CHEMISTRY LETTERS, pp. 1599-1600, 1982.

TAST POLAROGRAPHY OF OXOBIS(2,4-PENTANEDIONATO)VANADIUM(IV) IN AQUEOUS SOLUTIONS BY USING RAPIDLY DISLODGED MERCURY ELECTRODE

Nobuyuki TANAKA,* Yoshikiyo KATO, Shigeru SUZUKI, and Akifumi YAMADA+
Department of Chemistry, Faculty of Science,
Tohoku University, Sendai 980
+Faculty of Engineering, Technological
University of Nagaoka, Nagaoka 949-54

The tast polarography of $[VO(acac)_2]$ in aqueous solutions has been studied. Two well-defined separate waves of equal heights were obtained at a drop time of 0.5 s and a complex concentration of 0.23 mmol dm^{-3}. The ill-defined polarograms of $[VO(acac)_2]$ in aqueous solutions were interpreted by the adsorption of some vanadium species produced by electrolysis at the surface of electrode.

Electrochemical studies of vanadium chelates of high oxidation states have started on the basis of biological interest.[1,2)] The electrochemistry of oxobis(2,4-pentanedionato)vanadium(IV) ($[VO(acac)_2]$) is an extension of these studies.[2-6)] However, most of efforts on studying electrochemical properties were made in non-aqueous solvents because polarograms are ill-defined in aqueous solutions.[7)] Recently, it was found that the shape of the polarogram of $[VO(acac)_2]$ in aqueous solutions is strongly dependent on the dislodge interval of mercury drop and is also dependent on the bulk concentration of the complex.

$[VO(acac)_2]$ gives well-defined polarograms at a short drop time and a low complex concentration. Figure 1 shows examples of well-defined and ill-defined tast polarograms. Two separate waves of equal heights were obtained at a drop time of 0.5 s and a complex concentration of 0.23 mmol dm^{-3}. The corresponding current-time (i-t) curves during the life of a mercury drop are shown in Fig. 2. The i-t curve obtained under the same conditions as given in Fig. 1-b shows that the reduction of $[VO(acac)_2]$ was inhibited as the electrolysis proceeded during the life of a

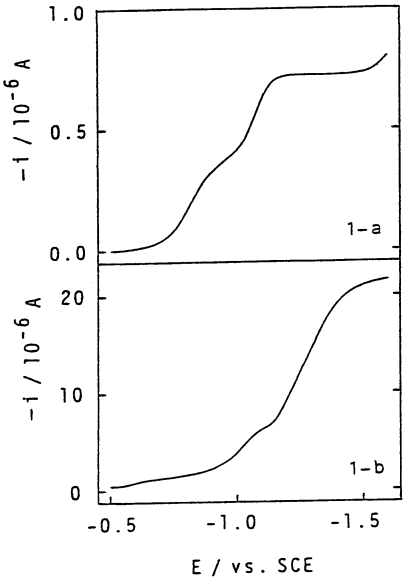

Fig. 1 Typical well-defined and ill-defined tast polarograms of [VO(acac)$_2$] in 0.1 mol dm^{-3} NaClO$_4$ containing 0.1 mol dm^{-3} AcOH-AcONa (pH 6.3) and 5 x 10^{-3} % gelatine at 25 $^{\circ}$C.
1-a: 0.23 mmol dm^{-3} [VO(acac)$_2$], t_d = 0.5 s
1-b: 4.97 mmol dm^{-3} [VO(acac)$_2$], t_d = 2.0 s

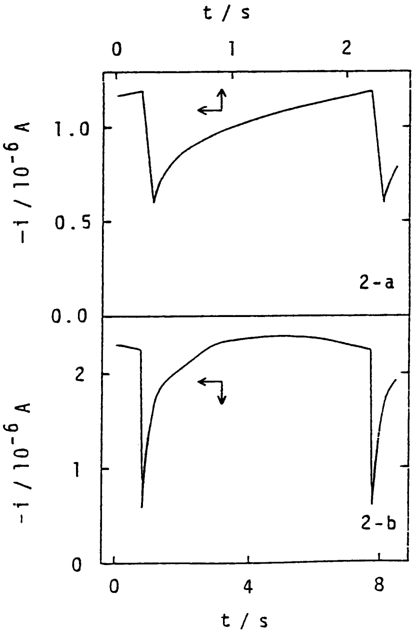

Fig. 2 Current-time curves during the life of a mercury drop measured under the same conditions as given in Figs. 1-a and 1-b.
2-a: at -0.95 V vs. SCE
2-b: at -0.70 V vs. SCE

mercury drop. These observations show that the electrode reaction of [VO(acac)$_2$] in aqueous solutions involves an auto-inhibition process attributable to some reduced vanadium species adsorbed at the electrode surface. The half wave potentials of two well-defined separate waves were found to be -0.812 and -1.072 V vs. SCE.

The two limiting currents of the well-defined polarogram were confirmed to be diffusion-controlled by the analysis of current-time curves during the life of a mercury drop. The electrode reaction was considered to be two conseqtive one-electron reduction processes from the magnitude of diffusion currents. The diffusion coefficient of [VO(acac)$_2$] was 4 x 10^{-6} cm^{2}s^{-1}.

References

1) I. G. Macara, Trends Biochem. Sci., 5, 92 (1980).
2) M. Asrinawi and T. L. Riechel, Inorg. Chem., 20, 1974 (1981).
3) M. Kitamura, K. Yamashita, and H. Imai, Bull. Chem. Soc. Jpn., 49, 97 (1976).
4) M. Kitamura, K. Yamashita, and H. Imai, Chem. Lett., 1975, 1071.
5) M. Kitamura, K. Sasaki, and H. Imai, Bull. Chem. Soc. Jpn., 50, 3199 (1977).
6) G. Gritzner, H. Murauer, and V. Gutmann, J. Electroanal. Chem., 101, 177 (1979).
7) M. Kitamura, Y. Niwa, A. Kitani, and N. Watanabe, Denki Kagaku, 46, 59 (1978).

(Received July 29, 1982)