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Adsorption and Inhibition Effect of Triton X at the Mercury/Solution Interface

Tetsuya Ohsaka, Hajime Yamamoto, and Tadashi Yoshida
Applied Electrochemical Laboratory, Graduate School of Science and Engineering,
Waseda University, Nishi-okubo, Shinjuku-ku, Tokyo 160

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The time dependence of differential capacity and that of polarographic current were observed to elucidate the adsorption behavior of Triton X. The adsorption showed a relatively ideal system of the diffusion-controlled type in which semi-infinite linear diffusion was assumed. The results from the two different observations agreed approximately. The Koryta equation was applied to obtain the maximum surface concentration Γ_m of Triton X in the adsorption of the monolayer. log Γ_m decreased linearly with increasing log $\bar{M}$ (mean molecular weight), the slope being *ca.* -1. In the case of high bulk concentration, the adsorption showed unusual phenomena considered to be caused by the formation of a multi-layer which tended to become marked with the decrease of $\bar{M}$. The inhibition effect of Triton X on reduction current revealed approximately the same tendency regardless of cations Cd^{2+} and Cu^{2+}. Though the dependence of inhibitive action on $\bar{M}$ was relatively small, the degree of inhibition became somewhat small with increasing $\bar{M}$ in contrast to the cases of PVP and PEG. The shape of instantaneous *i vs. t* curve was approximately elucidated by Matsuda's treatment of the system where the limiting current was depressed by diffusion-controlled adsorption. The *i-t* curve revealed that the degree of inhibition scarcely increases until attainment of a certain high coverage when a sharp increase takes place.

The adsorption of water-soluble polymer at the mercury/solution interface is mainly controlled by diffusion. The behavior is approximately explained by means of the Koryta equation,[1] as shown in the cases of polyvinylpyrrolidone (PVP)[2] and polyethyleneglycol (PEG).[3] Triton X (alkylphenoxy polyethoxy ethanols)[4] is often used as a suppressor of the maximum wave in polarography. We examined its interfacial behavior by means of measurements of differential capacity and instantaneous current.

Schmid and Reilley[5] showed instantaneous current *vs.* time curves classified into three extreme cases. The current-time curve depressed by Triton X is a typical example of diffusion-controlled adsorption. Barradas and Kimmerle[6,7] examined the maximum surface concentration Γ_m of Triton X by means of two methods; measurement of suppression of the oxygen maximum wave[6] and that of the potential dependence of interfacial tension.[7] The disagreement between Γ_m's obtained by the two methods seems to result from the formation of a multi-layer. In the present investigation, the formation of a monolayer was considered primarily, the formation of a multi-layer being also taken into account.

Experimental

A DME (dropping mercury electrode) was used as a test electrode. Its drop time was about 12 s for the measurements of differential capacity and instantaneous current, and about 3—4 s for the polarographic measurements. The counter electrode was a cylindrical platinum net with a sufficiently large surface. All potentials were referred to the saturated calomel electrode (SCE).

The differential capacity at the mercury/solution interface was measured with a transformer impedance bridge of 1 kHz whose input was kept less than 10 mV_{P-P}. A series equivalent circuit with resistance and capacitance was used for the bridge measurement.

The instantaneous current *vs.* time curves were determined from the *iR* drop observed with a recorder or an oscilloscope in parallel with 2 kΩ resistance which was connected in series

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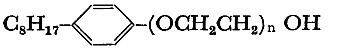
[1] J. Koryta, *Collect. Czech. Chem. Commun.*, **18**, 206 (1953).

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

[3] T. Yoshida, T. Ohsaka, and M. Suzuki, *ibid.*, **45**, 3245 (1972).

[4] Molecular formula: 

[5] R. W. Schmid and C. N. Reilley, *J. Amer. Chem. Soc.*, **80**, 2087 (1958).

[6] R. G. Barradas and F. M. Kimmerle, *J. Electroanal. Chem.*, **11**, 163 (1966).

[7] R. G. Barradas and F. M. Kimmerle, *ibid.*, **11**, 128 (1966).

with the DME and the polarization circuit.

Triton X-45, X-100, X-205, and X-405 (Rohm and Haas) were used without further purification, their degrees of polymerization for ethylene oxide groups being 5 ($\bar{M}$=430), 9—10 ($\bar{M}$=600—650), 20 ($\bar{M}$=1100), and 40 ($\bar{M}$=2000), respectively. Solutions were prepared from guaranteed reagent and triply-distilled water. All experiments were conducted in an atmosphere of purified nitrogen at 25°C in 1 N sulfuric acid.

