*Effect of Surface Active Reagents on Electrode Process in Oscillographic Polarography**

By Hideo IMAI and Shōkichi CHAKI

(Received February 7, 1956)

The effect of a surface active reagent on a polarographic reduction has been investigated from two points of view, one of which is the suppression of a maximum wave and the other is the retardation of an electron transfer process. Delahay[1], Randles[2], Gierst and Juliard[3], Heyrovský[4], and others studied the latter phenomenon, and from their experimental results Frumkin[5] proposed the "sieve" theory and Heyrovský suggested a mechanism with respect to the dismutation or disproportionation process of polyvalent cations. On the other hand, Loshkarev and Kryukova[6] observed that in solutions of 6 N-H_2SO_4 containing Ag^+ or Tl^+ ions their electrodeposition was hindered by surface active materials. More recently, Tamamushi[7] pointed out the similar effect on monovalent Tl^+.

An investigation of the same phenomenon has been carried out by one of the present authors[8]. The result of the more detailed investigation is presented in this report.

Experimental

A Ševčik type oscillographic polarograph was employed. The apparatus and the method of measurement were described in the previous report[9]. The details of the experimental conditions are as follows: the rate of variation of the applied voltage $(v)=40$ V./s. (in the case of gelatine solution), 50 V./s. (in the case of methyl cellulose solution); sweep frequency $=20$ c. p. s.; mercury head $=40$ cm.; the rate of mercury flow $=1.94_4$ mg./s.; the life time of the dropping mercury electrode (D. M. E.) $=3.1$–3.8 ± 0.02 sec.; the current measuring resistor (Rm) $=30$–$70\ \Omega$; temp. $=30\pm0.1$°C.

From reagent grade chemicals was prepared the test solution of a constant concentration of 0.5 mol./l. Tl^+, Cd^{++} or Zn^{++}, and each test solution contained 1 mol./l. KBr, KCl, KNO_3 or Na_2SO_4 as the supporting electrolyte and 0.002–0.01% gelatine (G.) or methyl cellulose (M.C.), respectively.

Purified nitrogen was used to remove the dissolved oxigen of the test solution prior to taking a polarogram.

Results and Discussion

The current-potential oscillograms are exemplified in Figs. 1 and 2 in the cases of Tl^+ in mol./l. KCl and Na_2SO_4 containing 0–0.01% M. C., respectively. From these polarograms the maximal peak current, i. e. the current at the maximum life time of the D. M. E., is plotted against the concentration of G. or M. C. as illustrated in Figs. 3, 4 and 5.

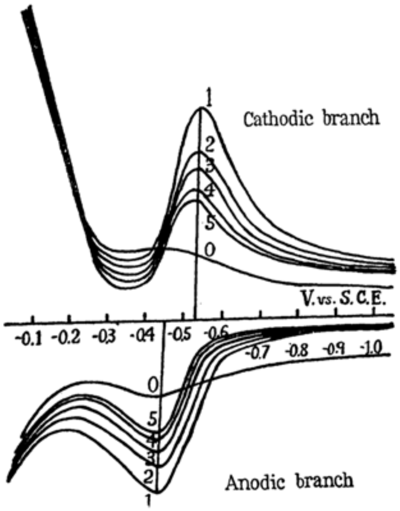

Fig. 1. Maximal peak current-potential oscillogram of 0.5 mM/l. Tl^+ in M KCl: Curve 1; 0% M.C., Curve 2; 0.002%, Curve 3; 0.005%, Curve 4; 0.008%, Curve 5; 0.01%, Curve 0; charging current. $R_m=40\ \Omega$, $t=3.1_4$ sec.

---

* Presented at the discussion on polarography held by the Chemical Society of Japan, the Electrochemical Society or Japan and the Japan Society for Analytical Chemistry in November, 1955.

1) P. Delahay, *J. Phys. Colloid Chem.*, **53**, 1279 (1949).

2) J. E. B. Randles, *Discs. Faraday Soc.*, **1**, 11 (1947).

3) R. Gierst and A. L. Juliard, *J. Phys. Chem.*, **57**, 70 (1953).

4) J. Heyrovský, *Collection Czechoslov. Chem. Communs.*, **19**, S. 58 (1954).

5) A. H. Frumkin, *Discs. Faraday Soc.*, **1**, 224 (1947), *Dokl. Akad. Nauk S.S.S.R.*, **85**, 373 (1952).

