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A SIMPLE CRITERION OF AN AUTOCATALYTIC PROCESS AT A STATIC MERCURY DROP ELECTRODE (SMDE)

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With the use of the SMDE, a simple criterion for distinguishing an autocatalytic process from a catalytic one is proposed; the limiting current for an autocatalytic wave increases with drop time, and the i–t curve shows a current increase with time on every drop. On the other hand, the limiting currents for diffusion, kinetic and catalytic waves decrease with drop time.

In a conventional dropping mercury electrode (DME), the drop area increases throughout the drop life. In DC polarography with the DME, the current which contains contributions from both Faradaic and charging currents is measured. With the SMDE, on the other hand, a drop is dispensed in a small fraction of time, and the stationary drop is held until the drop is dislodged.1) There is no charging current contribution arising from the growth of electrode area.

In DC polarography at the SMDE, Bond and Jones reported that a diffusion current was given by the Cottrell equation, and the detection limit was improved to as low as 10^{-7} M* level for both reversible and irreversible processes.2) According to Anderson et al.,3) adsorption and film-formation phenomena play more important roles at the SMDE than at the DME. However, studies on various types of the polarographic behavior at the SMDE have yet been quite few.

In the present paper, we describe the characteristics of catalytic polarographic currents at the SMDE. Since the current-time (i–t) curves characterize in a general manner the electrode process occurring on the individual mercury drops, attention is paid to record these curves at the SMDE.

The polarograms and i–t curves were obtained with a PAR (Princeton applied

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* 1 M = 1 mol dm^{-3}

Research) polarographic analyzer, Model 174A in conjunction with a PAR static mercury drop electrode (SMDE), Model 303. A Riken Denshi X-Y,T recorder, Model D-8CP was used to record them. The i–t curves were recorded with the use of a Riken Denshi transient time converter, Model TCA-1000. In all the measurements, the temperature was thermostated at 25 ± 0.1 °C.

The reduction of 1.0 mM Cd(II) in 0.1 M acetate buffer (pH 3.7) containing 10 mM nitrilotriacetic acid (NTA) was studied. Two reduction waves were observed under these conditions. The first wave is due to the reduction of $Cd(aq)^{2+}$ formed by the dissociation of Cd(II)-NTA complexes. The limiting current is governed by the rate of the dissociation reaction. The total current is diffusion-controlled.4) The i–t curves for the first and total limiting currents show a gradual decrease in current with time. Both limiting currents are plotted against $t^{-1/2}$, where t is the drop time (Fig. 1). For the diffusion current (the total current), a straight line plot which passed through the origin was obtained (curve a). This result is in line with that reported by Bond and Jones.2) For the kinetic current, on the other hand, the plot did not go through the origin (curve b). A similar result was obtained for the kinetic current of formaldehyde in 0.1 M NaOH (curve c). The aldehyde form of formalhyde is in equilibrium with the hydrated form, methyleneglycol, which is not reducible at the electrode. The reduction current of formaldehyde is controlled by the dehydration rate of the hydrated form.5)

The i–t curves for the Mo(VI)-nitrate,6) W(VI)-perchlorate,7) U(VI)-nitrate8) and Pb(II)-hydrogen peroxide9) systems were reported as examples of catalytic currents. As in the case of the diffusion and kinetic currents, the i–t curves for the catalytic currents also showed a current decrease with time on every drop.

As an example of autocatalytic currents, the reduction of formaldehyde in neutral unbuffered solutions was studied. In neutral unbuffered media, the dehydration reaction mentioned above is catalyzed by