Results and Discussion

Dependence of Differential Capacity on Potential (C-E Curves). Figures 1-(a) and (b) show the *C-E* curves of Triton X-45 and X-405 at adsorption time of 5 s. The anodic peaks due to adsorption or desorption were observed at *ca.* 0—0.1 V. No cathodic peak was observed. The adsorption or desorption peaks become large with the increase in bulk concentration. The potential dependence of the peak is seen to some extent except for the case of Triton X-405. Since the differential capacity decreases with the increase of Triton X concentration in a more cathodic potential than an anodic peak, adsorption occurs in this range.

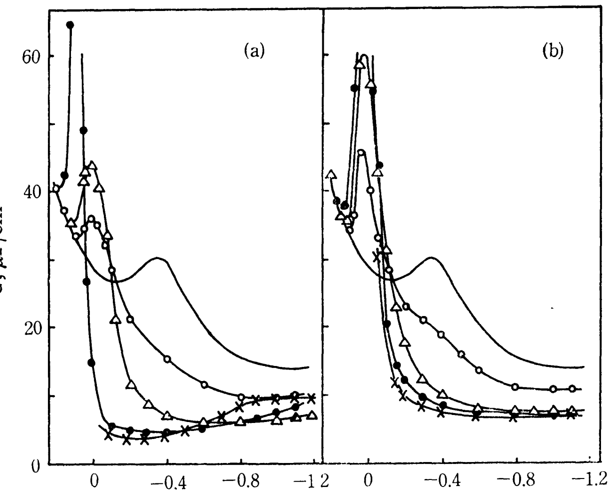


Fig. 1. The differential capacity *vs.* potential curves.
25 °C, adsorption time of 5 s, (a) 1 N aqueous sulfuric acid +Triton X-45 (solid line: 0 mg/l, ○: 10 mg/l, △: 20 mg/l, ●: 60 mg/l, ×: 200 mg/l), (b) 1 N aqueous sulfuric acid +Triton X-405 (solid line: 0 mg/l, ○: 10 mg/l, △: 20 mg/l, ●: 40 mg/l, ×: 100 mg/l).

In the case of high bulk concentration of Triton X-45, the differential capacity ascends gradually as the potential becomes more cathodic and finally becomes constant independent of potential. The ascent at the cathodic potential can hardly be ascribed to adsorption or desorption but rather to the formation of a multilayer of Triton X as stated by Barradas,[7] since the capacity after the ascent attains a constant value lower than that in the blank solution in a relatively wide range of potential. However, the ascent of differential capacity is scarcely seen in the case of Triton X-405. Since it becomes marked with decreasing $\bar{M}$ in the cathodic potential, it might be more easy for Triton X of low $\bar{M}$ to form the multi-layer.

Dependence of Differential Capacity on Adsorption Time. The differential capacity *vs.* time curve was measured at −0.6 V where the adsorption always attains equilibrium or saturation to form the monolayer. Figures 2-(a) and (b) show the C-$t^{1/2}$ relations of Triton X-45 and X-405, which indicate that the adsorption of Triton X is controlled by diffusion in a relatively low bulk concentration in the same way as in the cases of organic polymers.[2,3]

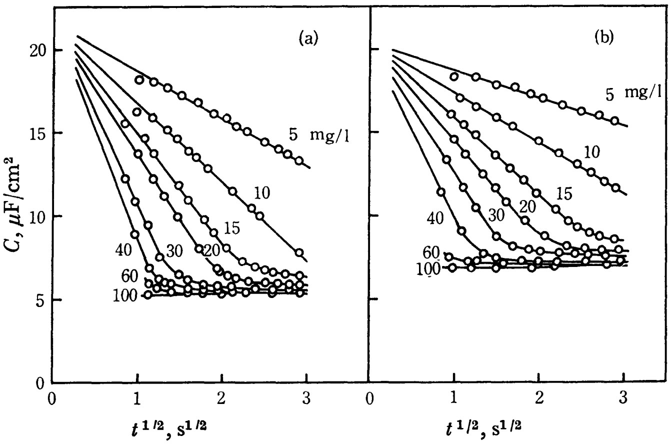


Fig. 2. The differential capacity *vs.* square root of time curves. 25 °C, −0.6 V, (a) 1 N sulfuric acid solution+Triton X-45, (b) 1 N sulfuric acid solution+Triton X-405.

