The Dual Effect of a Surface-active Substance on the Polarographic Electron-transfer Process

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The deceleration and the acceleration of the polarographic electron-transfer process by the adsorption of a surface-active substance have been studied in connection with the heterogeneous reaction mechanisms at the electrode surface[1-3]. Frumkin and his co-workers reported the dual effect of a surface-active substance on the reduction of $PtCl_4^{2-}$ ions; the $(C_5H_{11})_4N^+$ ion accelerates the reduction at its lower concentration and decelerates at its higher concentration[4].

In the course of our study of the polarographic reduction of manganese(III) in an alkaline tartrate solution, we found a remarkable deceleration and acceleration of the electron-transfer process upon the addition of trimethyloctadecylammonium chloride, $(CH_3)_3$-$(C_{18}H_{37})N^+Cl^-$, (TMOAC). An alkaline tartrate solution of manganese(III), which was obtained by air oxidation of that of manganese(II), gave the peculiar polarogram shown in Fig. 1 (curve 1)[5]. Current-potential curves obtained at various concentrations of TMOAC in alkaline tartrate solutions of pH 11.8 (Fig. 1) indicate that the addition of a small concentration of TMOAC depresses both the first round-shape and the second drawn-out wave, and that, at a higher concentration of TMOAC, the first wave was further depressed but the second, considerably improved. The dual (deceleration and acceleration) effect of a surface-active substance which is of a different type from that reported by Frumkin et al. is more clearly demonstrated by the current-time curves during the life of a mercury drop that were obtained at −0.82 V. vs. S. C. E. at varied concentrations of TMOAC (Fig. 2). In Fig. 2, curve 3 shows that the acceleration of the electron-transfer is controlled by the rate of adsorption of the surface-active cations.

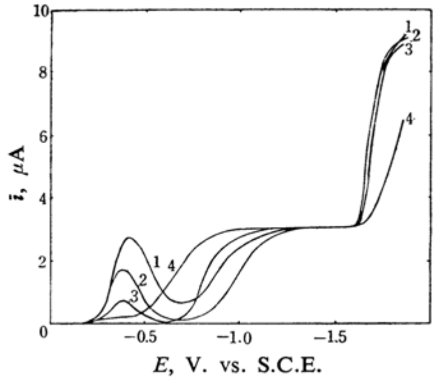

Fig. 1. Current-potential curves of Mn(III) in Britton-Robinson buffer of pH 11.8 containing 0.25 M sodium tartrate in the absence (curve 1) and in the presence of 0.13 mM (2), 0.25 mM (3), and 1.2 mM (4) trimethyloctadecylammonium chloride.

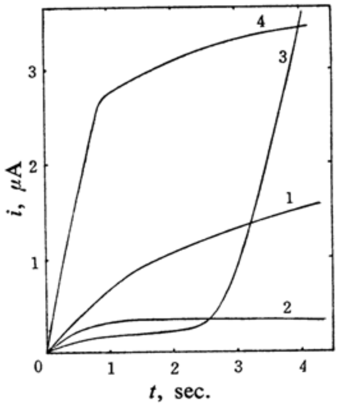

Fig. 2. Current-time curves at −0.82 V. vs. S.C.E. obtained with the same solutions as given in Fig. 1.

Manganese(III) is considered to form negatively-charged hydroxotartrato complexes in an alkaline tartrate solution. The adsorption of a sufficient amount of surface active cations, therefore, apparently lessens the repulsive interaction between the negatively-charged electrode and the electroactive anions, accelerating the electron transfer.

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[2] R. Tamamushi, T. Takeuchi and N. Tanaka, 18th International Congress of Pure and Applied Chemistry, Montreal, Canada (1961), No. B3-39.

[3] N. Tanaka and R. Tamamushi, 1st Australian Conference on Electrochemistry, Sydney and Hobart (1963).

[4] A. N. Frumkin, O. A. Petrii and N. V. Nikolaeva-Fedorovich, *Doklady Akad. Nauk S. S. S. R.*, **136**, 1158 (1961).

[5] The details of this study will be published elsewhere.