The Cation Effect on the Polarographic Reduction of Trioxalatochromate(III) Ions

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Recently, Pamfilov, Lopushans'ka and Zueva reported that trioxalatochromate(III) ($[Cr\cdot(ox)_3]^{3-}$) ions gave two irreversible polarographic waves, with half-wave potentials of -1.315 and -1.450 V. vs. NHE, in a 1.0 N potassium chloride solution.[1] This seemed to contradict our previous statement that $[Cr\cdot(ox)_3]^{3-}$ ions gave no reduction wave in a 0.1 M solution of tetramethylammonium bromide.[2] Therefore, the reduction of $[Cr(ox)_3]^{3-}$ ions has been investigated again; a marked cation effect on the half-wave potential and the limiting current of the wave has thus been revealed.

Typical one-step irreversible waves were obtained in various supporting electrolyte solutions. The limitting current was found to be diffusion-controlled and proportional to the concentration of the complex ions. The overall electrode process was considered to be of a three-electron reduction of chromium(III) to chromium(0), (cf. the reduction wave of cis-$[Cr(ox)_2(H_2O)_2]^-$).[3] The half-wave potentials obtained are given in Table I; they clearly indicate that the reduction potentials of $[Cr(ox)_3]^{3-}$ ions depend on the nature and the concentration of the cations present. The half-wave potentials shift to less negative potentials with the increasing ionic charge of the cation and, at the constant ionic charge, with the decreasing radius of the hydrated ion and the increasing concentration of the cations present. The diffusion current constants were also found to be dependent on the nature and the concentration of the cations present.

TABLE I. THE HALF-WAVE POTENTIALS OF THE POLAROGRAPHIC WAVES OF $[Cr(ox)_3]^{3-}$ IONS OBTAINED IN VARIOUS SUPPORTING ELECTROLYTE SOLUTIONS AT 25°C

Electrolyte soln.	$E_{1/2}$ V. vs. SCE
0.1 M $(CH_3)_4NBr$	—
1.0 M LiCl	-1.76
1.0 M NaCl	-1.70
0.1 M KCl	-1.83
0.3 M KCl	-1.76
1.0 M KCl	-1.68_5
3.0 M KCl	-1.64
1.0 M $MgCl_2$	-1.56
1.0 M $SrCl_2$	-1.51_5
1.0 M $BaCl_2$	-1.51

These facts may be explained by taking into account both the double-layer effect and the formation of ion-pairs.[4,5] The $[Cr(ox)_3]^{3-}$ ions are reduced at the negative side of the electrocapillary maximum. If the potential difference across the diffuse double layer decreases with the increasing concentration of electrolytes or by changing the nature of the cation of electrolyte in the solution, the electrostatic hindrance between the electrode and the $[Cr(ox)_3]^{3-}$ ions decreases and, consequently, the surface concentration of the complex anions increases. This and an increase in the effective potential difference in the Helmholtz layer accelerate the reduction of $[Cr(ox)_3]^{3-}$ ions, which therefore takes place at less negative potentials. The formation of ion-pairs, which is to be expected from the change in the diffusion current constant, lessens the total ionic charge of electroactive species and, consequently, facilitates the approach of $[Cr(ox)_3]^{3-}$ anions to the electrode surface.

These results lead to the conclusion that the $[Cr(ox)_3]^{3-}$ ions are reduced to give a one-step polarographic wave provided the electrostatic hindrance between the electrode and the complex ions is decreased by the change in the structure of the double layer and by the formation of the ion-pairs.

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