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Adsorption of Polyethyleneglycol at the Mercury/Solution Interface

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The adsorption of polyethyleneglycol (PEG) was investigated at the mercury/solution interface by the observation of the differential capacity and the inhibitive action on the deposition of cadmium or copper. From the differential capacity measurements, the adsorption of PEG was found to be controlled by the diffusion of the adsorbate to the dropping mercury electrode under the present experimental conditions. The relation between the time required to attain the saturated adsorption and the bulk concentration (a) was explained approximately by the Koryta equation, though its deviation from the Koryta equation was somewhat larger than that for polyvinylpyrrolidone. When the maximum surface concentration and the mean molecular weight of PEG were expressed by Γ_m and $\bar{M}$ respectively, the plot of log Γ_m-log $\bar{M}$ revealed two linear parts crossing each other at $\bar{M}$=*ca.* 600. The slope for $\bar{M} \geq 600$ was *ca.* -1, which implied the relation of "$\bar{M} \cdot \Gamma_m$=const.", *i.e.*, the segment numbers of PEG molecules adsorbed per unit area were constant, independently of $\bar{M}$, in the region of $\bar{M} \geq 600$. The configuration of PEG of $\bar{M} < 600$ at the interface was considered to be different from that of PEG of $\bar{M} \geq 600$ because the slope for $\bar{M} < 600$ was different from that for $\bar{M} \geq 600$. From the polarographic current measurements (*i.e.*, the inhibitive effect on the reduction of Cd^{2+} or Cu^{2+}), the time (t_{mi}) needed to achieve the maximum inhibition was obtained; it was then compared with that obtained from the capacity data. The relation of "$\log a = (-1/2)\log t_{mi}$+const." based on the Koryta equation was approximately applicable to the cases with a relatively large $\bar{M}$ value.

In many cases, organic high polymers are adsorbed so strongly at the electrode/solution interface, that the adsorption from its dilute solution is mainly controlled by the diffusion. Such a diffusion process was discussed for PVP (polyvinylpyrrolidone)[1] and the Koryta equation[2] was approximately applicable to the adsorption of PVP. Electrochemical studies on the adsorption of polyethyleneglycol (PEG) have been scarcely published, though Jehring and Horn[3] computed the maximum surface concentration (Γ_m) at the mercury interface by means of AC polarography. In this paper, the adsorption of PEG[4] at the mercury inter-

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[1] T. Yoshida, T. Ohsaka, and S. Tanaka, This Bulletin, **45**, 326 (1972).

[2] J. Koryta, *Collect. Czech. Chem. Commun.*, **18**, 206 (1953).

[3] H. Jehring and E. Horn, *Deut. Akad. Wiss. Berlin*, **10**, 295 (1968).

[4] Molecular formula: $H(OCH_2CH_2)_nOH$.

face was investigated by the observations of differential capacity and of inhibitive effect on the electrodeposition. The time (t_{mc}) needed to attain the saturated adsorption was observed by the capacity measurement and it was compared with that (t_{mi}) obtained from the inhibitive effect of PEG on the electrodeposition of cadmium or copper.

Experimental

Electrodes. For the measurements of the differential capacity and the instantaneous current, a DME (dropping mercury electrode) and a counter electrode of cylindrical platinum net were used. The drop time of DME was about 12 sec, while it was nearly 5 sec for the polarography. All the potentials were referred to the saturated calomel electrode (SCE).

Differential Capacity Measurements. The impedance bridge used for the capacity measurements was a condenser-connected type with both arms composed of 1 μF mica condensers; the input of 1 kHz sinusoidal wave was adjusted to be less than *ca.* 10 $\text{mV}_{\text{p-p}}$. The balance of the bridge was detected with a selective amplifier and a cathode-ray oscilloscope. The series-equivalent circuit with resistance and capacitance was assumed in balancing the bridge.

Instantaneous Current vs. Time Curves (i-t Curves). The instantaneous *i-t* curves were observed by connecting a recorder or oscilloscope in parallel with 2 kΩ resistance equipped in series with the polarizing circuit of DME.

Polarograph and Others. The polarograph was the PA102 type of Yanagimoto. The test cell and DME were the same as have been described previously;[1] all the experiments were conducted in an atmosphere of purified hydrogen at 25°C.

Materials. Seven kinds of chemical-grade PEG by the Sanyo Chemical Industry Co. were used without further purification. The mean molecular weights ($\bar{M}$) were calculated from those OH values obtained by end-group determination; they were 200, 300, 400, 600, 1000, 3100, and 8400 respectively. Mercury was distilled twice *in vacuo*, and all the solutions were prepared from chemical-grade reagents and triply-distilled water.

