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The Cation Effect on the Polarographic Reduction of *cis*-Dioxalatodiaquochromate(III) and Trioxalatochromate(III) Ions

By Nobuyuki TANAKA, Eiki ITABASHI* and Reita TAMAMUSHI**

Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho, Sendai

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The cation effect on the polarographic reduction of *cis*-dioxalatodiaquochromate(III) and trioxalatochromate(III) ions has been reported. *cis*-Dioxalatodiaquochromate(III) ions give an irreversible wave corresponding to a three-electron reduction in the solutions of univalent electrolytes, while they give a double wave in the solutions of bivalent electrolytes, the first wave being of a one-electron reduction and the second wave, of a two-electron reduction. Trioxalatochromate(III) ions are reduced to chromium(0) in the univalent and the bivalent electrolyte solutions at more negative potentials than *cis*-dioxalatodiaquochromate(III) ions. The reduction potentials of these complex anions depend on the nature and the concentration of cations of electrolytes present in the solution, and shift to less negative potentials with increasing ionic charges of the cation and, at the constant ionic charge, with decreasing radii of the hydrated ion and increasing concentrations of the cation present. The cation effect was explained by taking into consideration of both the structure of the electrical double layer and the formation of ion-pairs.

In the previous papers[1-3] evidences have been presented that *cis*-dioxalatodiaquochromate(III) ions gave an irreversible wave corresponding to three-electron reduction with a half-wave potential of -1.52 V. vs. SCE in a 0.3 M potassium chloride solution,[1] and that trioxalatochromate(III) ions gave no reduction wave in a 0.1 M solution of tetramethylammonium bromide,[2] but gave a well-defined reduction wave in the solutions of other electrolytes such as potassium chloride or barium chloride.[3] This result seemed to differ from that of Pamfilov and his co-workers,[4] who reported trioxalatochromate(III) ions gave two irreversible waves with the half-wave potentials of -1.315 and -1.450 V. vs. NHE in a 1.0 N potassium chloride solution.

In the present paper are reported the detailed results of the effects of the nature and the concentration of supporting electrolytes on the polarographic reduction of *cis*-dioxalatodiaquochromate(III) and trioxalatochromate(III) ions. The cation effect is discussed on the basis of the formation of ion-pairs and the change in the structure of the electrical double layer.

Experimental

Current-potential curves were recorded with a pen-recording polarograph, a Yanagimoto Galvarecorder Model PR-2 with an automatic potential scanner. A Yanagimoto Y-GR 2 Galvarecorder was used for recording alternating current (a.c.) polarograms. Kalousek polarograms were recorded with the same circuit as has been described previously.[5] To determine the integral capacity in the double layer, the capacitance was measured using the same circuit as given in the previous report.[6]

The dropping mercury electrode had an m value of 1.84_7 mg./sec., and a drop time, t_d, of 3.1 sec. being measured in an air-free 1 M potassium chloride solution containing 0.005% galatin at -1.70 V. vs. SCE at 45 cm. of the mercury reservoir.

The cell equipment was the same as has been reported previously.[7] The potentials were referred to a saturated calomel electrode (SCE). The dissolved oxygen in the solution was removed by bubbling pure nitrogen gas through the solution. All measurements were carried out in a thermostat of 25.0°C. All current-potential curves presented in this paper are corrected for the residual current and the ohmic drop (iR) across the electrolysis cell.

Potassium *cis*-dioxalatodiaquochromate(III)[8] and potassium trioxalatochromate(III)[9] were prepared with the procedures given in the literatures. All other chemicals used were of a guaranteed reagent grade. In the case of lithium chloride, it was dissolved in redistilled water, a small amount of insoluble substance was

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* Present address: Department of Chemistry, Faculty of Science, Osaka University Toyonaka, Osaka.

** Present address: The Institute of Physical and Chemical Research, Komagome, Bunkyo-ku, Tokyo.

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removed by decantation and pH of the solution was adjusted to about 7.0 by adding hydrochloric acid. Redistilled water was used to prepare the cell solution.