In the limiting case controlled by linear diffusion, the following relation (1)[8] can be derived from the Koryta equation[1] with the Frumkin parallel condenser model.[9]

$$C = C_0 - 0.736(C_0 - C_s)D^{1/2}\Gamma_m^{-1}at^{1/2} \quad \text{for } t < t_m \qquad (1)$$

where C_0 and C_s are unit area capacities (μF/cm²) for θ (coverage) = 0 and $\theta = 1$, a the bulk concentration (mol/cm³), D the diffusion coefficient (cm²/sec), t the adsorption time (sec), t_m the time required to attain the saturated adsorption to form the monolayer and Γ_m the maximum surface concentration (mol/cm²). Equation (1) holds for $t < t_m$. However, when $t \geq t_m$, the differential capacity becomes constant as follows.

$$C = C_s \qquad (2)$$

It is seen from Eqs. (1) and (2) that C decreases linearly with $t^{1/2}$ or a when the adsorption is controlled by diffusion ($t < t_m$), while C becomes constant at the saturated adsorption ($t \geq t_m$).

The C-$t^{1/2}$ relation in Fig. 2 consists of two linear portion; one corresponding to that of diffusion-controlled adsorption (C decreases with $t^{1/2}$), and the other to that of saturated adsorption (C is constant). Thus, the results in Fig. 2 are explained by Eqs. (1) and (2). Extrapolation of the two linear portions gives the value of t_m. Though the differential capacity at the adsorption equilibrium somewhat depends on bulk concentration, the initial linear portion was extrapolated

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[8] P. W. Board, D. Britz, and R. V. Holland, *Electrochim. Acta*, **13**, 1633 (1968).

[9] A. N. Frumkin, *Z. Phys.*, **35**, 792 (1926).

to that of C_s for the sake of convenience. The observed C_s may be the value for the multi-layer, but the error due to the selection of C_s is considered to be small because of the small concentration dependence of C at the adsorption equilibrium. It is possible to calculate Γ_m by substituting t_m into the Koryta equation on the assumption of D. Directly obtainable values of $at_m^{1/2}$ $(=\Gamma_m/0.736D^{1/2})$ are also given in Table 1.

Polarograms. The adsorption behavior of surface-active compounds can also be investigated by the inhibition effect on current. Γ_m can be calculated by use of the Koryta equation from the instantaneous current *vs.* time relation (*i-t* curve) where the limiting current is inhibited by diffusion-controlled adsorption.

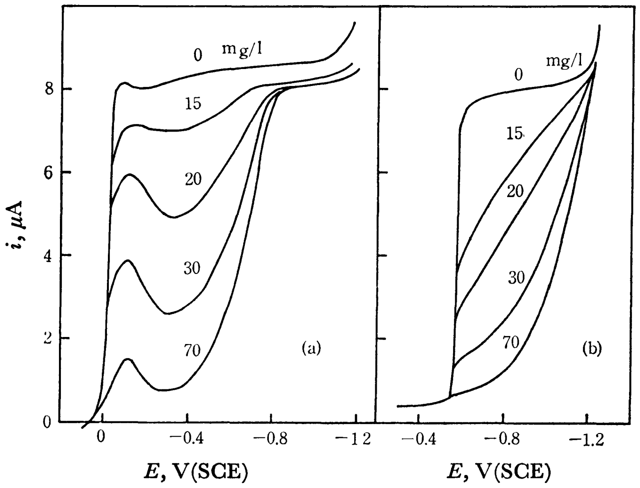

Fig. 3. Polarograms inhibited by Triton X-405.
1 N sulfuric acid solution + Triton X-405, (a) depolarizer: 1 mM Cu^{2+}, (b): depolarizer: 1 mM Cd^{2+}.

Figures 3-(a) and (b) give typical examples of the inhibition effect of Triton X-405 on the reduction of Cu^{2+} and Cd^{2+} in 1 N sulfuric acid. The reaction is depressed with increasing bulk concentration in both cases. The current peak at *ca.* −0.1 V for Cu^{2+} (Fig. 3-(a)) may be due to the desorption of Triton X-405 since the desorption peak is revealed at *ca.* −0.1 V in the *C-E* curves (*cf.* Fig. 1-(b)). The current begins to increase at *ca.* −0.7 V for Cu^{2+} and at *ca.* −1.0 V for Cd^{2+} (Fig. 3-(b)). The decrease of the inhibition effect can hardly be ascribed to the desorption of inhibitor but rather to the sufficient overpotential in view of the results in Fig. 1.