Results and Discussion

I) Differential Capacity Measurements. Differential Capacity vs. Potential Curves (C–E Curves): Some typical *C–E* curves of PEG $\bar{M}$=600 and 8400 in 1 N potassium chloride are shown in Fig. 1, where t_B is the duration from the beginning of a drop growth to the balancing the bridge. In Fig. 1-(a) with PEG $\bar{M}$=600, ad- or desorption peaks are observed at *ca.* −0.2 and *ca.* −0.6 V (SCE). Figure 1-(b) with $\bar{M}$=8400 is similar to the case of $\bar{M}$=600, though the anodic peak shows only a steep slope on the right side. The potential of the ad- or desorption peak for PVP[1] or PMA[5] has been reported to be almost independent of the bulk concentration; for PEG however, the peak potential is dependent to some extent on the bulk concentration. The peak becomes steeper with the increase in $\bar{M}$; this tendency suggests that the interaction among the adsorbed molecules becomes stronger with the increase in $\bar{M}$. The differential capacity is depressed as the concentration increases in the adsorption range of PEG between the two peaks. The increase in the adsorbability of PEG with $\bar{M}$ may be expected from the extension of the adsorption range by the increase in $\bar{M}$ under a constant *a*. When the saturated adsorption of PEG was attainable, the differential capacity became approximately constant at −0.9—−1.2 V, where the time-dependence of the capacity and of the instantaneous current were examined. The *C–E* curves for the adsorption of PEG in 1 N solutions of hydrochloric acid, sulfuric acid, and sodium sulfate were similar to Fig. 1; however, the cathodic peak in the acid solution was not revealed because of the hydrogen evolution.

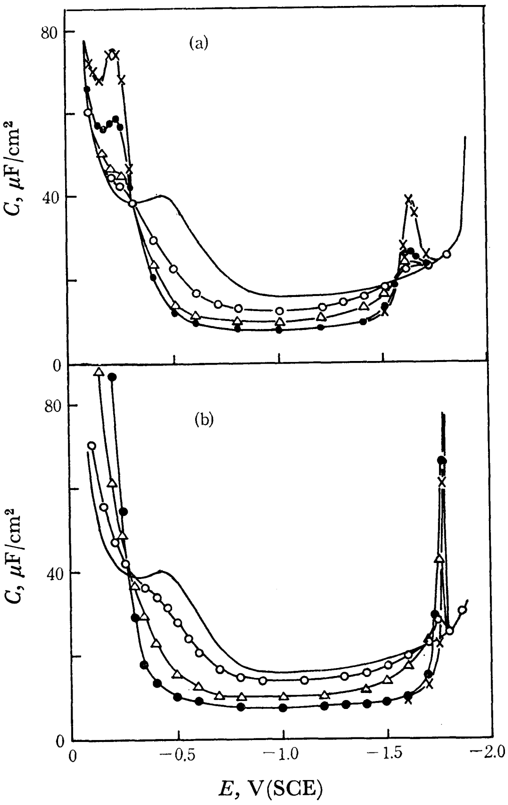

Fig. 1. Differential capacity *vs.* potential curves.
1 kHz, t_B=8 sec, (a) 1 N potassium chloride+PEG $\bar{M}$=600, —: 0 mg/*l* PEG, ○: 5 mg/*l*, △: 10 mg/*l*, ●: 50 mg/*l*, ×: 200 mg/*l*, (b) 1 N potassium chloride+PEG $\bar{M}$=8400, —: 0 mg/*l* PEG, ○: 6 mg/*l*, △: 15 mg/*l*, ●: 30 mg/*l*, ×: 100 mg/*l*.

Observed Capacity vs. Time Curves (C_E-t Curves): The C_E-*t* curves at −1.2 V in 1 N potassium chloride are shown in Fig. 2, where (a) and (b) are concerned with $\bar{M}$=600 and 8400. In the solution without adsorbates, the observed capacity (C_E) increases with $t^{2/3}$ or with the growth of a mercury drop;[6] further, the same tendency is also shown after the attainment of the adsorption equlibrium in a relatively concentrated PEG solution. In a relatively concentrated PEG solution the curve for the process controlled

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[5] PMA (polymethacric acid); I. R. Miller and D. C. Grahame, *J. Amer. Chem. Soc.*, **78**, 3577 (1956).

[6] $C_E=0.85\,C_0 m^{2/3} t^{2/3}$, where C_0 and m are the differential capacity (μF/cm²) in the solution without adsorbates and the flow rate of mercury (g/sec).