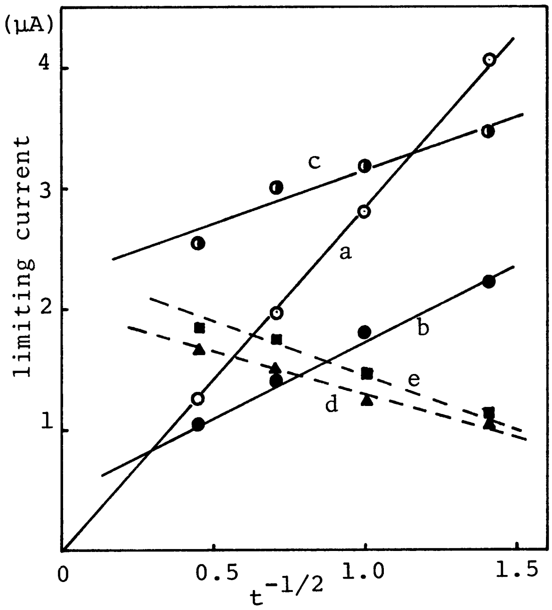

Fig. 1

a) The total wave and b) the first wave of 1.0 mM Cd(II) in 0.1 M acetate buffer (pH 3.7) containing 10 mM NTA.
c) 2.5 mM HCHO in 0.1 M NaOH.
d) 10 mM HCHO in 0.1 M KCl.
e) 5 mM OHCCOOH in 0.1 M KCl.

hydroxide ions. The autocatalytic effect is caused by hydroxide ions produced by the reduction of formaldehyde.[5)]

$$HCHO + 2H_2O + 2e = CH_3OH + 2OH^-$$

Contrary to the cases of the diffusion and kinetic currents, the limiting current decreases with an increase in $t^{-1/2}$ (curve d), i.e., the i–t curve showed a gradual increase of current with time. Similar results were obtained for the autocatalytic current of glyoxylic acid in a neutral unbuffered solution (curve e).[5)]

The catalytic polarographic wave of the Co(II)-nitrite system was studied. The DC polarogram and i–t curves at the SMDE are shown in Fig. 2. As reported previously,[10)] the reaction mechanism for the catalytic wave is as follows; in the presence of hydroxide ions, $Co(OH)^+$ is reduced to the metal, which is then reoxidized to Co(II) by nitrite. By the reduction of nitrite, hydroxide ions are liberated in the vicinity of the electrode, which in turn increases the concentration of $Co(OH)^+$ (autocatalysis). The Fe(II)-nitrate or chlorate system in neutral unbuffered media also produces an autocatalytic polarographic wave which is due to the oxidation of colloidal $Fe(OH)_2$ with nitrate or chlorate. The reduction of nitrate or chlorate produces hydroxide ions, which are available for the formation of colloidal $Fe(OH)_2$ [11,12)] The i–t curves for these autocatalytic waves show a current increase with time, which is similar to the behavior of formaldehyde in neutral unbuffered solutions (curve a in Fig. 2). The catalytic waves resemble the usual polarographic maxima in shape. For the maxima, however, such a current increase in the i–t curves was not observed.

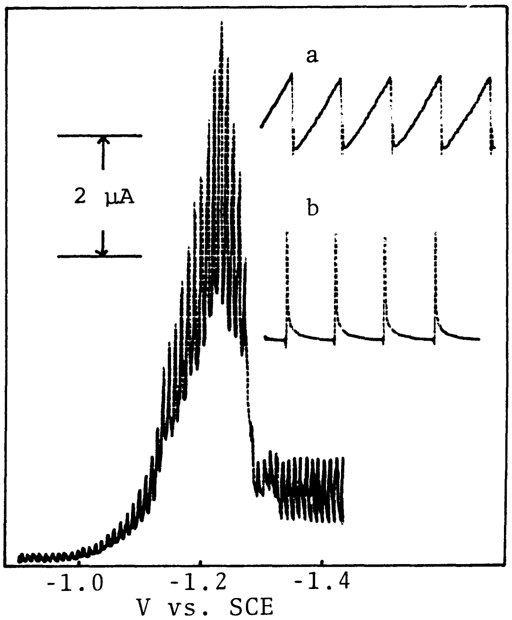

Fig. 2
A DC polarogram and i–t curves of 0.4 mM Co(II) in 0.1 M KCl (pH 5.6) containing 20 mM NO_2^-.
Drop time ; 5 s.
a) at -1.2 V, b) at -1.4 V.

In the past, the i–t curves have been recorded with the use of DME. For catalytic (kinetic) and autocatalytic currents, the i–t curves are parabolic with exponents of 2/3 and 7/6, respectively.[13)] From the i–t curves at the DME, however, it is rather difficult to determine whether the electrode process acquires an autocatalytic character. With the SMDE, the i–t curves for autocatalytic currents exhibit a current increase with time. The dependence of the limiting current on drop time (Fig. 1) or the unusual i–t profile can be used as a simple test for an autocatalytic reaction.

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