Instantaneous Current vs. *Time Curves.* The *i-t* relations for the reduction of Cu^{2+} and Cd^{2+} were examined at the potentials of −0.3 and −0.8 V, where the currents are most depressed. Since the *i-t* curves for the inhibition effect of Triton X on cadmium deposition showed a tendency similar to that on copper deposition, the latter is discussed herewith. Figures 4-(a) and (b) show the *i-t* curves of copper deposition inhibited by Triton X-100 and X-405. The initial portion of the *i-t* curve for the process inhibited by Triton X coincides with that for the process with no inhibitor, while the limiting current decreases rapidly at a certain time and finally the reaction is depressed almost completely after full coverage is attained. The time required to attain complete inhibition becomes shorter as the content of Triton X is increased.

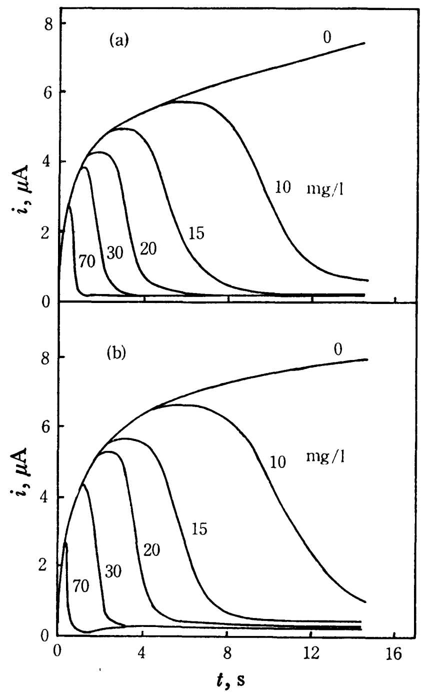

Fig. 4. Instantaneous current *vs.* time curves.
25 °C, −0.3 V, 1 mM Cu^{2+}, (a) 1 N sulfuric acid solution + Triton X-100, (b) 1 N sulfuric acid solution + Triton X-405.

The tendency of *i-t* curves for the process inhibited by PVP in 1 N sulfuric acid is similar to that in the case of Triton X. However, the *i-t* curves for the process inhibited by PEG[3] show a different tendency, complete inhibition not being attained even at $\theta=1$. The tendency becomes more marked as $\bar{M}$ decreases, that is, the current after attainment of the full coverage depends distinctly on the bulk concentration especially in the case of a relatively low $\bar{M}$ of PEG. Such a tendency can be expected from the behavior of differential capacity which depends on the bulk concentration after attainment of adsorption equilibrium. As seen in Fig. 4, the current after t_m is almost completely inhibited by Triton X in spite of the concentration dependence of differential capacity after attainment of adsorption equilibrium (Fig. 2). Thus, the concentration dependence of C after $t \geq t_m$ may be caused by the formation of a multi-layer.

The time required to attain complete inhibition is given by extrapolating the portion of rapidly decreasing current in *i-t* curve to $i=0$. The t_m values obtained from the relations of C-$t^{1/2}$ and *i-t* are expressed by t_{mc} and t_{mi}, respectively.

Maximum Surface Concentration of Triton X. The values of $at_{mc}^{1/2}$ and $at_{mi}^{1/2}$ are given in Table 1, since the directly obtainable term in the Koryta equation is $at_m^{1/2}$ which corresponds to the ratio of Γ_m to $D^{1/2}$. The $at_{mc}^{1/2}$ (or $at_{mi}^{1/2}$) value somewhat depends on a, *viz.*, $at_{mc}^{1/2}$ (or $at_{mi}^{1/2}$) becomes somewhat large with a. Such a phenomenon was also observed in the case of PVP[2] and the variation of $at_{mc}^{1/2}$ with a was explained by means of the concentration dependence of diffusion coefficient or the effect of spherical diffusion.

Table 1. Comparison of $at_{mc}^{1/2}$ with $at_{mi}^{1/2}$.