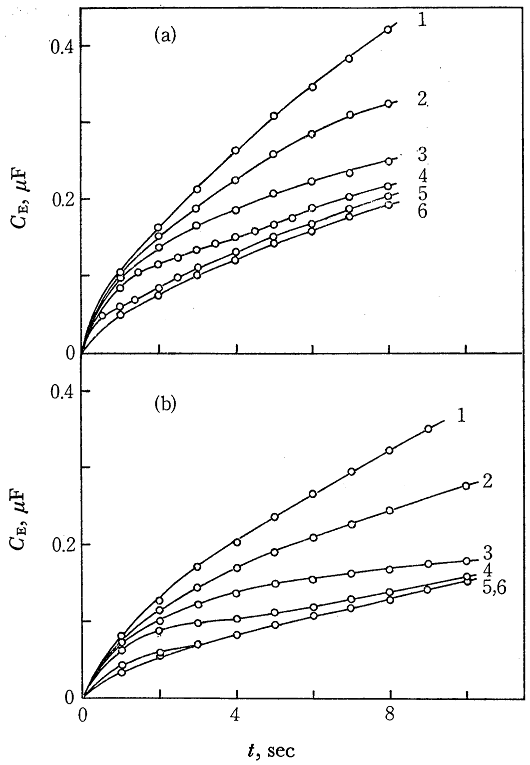

Fig. 2. Observed differential capacity *vs.* time curves.
1 kHz, at $E=-1.2$ V, (a) 1 N potassium chloride+PEG $\bar{M}=600$, 1: 0 mg/*l*, 2: 4.3 mg/*l*, 3: 8.6 mg/*l*, 4: 14.0 mg/*l*, 5: 33.2 mg/*l*, 6: 864 mg/*l*, (b) 1 N potassium chloride+PEG $\bar{M}=8400$, 1: 0 mg/*l* PEG, 2: 10.0 mg/*l*, 3: 20.0 mg/*l*, 4: 30.0 mg/*l*, 5: 70.0 mg/*l*, 6: 200 mg/*l*.

mainly by the diffusion seems to approach that of the adsorption equilibrium with the increase in time. Such a transition from a diffusion-controlled adsorption to an equilibrium one is clearly revealed in the adsorption of PVP,1) whereas the transition range for PEG is not so clear.

Differential Capacity vs. Square Root of the Time Curves (C-$t^{1/2}$ Curves): For the adsorption controlled by the diffusion of adsorbates, the surface concentration (Γ_t) on a DME at the time (t) was introduced by Koryta;2)

$$\Gamma_t = 0.736D^{1/2}at^{1/2} \qquad (1)$$

where Γ_t, D, a, and t are the surface concentration of adsorbates at time t in mol/cm^2, the diffusion coefficient in cm^2/sec, the bulk concentration in mol/cm^3, and the time from the beginning of its adsorption in sec. For the sake of convenience, the bulk concentration in mg/*l* was used for the experiments instead of that in mol/cm^3. By replacing Eq. (1) in the relation of Frumkin's parallel condencer model with $\theta=\Gamma_t/\Gamma_m$, the time-dependence of C on the diffusion-controlled adsorption is obtained as follows:

$$C = C_0 - 0.736(C_0-C_1)D^{1/2}\Gamma_m^{-1}at^{1/2} \qquad (2)$$

where C is the differential capacity in μF/cm^2, θ, the coverage; C_0 or C_1, the differential capacity at $\theta=0$ or $\theta=1$, and Γ_m, the maximum surface concentration. When t_{mc} is the time required to attain the saturated adsorption, Eq. (2) holds for $t \leq t_{mc}$. For $t > t_{mc}$,