Results

The current-potential curves of *cis*-dioxalatodiaquochromate(III) and trioxalatochromate(III) ions were obtained in the solutions of various supporting electrolytes and at various concentrations of the electrolytes in the presence of 0.005% gelatin added as a maximum suppressor. The typical current-potential curves of *cis*-dioxalatodiaquochromate(III) ions are given in Figs. 1 and 2. Figure 1 shows the current-potential curves obtained in the solutions of univalent electrolytes. The limiting current was found to be diffusion-controlled and proportional to the concentration of the complex ions. The current-potential curves obtained in the bivalent electrolyte solutions are reproduced in Fig. 2. In a solution of strontium chloride or barium chloride, especially, the wave was found to split into two steps; the first wave was observed in the potential range from −1.2 to −1.45 V. vs. SCE, which was not observed in the univalent electrolyte solutions. The limiting currents of both the first and the second wave are diffusion-controlled and proportional to the concentration of the complex ions. The gradual increase in the current was observed in the bivalent electrolyte solutions at more negative potentials than −1.75 V. vs. SCE. A maximum was observed at the potentials of the limiting current plateau when the measurement was made in a barium chloride solution, and the height of the maximum increases with increasing concentrations of barium chloride. The maximum was not suppressed by the addition of relatively high concentrations of gelatin, but suppressed by the addition of a small amount of hydrogen ion.

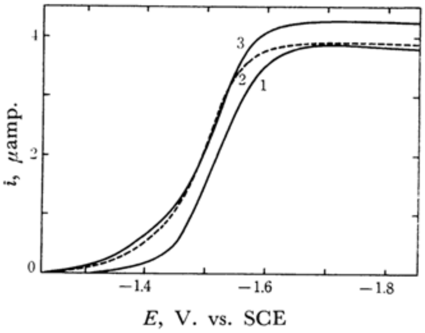

Fig. 1. Current-potential curves of 0.5 mM *cis*-dioxalatodiaquochromate(III) ions in the univalent electrolyte solutions containing 0.005% gelatin: (1) 1.0 M LiCl, (2) 1.0 M NaCl, (3) 1.0 M KCl.

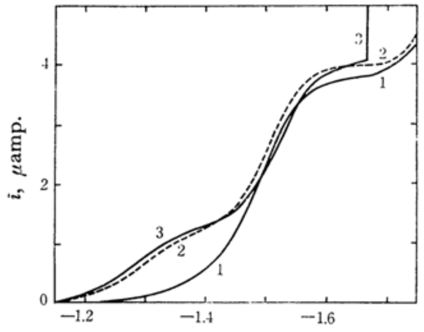

Fig. 2. Current-potential curves of 0.5 mM *cis*-dioxalatodiaquochromate(III) ions in the bivalent electrolyte solutions containing 0.005% gelatin: (1) 0.5 M $MgCl_2$, (2) 0.5 M $SrCl_2$, (3) 0.5 M $BaCl_2$.

The diffusion current constants and the reduction potentials at $\bar{i}=\bar{i}_l/6$ and $\bar{i}=2\bar{i}_l/3$ on the reduction of *cis*-dioxalatodiaquochromate(III) ions which were obtained in the solutions of various electrolytes and at various concentrations of the electrolytes in the presence of 0.005% gelatin are given in Table I. The half-wave potential was not used because of the irregular shapes of the waves.

TABLE I. DIFFUSION CURRENT CONSTANTS AND REDUCTION POTENTIALS OE *cis*-DIOXALATODIAQUOCHROMATE(III) IONS OBTAINED IN VARIOUS ELECTROLYTE SOLUTIONS CONTAINING 0.005% GELATIN

Electrolyte soluiton	$I_{obs.}$*	$I_{corr.}$*	$E_{1/6}$** V. vs. SCE	$E_{2/3}$** V. vs. SCE
1.0 M LiCl	4.26	4.47	−1.46	−1.54
1.0 M NaCl	4.24	4.41	−1.41	−1.52
0.1 M KCl	4.30	4.30	−1.47	−1.55
0.5 M KCl	4.58	4.59	−1.44	−1.53
1.0 M KCl	4.61	4.60	-1.40_5	−1.52
2.0 M KCl	4.58	4.58	−1.38	−1.53
0.5 M $MgCl_2$	4.15	4.55	−1.41	−1.51
0.1 M $SrCl_2$	4.63	4.68	−1.35	−1.51
0.3 M $SrCl_2$	4.48	4.66	−1.32	−1.51
0.5 M $SrCl_2$	4.37	4.63	−1.30	−1.51
0.5 M $BaCl_2$	4.35	4.61	−1.29	−1.52

* $I_{obs.}$ and $I_{corr.}$ represent the obserbed diffusion current constant and the diffusion current constant corrected for the relative viscosity of the electrolyte solutions, respectively.

