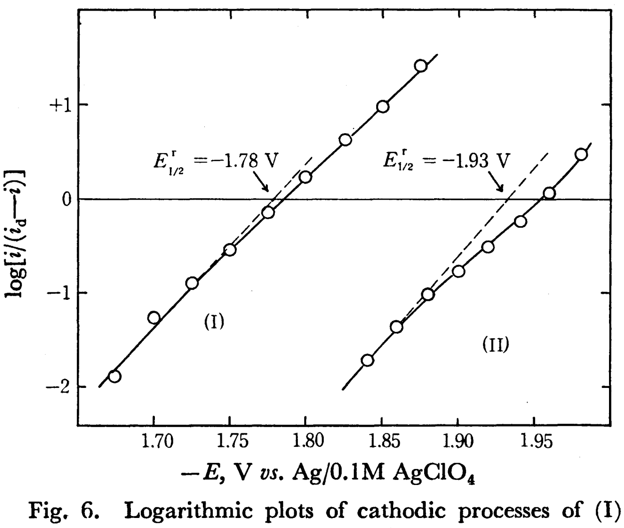

Fig. 6. Logarithmic plots of cathodic processes of (I) $[V(acac)_3]$ and (II) $[VO(acac)_2]$ as assumed to be one-electron transfer process.

The reaction mechanism can be summarized as follows:

(1) The first electron transfer to $[VO(acac)_2]$:

$$[VO(acac)_2] + Hacac + e^- \longrightarrow (V(acac)_2{\cdot}O{\cdot}Hacac^-)^*$$

where * denotes the activated state.

(2) The successive electron transfer to the activated state:

$$(V(acac)_2{\cdot}O{\cdot}Hacac^-)^* + e^- \longrightarrow [V(acac)_3]^- + OH^-$$

(3) The second electron transfer after the ligands rearrangement:

$$[V(acac)_3] + e^- \longrightarrow [V(acac)_3]^-$$

(4) The coupled chemical reactions:

(4-1) the ligands rearrangement:

$$(V(acac)_2{\cdot}O{\cdot}Hacac^-)^* \longrightarrow [V(acac)_3] + OH^-$$

(4-2) A possible following reaction of (4-1):

$$OH^- + Hacac \longrightarrow acac^- + H_2O$$

(4-3) the reduction of V(IV) by V(II):

$$[VO(acac)_2] + [V(acac)_3]^- + Hacac \longrightarrow 2[V(acac)_3] + OH^-$$

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