6) M. A. Loshkarev and A. A. Kryukova, *Dokl. Akad. Nauk S.S.S.R.*, **62**, 97 (1948).

7) R. Tamamushi, *Polarography*, **3**, 56 (1955); R. Tamamushi and T. Yamanaka, This Bulletin, **28**, 673 (1955).

8) M. Shinagawa and H. Imai, *J. Electrochem. Soc. Japan*, **23**, 187 (1955). Presented at the discussion on analytical chemistry held by the Chemical Society of Japan in November, 1953.

9) H. Imai, This Bulletin, **29**, 276 (1956).

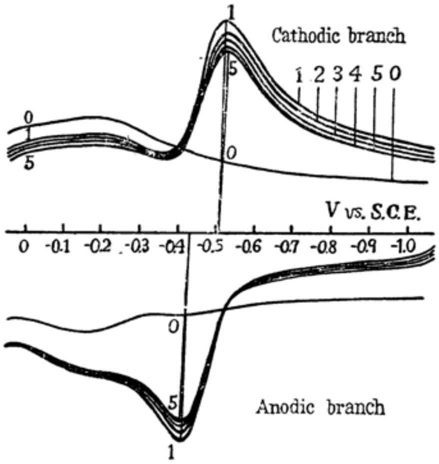

Fig. 2. Maximal peak current-potential oscillogram of 0.5 mM/l. Tl^+ in M Na_2SO_4: The curve numbers correspond to those of Fig. 1. $R_m = 70\ \Omega$, $t = 3.3_0$ sec.

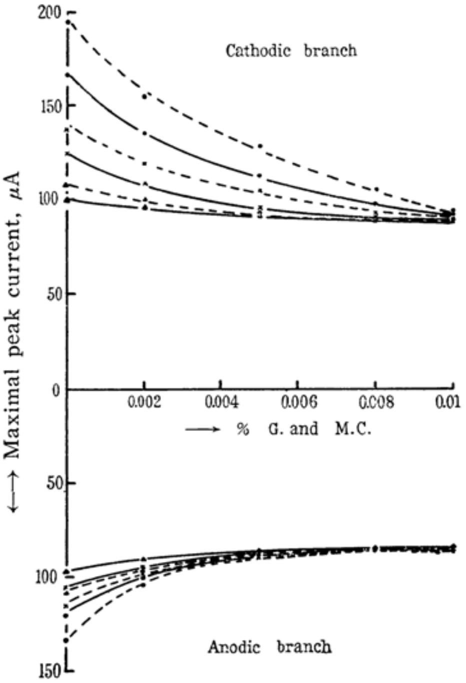

Fig. 3. Variation of the maximal peak current of 0.5 mM/l. Tl^+ with the concentration of G. or M. C.: G.; full curve, M. C.; interrupted curve. G: full curve, M.C: interrupted curve, -●- Cl^-, -×- NO_3^- -▲- SO_4^{--}.

In Fig. 4 it is evident that the cathodic peak current of the solution containing no surface active reagent increases in the solution of SO_4^{--}, NO_3^-, Cl^-, Br^- in the order given. This trend is emphasized in the case of Tl^+ (Fig. 3) and is weakened in the case of Zn^{++} (Fig. 5). Since the peak potential of Tl^+ is more positive than that of Cd^{++} and the peak potential of Zn^{++} is more negative than that of Cd^{++}, it is assumed that the above mentioned trend becomes weaker as the reduction potential shifts toward more negative potentials. In the anodic branch the same trend is also observed, although the net variation of the peak current is in any case less than the cathodic one.