** $E_{1/6}$ and $E_{2/3}$ represent the reduction potentials at $\bar{i}=\bar{i}_l/6$ and $\bar{i}=2\bar{i}_l/3$, respectively.

Figure 3 shows the current-potential curves of trioxalatochromate(III) ions obtained in 1.0 M solutions of univalent electrolytes containing 0.005 % gelatin. The typical current-potential curves obtained in 1.0 M solutions of bivalent electrolytes containing 0.005% gelatin are reproduced in Fig. 4.

The limiting current was found to be diffusion-controlled and proportional to the concentration of trioxalatochromate(III) ions. The overall

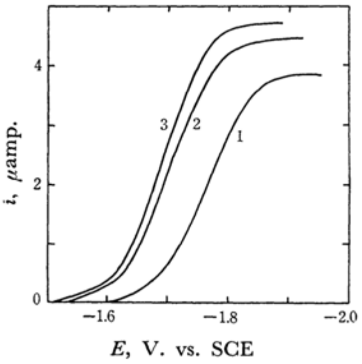

Fig. 3. Current-potential curves of 0.5 mM trioxalatochromate(III) ions in the univalent electrolyte solutions containing 0.005% gelatin: (1) 1.0 M LiCl, (2) 1.0 M NaCl, (3) 1.0 M KCl.

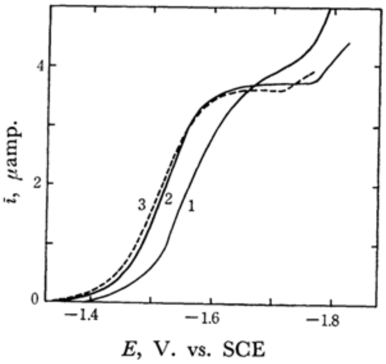

Fig. 4. Current-potential curves of 0.5 mM trioxalatochromate(III) ions in the bivalent electrolyte solutions containing 0.005% gelatin: (1) 1.0 M $MgCl_2$, (2) 1.0 M $SrCl_2$, (3) 1.0 M $BaCl_2$.

TABLE II. DIFFUSION CURRENT CONSTANTS AND HALF-WAVE POTENTIALS OF TRIOXALATOCHROMATE(III) IONS OBTAINED IN VARIOUS ELECTROLYTE SOLUTIONS CONTAINING 0.005% GELATIN

Electrolyte solution	$I_{obs.}$	$I_{corr.}$	$E_{1/2}$ V. vs. SCE	Reciprocal slope of log-plot, mV.
1.0 M LiCl	4.34	4.48	−1.76	85
1.0 M NaCl	4.93	5.16	−1.70	85
0.1 M KCl	4.97	4.97	−1.83	90
0.3 M KCl	5.07	5.07	−1.76	87
1.0 M KCl	5.19	5.17	-1.68_5	85
3.0 M KCl	5.07	5.14	−1.64	80
1.0 M $MgCl_2$	4.25	4.80	−1.56	—
1.0 M $SrCl_2$	4.11	4.59	-1.51_5	75
0.1 M $BaCl_2$	4.69	4.73	−1.55	70
0.3 M $BaCl_2$	4.42	4.57	−1.53	69
1.0 M $BaCl_2$	4.04	4.56	-1.50_5	72

electrode process was considered to be of a three-electron reduction of chromium(III) to chromium(0), being compared with the reduction wave of *cis*-dioxalatodiaquochromate(III) ions previously reported.[1] The relation between E and $\log \bar{i}/(\bar{i}_l-\bar{i})$, Kalousek polarograms and a. c. polarograms indicated the electrode processes of trioxalatochromate(III) ions to be irreversible.

Table II shows the diffusion current constants, the half-wave potentials and the reciprocal slopes of log-plots obtained in the solutions of various supporting electrolytes and at various concentrations of the electrolytes.