$$C = C_1 \qquad (2)'$$

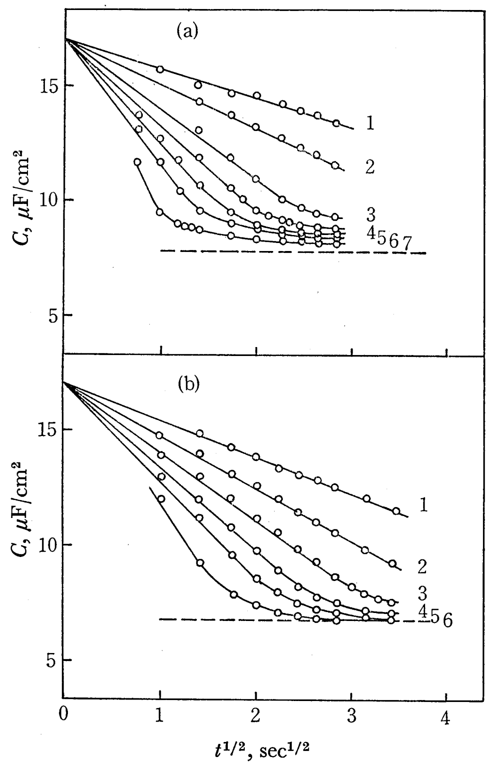

Fig. 3. Differential capacity *vs.* square root of time curves.
1 kHz, at $E=-1.2$ V, (a) 1 N potassium chloride+PEG $\bar{M}=600$, 1: 4.3 mg/*l*, 2: 8.6 mg/*l*, 3: 10.8 mg/*l*, 4: 14.0 mg/*l*, 5: 17.3 mg/*l*, 6: 21.6 mg/*l*, 7: 33.2 mg/*l*, ----: C_{min} (minimum differential capacity), (b) 1 N potassium chloride+PEG $\bar{M}=8400$, 1: 10.0 mg/*l*, 2: 15.0 mg/*l*, 3: 20.0 mg/*l*, 4: 25.0 mg/*l*, 5: 30.0 mg/*l*, 6: 40.0 mg/*l*, ----: C_{min}.

Figure 3 is obtained from C_E-t curves with Eqs. (2) and (2)′, where (a) and (b) are concerned with $\bar{M}=600$ and 8400. The linear decrease in C with $t^{1/2}$ is due to the diffusion-controlled adsorption, while a nearly constant C is revealed, independently of t,

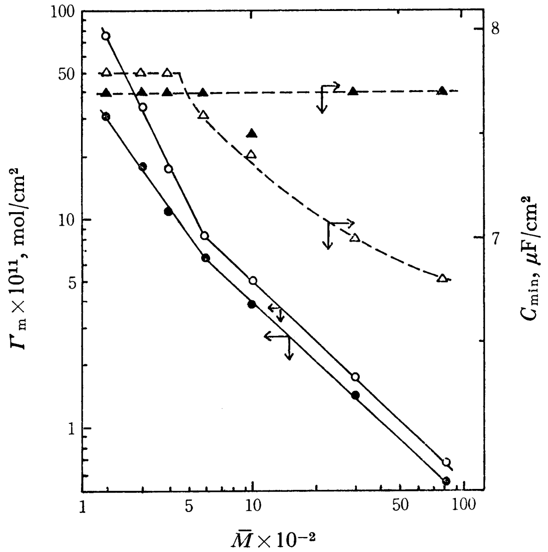

Fig. 4. Relation between mean molecular weight and maximum surface concentration (solid lines) or minimum differential capacity (broken lines).
solid lines: Γ_m—$\bar{M}$ curves (○: 1 N potassium chloride+PEG, ●: 1 N hydrochloric acid+PEG), broken lines: C_{min}—$\bar{M}$ curves (△: 1 N potassium chloride+PEG, ▲: 1 N hydrochloride acid+PEG).

with the adsorption equilibrium. The behavior of PEG deviated somewhat from Eqs. (2) and (2)′, unlike that of PVP,[1] which was approximately consistent with the Koryta equation based on pure diffusion except for the transient range from the diffusion-controlled to the saturated adsorption. Such a deviation is obviously revealed by the curves for PEG of an especially low $\bar{M}$, as is shown in Fig. 3-(a), where each curve seems to attain an individual capacity at the adsorption equilibrium dependent on the concentration. This tendency is due to the lower adsorbability of PEG as compared with that of PVP. The time (t_{mc}) needed to attain Γ_m can be estimated by extrapolating the linear relation of C-$t^{1/2}$ to the minimum differential capacity; then, Γ_m is obtainable from the Koryta equation [Eq. (1)] on the assumption of its diffusion coefficient.

Relation between the Maximum Surface Concentration and the Mean Molecular Weight (Γ_m–$\bar{M}$ Curves): It is necessary to assume the diffusion coefficient (D) of adsorbates in order to evaluate Γ_m from the Koryta equation. Scholtan's relation[7] between D and $\bar{M}$, which is used for the assumption of D, is as follows:

$$D^2\bar{M} = 10^{-8} \qquad (3)$$

In Fig. 4, the Γ_m obtained from Eq. (1) is plotted against $\bar{M}$ by the solid line; the values of Γ_m in 1 N potassium chloride are larger than those in 1 N hydrochloric acid by *ca.* 20%. Both plots of log Γ_m *vs.* log $\bar{M}$ reveal linear relations with the slope of *ca.* -1 in the range of $\bar{M} \geq 600$. The relation of the $\bar{M}\cdot\Gamma_m =$ const. may be found from the above slope. From this relation, obtained also for PVP,[1] the total segment numbers of PEG molecules adsorbed per unit area at the interface can be considered to be constant, regardless of $\bar{M}$. In the range of $\bar{M} < 600$, each slope of logΓ_m *vs.* log$\bar{M}$ plots is different from that for $M \geq 600$; therefore, the configuration for $\bar{M} < 600$ at the interface can be considered to be different from that for $M \geq 600$. The Γ_m values dependent on the electolyte may result from a small change in the adsorbed layer influenced by the pH value of the solution.