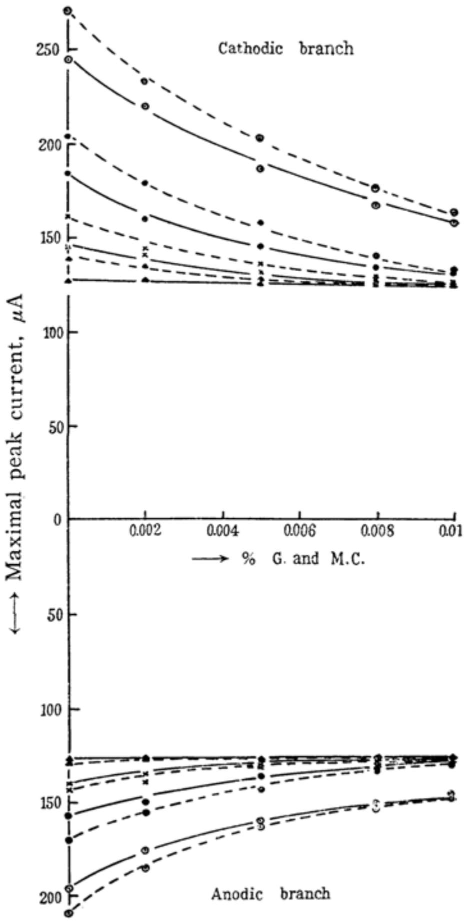

Fig. 4. Variation of the maximal peak current of 0.5 mM/l. Cd^{++} with the concentration of G. or M. C.: G: full curve, M. C.: interrupted curve, -⊙- Br^-, -●- Cl^-, -×-NO_3^-, -▲- SO_4^{--}.

The above mentioned effect of anions has already been reported by Heyrovský[10], Randles[2], Doss and Agarwal[11], and others[5,12]. One of the present authors[13] has pointed out the parallelism between the catalytic

---

[10] J. Heyrovský, *Discs. Faraday Soc.*, **1**, 212 (1947).

[11] K.S.G. Doss and H.P. Agarwal, *J. Phys. Coloid Chem.*, **54**, 804 (1950).

[12] P. Lukovtsev, S. Levina and A.H. Frumkin, *Acta Physicochim. U.R.S.S.*, **11**, 21 (1939). J'OM. Bockris, *Chem. Revs.*, **43**, 525 (1948). R. Pointelli, Int. Comm. Electrochem. Therm. Kin., Proc. 2nd meeting, Tamburini, Milan, 1950, p. 185.

[13] H. Imai, Presented at the discussion on polarography held by the Chemical Society of Japan etc. in November, 1955.

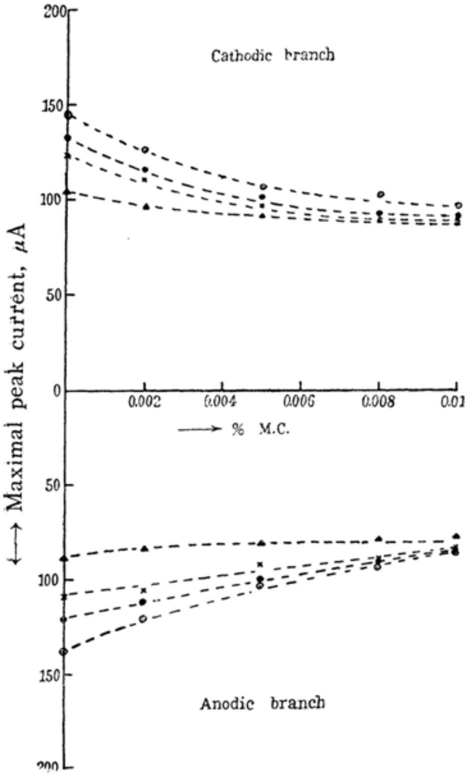

Fig. 5. Variation of the maximal peak current of 0.5 mM/l. Zn^{++} with the concentration of M. C.: -⊙- Br^-, -●- Cl^-, -×- NO_3^-, -△- SO_4^{--}.

effect of an anion and the charging current[14] resulting from anions adsorbed on the surface of the D. M. E.; namely, the charging current becomes more pronounced in the solution containing SO_4^{--}, NO_3^-, Cl^-, Br^-, I^- in the order given and it decreases as the applied potential shifts toward more nagative potentials in the cathodic branch. In the anodic branch a less charging current than the cathodic current is observed in every supporting electrolyte solution. Assuming that the adsorptive density of an anion is proportional to the charging current, one can conclude that the catalytic effect originates from the establishment of the combination such as Hg (electrode)—Adsorbed Anion—Depolarizer Ion, through which the electrone transfer is facilitated.

In the presence of G. or M. C. the catalytic process of an anion is retarded as is illustrated in Figs. 3, 4 and 5. Namely, the effect of G. or M. C. becomes more pronounced in the test solution of the same depolarizer (Tl^+, Cd^{++} or Zn^{++}) containing SO_4^{--}, NO_3^-, Cl^-, Br^- in the order given, and also in the solution of the same supporting electrolyte containing Zn^{++}, Cd^{++}, Tl^+ in the order given. In the anodic process the effect is less than the cathodic one. The parallelism between the catalytic effect and the retarding effect is best realized in the solution containing 0.01% G. or M. C.; that is, in this solution the catalytic effect of an anion is almost perfectly reduced, and accordingly, the cathodic current is nearly equal to the anodic current regardless of the anion constituent.