Discussion

The polarographic reduction of *cis*-dioxalatodiaquochromate(III) and trioxalatochromate(III) ions was affected by the nature and the concentration of the cation of electrolyte present in the solution.

The reduction of *cis*-dioxalatodiaquochromate(III) ions at the DME in the solutions of univalent electrolytes proceeds irreversibly according to the equation,

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- + 3e \rightarrow Cr(0) + 2\ ox^{2-} + 2H_2O$$

In the solutions of bivalent electrolytes, on the other hand, two waves are observed as mentioned above. The electrode processes of these waves are considered as follows:

The first wave is of a one-electron reduction corresponding to the reaction,

$$cis\text{-}[Cr(ox)_2(H_2O)_2]^- + 2pH_2O + e \rightarrow [Cr(ox)_{2-p}(H_2O)_{2p+2}]^{(2-2p)-} + p\ ox^{2-}$$

The second wave is of a two-electron reduction, which proceeds as,

$$cis\text{-}[Cr(ox)_{2-p}(H_2O)_{2p+2}]^{(2-2p)-} + 2e \rightarrow Cr(0) + (2-p)ox^{2-} + (2p+2)H_2O$$

In the case of trioxalatochromate(III) ions, an irreversible wave corresponding to the reduction from chromium(III) to chromium(0) was found to appear at more negative potentials than those of *cis*-dioxalatodiaquochromate(III) ions in the solutions of both univalent and bivalent electrolytes. The result seems to contradict the result obtained by Pamfilov and his co-workers.[4]

The shifts of the reduction potential and the changes in the diffusion current constants given in Tables I and II indicate that the effect of the cations of electrolytes on the reduction potentials increases with the increase in the ionic charge, and at constant ionic charge, with the increase in the radius of the hydrated cation and the increase in the concentration of the electrolytes present in the solution. These facts may be explained by taking into account of both the structure of the electrical double layer and the formation of ion-pairs.[10-12]

Since both *cis*-dioxalatodiaquochromate(III) and trioxalatochromate(III) ions are reduced at the negative side of electrocapillary maximum, the reduction of these complex anions are more difficult at lower concentrations of electrolytes because of greater electrostatic repulsion between the electrode surface and the electroactive complex anions. Trioxalatochromate(III) ions gave actually no reduction wave at lower concentrations of the univalent electrolytes in the solution.

If the potential difference across the diffuse double layer is decreased with increasing concentrations of electrolyte or by changing the nature of the cation of electrolyte, the electrostatic repulsion, which hinders the approach of the electroactive complex anions to the electrode surface, decreases so that the surface concentration of the complex anions increases. This and an increase in the effective potential difference in the Helmholtz double layer facilitate the reduction of the complex anions, as pointed out by Vlček[13] on the reduction of hexacyanocobaltate(III) ions. He reported that the reduction potential of hexacyanocobaltate(III) ions at the DME shifted to less negative potentials with increasing concentrations of potassium chloride and increasing radii of the univalent cation in the solution.

The shifts of the half-wave potential, $\Delta E_{1/2}$, with the change in the concentration of electrolyte is approximately given by the relationship,[14,15]

$$\Delta E_{1/2}=\frac{\alpha n_a - z_0}{\alpha n_a}\Delta(\phi_H-\phi_S)_{1/2} \qquad (1)$$

where α is the transfer coefficient, n_a the number of electron involved in the electron-transfer process, z_0 the valency, with sign, of the reducible species and $\Delta(\phi_H-\phi_S)_{1/2}$ the change in the potential difference across the diffuse double layer at the half-wave potential of the reduction wave.

The relation between the electrode potential, E, and the value of $(\phi_H-\phi_S)$ can be calculated on the basis of the classical Gouy-Chapmann theory for the z-z type electrolyte,

$$K_i[(E-E_z)-(\phi_H-\phi_S)]=\left(\frac{2\boldsymbol{R}T\varepsilon C_t}{\pi}\right)^{1/2}\sinh\left\{\frac{|z|\boldsymbol{F}(\phi_H-\phi_S)}{2\boldsymbol{R}T}\right\} \qquad (2)$$

where K_i is the integral capacity of the Helmholtz double layer, E_z the potential at zero charge of the electrode, ε the dielectric constant, C_t the bulk concentration of ions with valence z.