Relation between the Minimum Differential Capacity and the Mean Molecular Weight ($C_{\min}$–$\bar{M}$ Curves): The thickness of the adsorbed layer can be examined by means of the following well-known relation:

$$C_{\min} = \varepsilon/(4\pi\delta) \qquad (4)$$

where $C_{\min}$, ε, and δ are the minimum differential capacity, the dielectric constant, and the thickness of the adsorbed layer. In the case of $\bar{M} \geq 600$, the $\bar{M}$-dependence of $C_{\min}$ may be negligible because of nearly constant segment numbers adsorbed per unit area, as found previously from the Γ_m–$\bar{M}$ relation, and the $C_{\min}$ observed in 1 N hydrochloric acid is independent of $\bar{M}$, whereas the $C_{\min}$ in 1 N potassium chloride depends on $\bar{M}$ in the range of $\bar{M} \geq 600$, as is shown by the broken line in Fig. 4. The maximum difference between $C_{\min}$'s in 1 N solutions of potassium chloride and hydrochloric acid is about 1 μF/cm^2; it may be caused by the variation in the thickness or in the dielectric constant of adsorbed layer. From such a difference as about 10% of $C_{\min}$, however, hardly no basic variation in the adsorbed structure is considered to take place. In this connection, it may be considered, with a constant segment numbers per unit area, that the decrease in $C_{\min}$ in aqueous potassium chloride is mainly due to the change in the compactness of the adsorbed layer, which is itself related to the inhibitive action of PEG.

Consequently, for PEG of $\bar{M} \geq 600$, the configuration at the interface may be a spread or flat form consisting of a chain, as may be expected from the Γ_m–$\bar{M}$ relation, and the compactness of the adsorbed layer somewhat depends on $\bar{M}$ in some cases, while in relation to the PEG of $\bar{M} < 600$, the configuration at the interface may be quite different from that for PEG of $\bar{M} \geq 600$, in view of the results shown in Fig. 4.

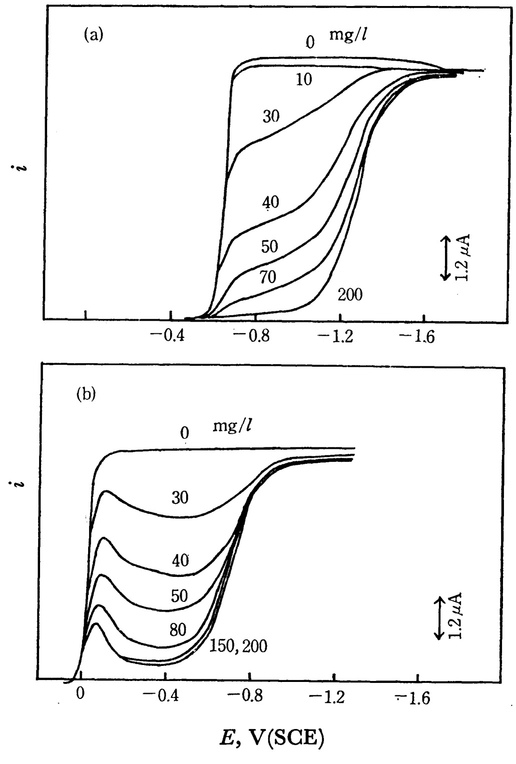

Fig. 5. Polarograms inhibited by PEG.
1 N sodium sulfate+PEG $\bar{M}$=8400, (a) depolarizer: 1 mM Cd^{2+}, (b) depolarizer: 1 mM Cu^{2+}.

II) Inhibitive Effect of Adsorbed PEG. Polarograms: Figure 5 consists of typical polarograms which show the inhibitive effect of the PEG of $\bar{M}$=8400 on the reduction of Cd^{2+} or Cu^{2+} in 1 N sodium sulfate. In Fig. 5-(a) for Cd^{2+}, the reaction current is depressed as the bulk concentration of PEG is increased, and the depression becomes less with the negative potential. The maximum depression of the reaction current is revealed at nearly -0.9 V, where the instantaneous *i-t* relations are observed, as will be shown later. Judging from the results shown in Fig. 1-(b), it is difficult to consider the current rise at *ca.* -1.2 V to be due to the desorption of PEG, but it may be ascribed to the inhibition weakened at a sufficiently negative potential.