In the test solution containing Tl^+ no appreciable shifts of the peak potential owing to the presence of G. or M. C. was observed either in the cathodic branch or in the anodic branch. $E_p - E_{p1/2}$ (E_p; the peak potential, $E_{p1/2}$; the half peak potential), however, slightly increases within a few millivolts as the concentration of G. or M. C. increases. The increase of $E_p - E_{p1/2}$ results from the retardation of the rate of the electrode process as is indicated theoretically by Matsuda and Ayabe[15].

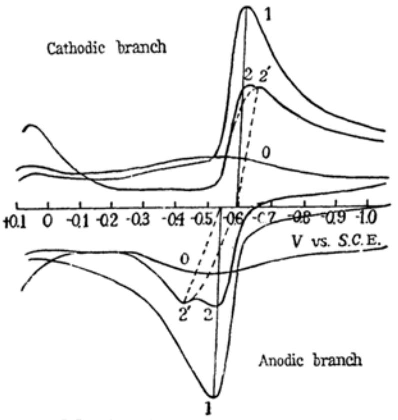

Fig. 6. Maximal peak current-potential oscillogram of 0.5 mM/l. Cd^{++} in M KNO_3: Curve 1; no M. C., Curve 2; 3/4 life time of D. M. E. (0.008% M. C.), Curve 2′; just before the drop falls. (0.008% M. C.)

In the case of Cd^{++} in KNO_3 solution containing more than 0.008% M. C. the peak remarkably shifts toward more negative or more positive potentials in the cathodic or the anodic branch, respectively, as the mercury drop grows ripe. The current-potential oscillogram is illustrated in Fig. 6. Zn^{++} behaves likewise. It is assumed that the phenomenon results from the steric hindrance by the film formation of surface active molecules.

Finally the molecules of a surface active reagent, the concentration of which is as low as 0.002–0.01%, exchange with the anions

---

[14] H. Imai, This Bulletin, 29, 281 (1956).

[15] H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, 59, 494 (1955).

existing in the electrode surface (Helmholtz layer) and result in the retardation of the catalytic process displayed by the anions. Hereupon, not only a polyvalent cation but also a monovalent cation (Tl^+) suffer from the catalytic effect of the anion and the retarding effect of the surface active reagent. In this conncetion Heyrovský[4] observed that the electrodeposition of Tl^+ is reversible and is not hindered by the presence of gelatine. From Matsuda and Ayabe's theory[15] it is reasoned that the electrode process of Tl^+ is quasi-reversible and is controlled not only by the diffusion of Tl^+ but also by the rate of the electrode process as far as the rate constant, k_G, of the electrode process does not exceed 2 cm./sec. This value is estimated by substituting the numerical values of n and v in $0.3\sqrt{nv}$, where n is the number of electrons transferred per ion and v is the rate of variation of the applied voltage. By the way, the value of k_G of Tl^+ in mol./l. KNO_3 solution is given as great as>1 cm./sec. by Randles and Somerton[16]. Since the electrode process of Tl^+ suffered from the catalytic action of anions in this experiment, it seems that the value of k_G will not be greater than 2.

The phenomenon occurring in the concentration region greater than 0.008% of the surface active reagent is mentioned above, and in the region from 0.008% to 0.04% the diffusion controlled current of an ordinary polarograph is scarcelly retarded, but the peak potential in the oscillographic polarograph shifts remarkably. This effect can be assigned to the film formation of the surface active reagent. The retardation of the diffusion controlled current of an ordinary polarograph in the concentration region of the surface active reagent more than 0.04% is probably explicable on the basis of the "sieve" effect.

Randles[2] observed that the rate constant of the electrode process of Cd^{++} in mol./l. KCl solution is reduced in two steps as the concentration of gelatine increases, and the first step appears in the concentration region from 0 to 0.01% of gelatine and the second step appears in the concentration region of more than 0.04% gelatine. Since these results coincide with those of the present authors, the mechanisms of Randles's results are reasonably explicable by adopting the above mentioned conclusion.

The authors wish to express their hearty gratitude to Dr. Takeshi Taketa and Dr. Mutsuaki Shinagawa for their encouragement throughout this study.

Laboratory of Chemistry, Minami College
Hiroshima University, Hiroshima

---

[16] C.W. Conway, "Electrochemical Data", Elsevier Publ. Co., Amsterdam (1952), p. 356.