Triton X	$at_{mc}^{1/2}$ a) (mg/l·s$^{1/2}$)	$at_{mi}^{1/2}$ b) (mg/l·s$^{1/2}$)	
		Cu^{2+}	Cd^{2+}
X- 45	35.2	34.8	35.1
X-100	35.4	39.7	42.1
X-205	30.7	37.5	40.6
X-405	43.5	42.5	47.3

a) The mean values of $at_{mc}^{1/2}$ at 5, 10, 15, and 20 mg/l.
b) The mean values of $at_{mi}^{1/2}$ [12] at 10, 20, and 30 mg/l.

The $at_{mc}^{1/2}$ values in Table 1 are the mean values of *a* at 5, 10, 15, and 20 mg/l, and the $at_{mi}^{1/2}$ values are those at 10, 20, and 30 mg/l. The Γ_m values of Triton X were calculated from the mean values of $at_{cm}^{1/2}$ (or $at_{mi}^{1/2}$) and D[10] assumed by Scholtan's relation[11] ($\bar{M}D^2=10^{-8}$).

Barradas and Kimmerle[6,7] give Γ_m values of Triton X-100 as follows: 22×10^{-10} mol/cm^2 by the interfacial tension measurement[7] and 1.3—1.4×10^{-10} mol/cm^2 by the observation of suppression of polarographic oxygen wave.[6] They have ascribed the disagreement of the results to the formation of a multi-layer, namely, Γ_m by the electrocapillary data corresponds to that of the multi-layer adsorbed perpendicularly with the alkyl end in contact with mercury, while Γ_m by the suppression effect corresponds to that of nearly monolayer which is adsorbed on mercury with planar configuration. The Γ_m values given in Table 2 are considered to be those of the monolayer, since the dependence of differential capacity and that of inhibition upon the diffusion process of adsorbates may be caused mainly by the monolayer formation. From the linear relation of log Γ_m *vs.* log $\bar{M}$ with a slope of *ca.* -1, the configuration of monolayer of Triton X is expected to be flat, which is similar to the cases of PVP[2] and PEG ($\bar{M}\geq600$).[3]

The relation between C_s and thickness of adsorbed layer can be expressed by

$$C_s = \varepsilon/(4\pi\delta) \tag{3}$$

where ε and δ are the dielectric constant and thickness of the adsorbed layer, respectively. The C_s of Triton X may correspond to that of the multi-layer, since it is relatively low and varies considerably with $\bar{M}$ as compared with the cases of PVP[2] and PEG.[3] The considerable dependence of C_s on $\bar{M}$ is inconsistent with the planar configuration of monolayer at the interface under the assumption of ε=constant. The fact that C_s becomes larger with the increase in $\bar{M}$ is also inconsistent with the configuration of monolayer adsorbed perpendicularly, because C_s should become small with increasing $\bar{M}$ in view of the inverse proportionality between δ and C_s (*cf.* Eq. (3)). Consequently, the configuration of multi-layer adsorbed perpendicularly, assumed by Barradas, is applicable to the results of C_s. It must be taken into account that Triton X of low $\bar{M}$ is apt to form the multi-layer as shown in Fig. 1.

Shape of Instantaneous Current vs. *Time Curve.* Some theoretical approaches to elucidate the polarographic current *vs.* time curve have been given.[1,12,13] The *i-t* curve for the system where the limiting current is inhibited by diffusion-controlled adsorption will be discussed, Weber *et al.*[12] and Kůta and Smoler[13] solved the problem of the inhibition effect on the rate constant of electrode reaction. Matsuda[14] has recently introduced the following theoretical equation for the *i-t*