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[7] W. Scholtan, *Makromol. Chem.*, **7**, 209 (1951).

In Fig. 5-(b) for Cu^{2+}, a current peak appears at *ca.* −0.1 V; it seems to be due to the desorption of PEG because of the increase in capacity at *ca.* −0.1 V in Fig. 1-(b), though the formation of an intermediate product[8] should also be taken into account. For the copper deposition, instantaneous *i-t* curves were observed at −0.4 V.

In 1 N solutions of potassium chloride and hydrochloric acid, no inhibitive effect of adsorbed PEG was revealed because of the effect of the chloride ion, as has been discussed by Delahay.[9] Therefore, the inhibitive effect of PEG was examined in 1 N solution of sodium sulfate or sulfuric acid.

Instantaneous Current vs. Time Curves (i-t Curves): The instantaneous *i-t* curves for the inhibitive effect of PEG on the reduction of Cu^{2+} revealed a tendency similar to that for Cd^{2+}; therefore, only the latter will be discussed here as an example. Figure 6 shows the *i-t* curves for the reduction of Cd^{2+} in 1 N sodium sulfate with several concentrations of PEG, where (a) and (b) are related to the PEG of $\bar{M}=600$ and 8400 These curves are nearly analogous to the results by Schmid and Reilley[10] obtained for the adsorption of Triton X, which is controlled by the diffusion. The time t_{mi} (or t_{mc}) needed to complete a monolayer or the full coverage may be computed from Eq. (1) or (5)[11] modified as follows on the assumption that the complete inhibition takes place under full coverage by the adsorbates, whose process is controlled by the diffusion.

$$t_{mi} = t_{mc} = 1.82\Gamma_m^2/a^2D \qquad (5)$$

Therefore, t_{mi} should be in accordance with the t_{mc} obtained from the C-$t^{1/2}$ relation in Fig. 3.

In the adsorption of PVP,[12] t_{mi} was in good agreement with t_{mc}; in this case, t_{mi} was estimated by extrapolating the steeply depressed part to the time of zero current in the *i-t* relation.

In the case of PEG, the adsorption behavior somewhat deviates from that of the process simply controlled by the diffusion as has been stated previously, and a complete inhibition can not always be expected, even for the full coverage. Therefore, the value of t_{mi} for PEG was determined from the intersection obtained by extrapolating the steeply depressed part of the current to the extremely inhibited current in a considerably concentrated solution of PEG, on the assumption that the extremely inhibited current corresponded to the minimum current in the case of the maximum inhibition.

Comparison of t_{mc} with t_{mi}: The relations of log *a* *vs.* log t_{mi} are shown in Fig. 7. Further, the values of $at_{mc}^{1/2}$ and $at_{mi}^{1/2}$ are listed in Table 1, where $at_{mi}^{1/2}$ and $at_{mi}^{1/2}$ are shown instead of Γ_m since they are the values obtained directly without assuming the diffusion coefficient. The result for $at_{mc}^{1/2}$ shown in Table 1 was evaluated by extrapolating the C in the C-a relation to the minimum differential capacity at a constant t on the basis of Eq. (2). The value of $at_{mc}^{1/2}$ or $at_{mi}^{1/2}$ should be equal to a at $t_{mi}=1$ in Fig. 7.

Equation (5) can be rewritten as follows:

$$\log a = (-1/2) \log t_{mi} + \text{const.}$$

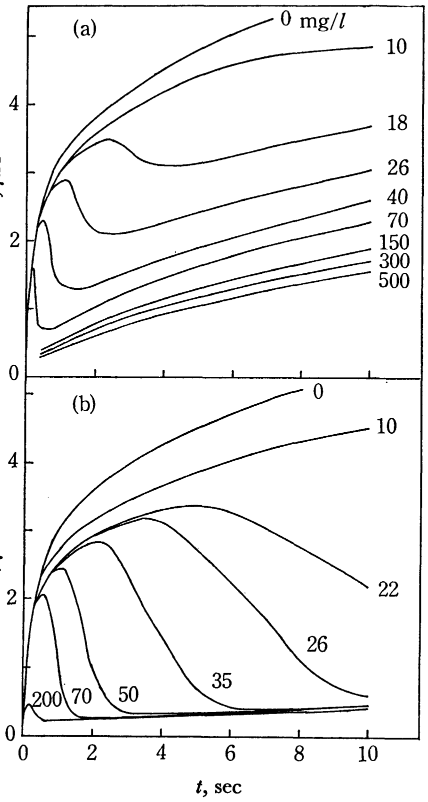

Fig. 6. Instantaneous current *vs.* time curves.
1 N sodium sulfate+1 mM Cd^{2+}+PEG, at $E=-0.9$ V, (a) PEG of $\bar{M}=600$, (b) PEG of $\bar{M}=8400$.