In the calculation of Eq. 2, E_z and K_i which were determined from the electrocapillary curve and the capacitance measurements, respectively. The value of αn_a in Eq. 1 was obtained from the plot of E vs. $\log \bar{i}/(\bar{i}_d-\bar{i})$. The values of E_z and K_i obtained at varied concentrations of potassium chloride are given in Table III.

TABLE III. THE POTENTIAL OF ZERO CHARGE OF THE ELECTRODE (E_z) AND THE INTEGRAL CAPACITY IN THE HELMHOLTZ DOUBLE LAYER (K_i) OBTAINED AT VARIED CONCENTRATIONS OF POTASSIUM CHLORIDE

Concn. of KCl in the solution* M	E_z V. vs. SCE	K_i μF/cm^2
0.1	-0.510	16.7_4
0.3	-0.51_5	18.0_5
1.0	-0.52_0	19.3_3
2.0	-0.55_0	20.4_8
3.0	-0.60_0	20.7_5

* All solutions contain 0.005% gelatin.

Equation 1 was not able to apply to the electrode process of *cis*-dioxalatodiaquochromate(III) ions because no straight line was obtained in the log-plot analysis.

The experimental and the calculated values for the shift of the half-wave potential on the reduction of 0.5 mM trioxalatochromate(III) ions with varied amounts of potassium chloride are given in Table IV. The calculation was made with three different values of the valency of the complex anion participating in the electron-transfer process. Table IV shows that the experimental shifts of the half-wave potential agree to the calculated ones which were obtained with $z_0=-1$. This suggests that the species which is involved in the electron-transfer process is probably a $K_2[Cr(ox)_3]^-$ ion.

The concentration of the species, $K_2[Cr(ox)_3]^-$, in the bulk of the solution is estimated to be much smaller than that of the species, $K[Cr(ox)_3]^{2-}$, from the calculation with the association constants of these ion-pairs. Consequently, it is presumed that the species, $K_2[Cr(ox)_3]^-$ is present predominantly only at the electrode surface, and that one of the potassium ions of $K_2[Cr(ox)_3]^-$ plays a role of bridging the electrode surface and the electroactive species at the electron-transfer process. The formation of ion-pairs lessens the ionic charge of trioxalatochromate(III) ions, so that it facilitates their approach to the electrode surface. The electrode process for the reduction of trioxalatochromate(III) ions, therefore, may be written as follows:

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TABLE IV. EXPERIMENTAL AND CALCULATED SHIFTS OF THE HALF-WAVE POTENTIAL FOR THE REDUCTION OF 0.5 mM TRIOXALATOCHROMATE(III) IONS IN THE SOLUTIONS OF VARIOUS CONCENTRATIONS OF POTASSIUM CHLORIDE CONTAINING 0.005% GELATIN

Concn. of KCl, M	$E_{1/2}$ V. vs. SCE	$\Delta E_{1/2\text{obs.}}$ V.	$(\phi_H-\phi_S)_{1/2}$ V.	$\Delta E_{1/2\text{calc.}}$, V.		
				$z_O=-3$	$z_O=-2$	$z_O=-1$
0.1	-1.83	—	-0.12_2	—	—	—
0.3	-1.76	0.07	-0.09_7	0.13_3	0.09_7	0.06_1
0.5	-1.73	0.10	-0.08_6	0.19_2	0.14_0	0.08_8
1.0	-1.68_5	0.14_5	-0.06_8	0.28_7	0.20_9	0.13_1
2.0	-1.65	0.18	-0.05_5	0.35_6	0.25_9	0.16_3
3.0	-1.64	0.19	-0.04_5	0.40_9	0.29_8	0.18_8

$$\mathrm{K[Cr(ox)_3]^{2-} + K^+ \rightleftharpoons K_2[Cr(ox)_3]^-}$$

$$\mathrm{K_2[Cr(ox)_3]^- + 3e \longrightarrow Cr(0) + 3ox^{2-} + 2K^+}$$

In conclusion, it may be said that the reduction processes of *cis*-dioxalatodiaquochromate(III) and trioxalatochromate(III) ions depend on the nature and the concentration of the cation of the electrolyte in the solution and that this cation effect may be understood by the consideration of the formation of ion-pairs as well as the change in the electrical double layer.

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