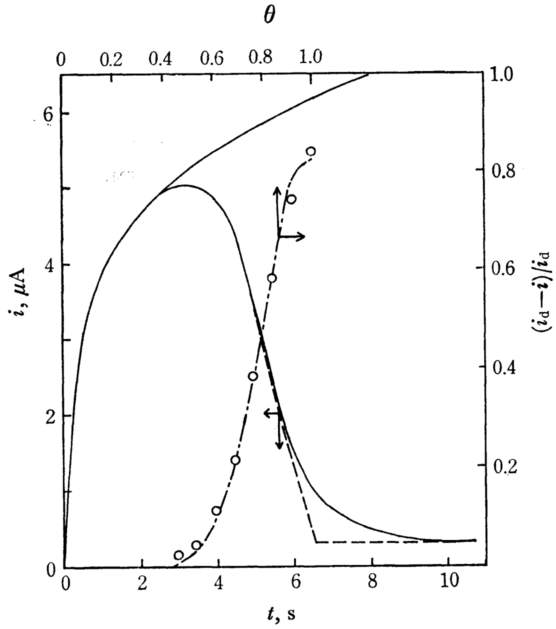

Fig. 5. The time-dependence of instantaneous current inhibited by Triton X, observed or calculated, and the coverage-dependence of inhibition by Triton X.
1N sulfuric acid solution + Triton X-100 of 15 mg/l, 1 mM Cu^{2+}, -0.3 V, *i-t* curves (solid lines: observed curves with and without Triton X, broken line: theoretical curve), $[(i_d-i)/i_d]$-θ curve (circles: observed curve with 15 mg/l Triton X, dashed-dotted line: theoretical curve).

Table 2. Maximum surface concentration and minimum differential capacity of Triton X.

Triton X	Γ_m a)	Γ_m b)	Γ_m c)	C_s
X- 45	1.38×10^{-10}	1.32×10^{-10}	1.33×10^{-10}	5.2
X-100	8.00×10^{-11}	8.96×10^{-11}	9.53×10^{-11}	6.1
X-205	3.62×10^{-11}	4.42×10^{-11}	4.79×10^{-11}	6.5
X-405	2.45×10^{-11}	2.39×10^{-11}	2.66×10^{-11}	6.9

a) Γ_m by means of differential capacity measurenents.
b) Γ_m by means of measurements of the inhibition effect on electrodeposition of copper.
c) Γ_m by means of measurements of the inhibition effect on electrodeposition of cadmium.

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10) The values of the diffusion coefficient estimated with $MD^2=10^{-8}$ are 4.84×10^{-6} cm^2/s for Triton X-45, 3.94×10^{-6} for X-100, 3.04×10^{-6} for X-205, and 2.26×10^{-6} for X-405.

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

12) J. Weber, J. Koutecky, and J. Koryta, *Z. Electrochem.*, **63**, 583 (1959).

13) J. Kůta and I. Smoler, *ibid.*, **64**, 285 (1960).

14) H. Matsuda, *Rev. Polarog.* (Kyoto), **14**, 87 (1967).

curve assuming that the adsorbed films are perfectly immobile.

$$i = i_{\mathrm{d}}\frac{(1.35\lambda_{\infty}t^{1/2})^{1.091}}{1+(1.35\lambda_{\infty}t^{1/2})^{1.091}} \tag{4}$$

where i and i_{d} are the instantaneous currents with and without adsorbates, respectively, and λ_{∞} is given by the following:

$$\lambda_{\infty} = [\lambda_2 + (1-\theta)A/[(1-\theta)\{-\ln(1-\theta)\}]^{1/2}]\theta^{-1}$$

$$\lambda_2 = k_2/D_0^{1/2}, \qquad A = D_0/R_{\mathrm{m}} = K'\theta^{z}$$

where k_2, D_0, and R_{m} are respectively the rate constant of forward reaction on the adsorbed surface, the diffusion coefficient of oxidized form of depolarizer and the mean radius of the congregated molecules adsorbed at the interface. K' and z are the arbitrary constants. A typical example in which the limiting current of copper deposition is inhibited by Triton X of 15 mg/l is given in Fig. 5 and shown by the solid line. The theoretical curve whose parameters ($\lambda_2=0.020$, $K'=0.347$, $z=-11.0$, and $t_{\mathrm{mi}}=6.5$) are estimated from experimental data is given by the broken line. The shape of *i-t* curve is well explained by Matsuda's equation except for the region in the neighborhood of $t=t_{\mathrm{mi}}$. Figure 5 shows also the inhibition effect by means of $(i_{\mathrm{d}}-i)/i_{\mathrm{d}}$ *vs.* θ relation. The coverage is given by the Koryta equation as $\theta=(t/t_{\mathrm{mi}})^{1/2}$. Inhibition is hardly seen at a small coverage and then a sharp rise occurs at a certain coverage. Such a tendency is always revealed by the limiting current which is depressed by diffusion-controlled adsorption. The coverage at which the sharp rise of inhibition occurs may be dependent on the properties of the adsorbates and on the parameter, z, in Eq. (4). The shape of the *i-t* curve in a relatively ideal system can be explained with Eq. (4). However, further approaches must be made to explain the behavior somewhat deviating from the ideal one, *e.g.*, the *i-t* curve inhibited by PEG of a relatively low $\bar{M}$.[3]