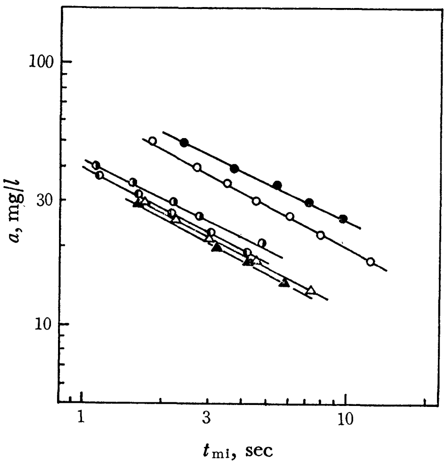

Fig. 7. Relation between saturation time (t_{mi}) and bulk concentration.
1 N sodium sulfate+PEG (◑: $\bar{M}=600$, ▲: $M=1000$, ●: $\bar{M}=8400$), 1 N sulfuric acid+PEG (◐: $\bar{M}=600$, △: $\bar{M}=1000$, ○: $\bar{M}=8400$).

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[8] I. M. Kolthoff and Y. Okinaka, *J. Amer. Chem. Soc.*, **81**, 2296 (1959).

[9] P. Delahay and I. Trachtenberg, *ibid.*, **80**, 2094 (1958).

[10] R. W. Schmid and C. N. Reilley, *ibid.* **80**, 2087 (1958).

[11] t_{mi} and t_{mc} are the times needed to attain the maximum inhibition and the minimum differential capacity respectively, when $\Gamma_t=\Gamma_m$, $t=t_{mi}=t_{mc}$. Then, Eq. (5) can be given by Eq. (1).

[12] T. Yoshida and T. Ohsaka, *Bull. Sci. Eng. Res. Lab. Waseda Univ.*, **58**, 34 (1972).

TABLE 1. COMPARISON OF $at_{mc}^{1/2}$ WITH $at_{mi}^{1/2}$

PEG $\bar{M}$	$at_{mc}^{1/2}$ (mg·sec$^{1/2}$·l^{-1})[a]		$at_{mi}^{1/2}$ for Cd^{2+} [b]	
	1N KCl	1N HCl	1N Na_2SO_4	1N H_2SO_4
200	76.2 (−0.9 V)	89.2 (−0.9 V)		
300	60.5 (−1.2 V)	34.7 (−0.9 V)		
400	40.3 (−1.2 V)	29.1 (−1.0 V)		
600	32.8 (−1.2 V)	25.1 (−1.0 V)	43.6 (−0.9 V)	40.9 (−0.9 V)
1000	35.5 (−1.2 V)	27.8 (−1.0 V)	36.0 (−0.9 V)	38.7 (−0.9 V)
3100	55.3 (−1.2 V)	45.8 (−1.0 V)		
8400	71.8 (−1.2 V)	59.2 (−1.0 V)	79.4 (−0.9 V)	79.4 (−0.9 V)

a) The mean values of $at_{mc}^{1/2}$ at t of 3, 5, and 7 sec from *C-a* curves.

b) The mean values of $at_{mi}^{1/2}$ at several concentrations from *i-t* curves.

As can be expected from this relation, the log t_{mi} *vs.* log a plot in Fig. 7 reveals a nearly linear relation with the slope of *ca.* $-1/2$, regardlesss of $\bar{M}$, and so the adsorption process of PEG is controlled by the diffusion under the present experimental conditions.

The data in Table 1 are markedly scattered. In the case of $\bar{M}=1000$, however, the result of $at_{mc}^{1/2}$ in aqueous potassium chloride is approximately accordance with that of $at_{mi}^{1/2}$ in aqueous sodium sulfate or sulfuric acid. The results of t_{mi} for PEG of $\bar{M}=1000$ and 8400 are considered to be approximately reliable. For $\bar{M}=600$,, the data are too scattered, perhaps because the behavior deviates somewhat from that of the adsorption simply controlled by the diffusion, as is revealed in Fig. 3-(a). The result in aqueous hydrochloric acid differs considerably from those in other solutions, though the dependence on the supporting electrolyte remains to be explained.

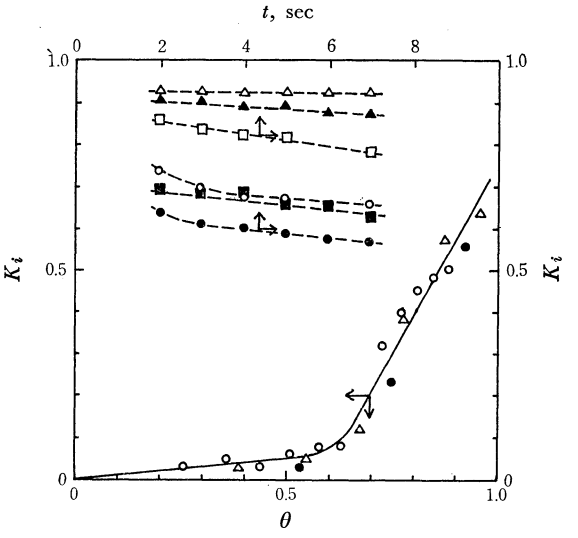

Fig. 8. Dependence of inhibitive efficiency on coverage, or on time after the attainment of saturated adsorption. at $E=-0.9$ V, depolarizer: 1 mM Cd^{2+}, solid line: $K_i-\theta$ ($t \leq t_{mi}$) curve, 1N sodium sulfate+PEG of $\bar{M}=1000$ (○: 10 mg/l PEG, △: 15 mg/l, ●: 20 mg/l), broken lines: K_i-t ($t > t_{mi}$) curves, 1N sodium sulfate+PEG (○: PEG of $\bar{M}=600$, □: $\bar{M}=1000$, △: $\bar{M}=8400$), 1N sulfuric acid+PEG (●: PEG of $\bar{M}=600$, ■: $\bar{M}=1000$, ▲: $\bar{M}=8400$).

Relation between the Inhibitive Efficiency and the Coverage (K_i-θ Curve): The inhibitive efficiency (K_i) is given by $(i_b-i)/i_b$, where i and i_b are the instantaneous currents in the solution with and without PEG. At the time $t \leq t_{mi}$ during the diffusion-controlled adsorption, the coverage can be written by means of the Koryta equation as follows: $\theta=\Gamma_t/\Gamma_m=(t/t_{mi})^{1/2}$. The solid line in Fig. 8 is a typical plot of the K_i-θ relation, where the inhibition is hardly shown until $\theta=0.6$; then, the sharp increase in K_i is revealed. When the inhibitor and the depolarizer are adsorbed by the process controlled the diffusion, the inhibitive effect on the reaction current is hardly revealed soon compared with t_{mi}; this tendency is clearly shown in Fig. 8. The tendency is revealed by the adsorption of the PEG or PVP of several $\bar{M}$, regardlesss of a. If a blocking effect of adsorbates is solely considered, K_i should be proportional to θ, however, this relation hardly holds usually and other effects must be taken into account in order to explain the behavior of the solid line in Fig. 8. The behavior of the K_i-θ plot may be explained by the geometrical relation between the effective radius of the congregated molecules adsorbed at the interface and the thickness of diffusion paths of the depolarizer. Matsuda[13] derived a theoretical *i-t* relation similar to the above case from the fundamental model assumed for the adsorbed layer; recently he has introduced a relation even more useful for analysis.

In the case of $t > t_m$, the K_i-t relations after the attainment of the saturated adsorption are plotted by the broken lines in Fig. 8. For the purpose of making the inhibitive condition uniform, regardless of $\bar{M}$, the value of K_i for any $\bar{M}$ is always determined in a solution containing PEG of 100 mg/l, because the segment numbers of the PEG adsorbed per unit area are nearly constant, independent of $\bar{M} \geq 600$, and the concentration in mg/l may be approximately proportional to that in segment numbers/l.

The variation in K_i after the completion of the saturated adsorption is shown somewhat in the figure, and it may be discussed from the viewpoint of the rehomogeneity proposed by Kastening.[14] The broken lines also reveal some dependence of K_i on $\bar{M}$ or on the supporting electrolyte. The inhibitive efficiency, K_i, after the attainment of the saturated adsorption increases with $\bar{M}$, which can be expected from the $\bar{M}$-dependence of adsorbability, as is revealed in Figs. 1—3. In the reduction of Cd^{2+}, the observed K_i in 1N sodium sulfate is always higher than that in 1N sulfuric acid; however, the reverse is the case in the reduction of Cu^{2+}, though the cause remains to be explained.

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13) H. Matsuda, *Rev. Polaro.* (Japan), **14**, 87 (1969).

14) B. Kastening, *J. Electroanal. Chem.*, **9**, 41 (1965).