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Adsorption of Organic Polymers on Platinum Electrode

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The adsorption behavior of polyvinylpyrrolidone (PVP), polyethyleneglycol (PEG), and alkylphenoxy polyethoxy ethanols (Triton X) on a smooth platinum electrode was investigated by observation of the inhibition effect on the electrosorption of hydrogen and oxygen in the potential range between hydrogen and oxygen evolution. The adsorption of PVP, PEG, and Triton X on platinum always took place within the potential range from −0.20 to 1.25 V *vs.* SCE, the inhibition effect on the electrosorption of hydrogen and oxygen being distinctly shown. The order of inhibition of these adsorbates was Triton X$>$PVP$>$PEG. The inhibition effect became larger in most cases with decreasing mean molecular weight of adsorbate. In contrast to the case with a mercury, the adsorbates were oxidized or reduced on the platinum electrode in the adsorption range, the anodic peak due to oxidation being distinctly revealed in the case of PEG.

Many organic polymers are adsorbed so strongly on a DME that the adsorption process is mainly controlled by diffusion.[1–5] The adsorption behaviors of PVP (polyvinylpyrrolidone),[1,6] PEG (polyethyleneglycol),[2,7] and Triton X (alkylphenoxy polyethoxy ethanols)[5,8] investigated at the mercury/solution interface, are explained by means of the Koryta equation,[9] their saturated adsorption being established after diffusion process.

The adsorption of various organic substances on a solid electrode has been investigated by many authors from the viewpoint of corrosion inhibitors and organic additives in electrodeposition, but the adsorption of organic polymers on a solid electrode has been given little attention. We investigated the adsorption of water-soluble polymers on a smooth platinum electrode by observing the inhibition effect on the electrosorption of hydrogen and oxygen.

PVP has high adsorbability due to pyrrolidone radicals containing ketone radical and nitrogen atom. PEG is a polymer of ethylene oxide, extensible and highly crystalline. Triton X is a surface active agent

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

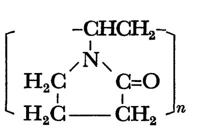
2) T. Yoshida, T. Ohsaka, and M. Suzuki, *ibid.*, **45**, 3245 (1972).

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

4) H. Jehring and E. Horn, *Monatsber. Deut. Akad. Wiss. Berlin*, **10**, 295 (1968).

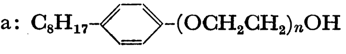
5) T. Ohsaka, H. Yamamoto, and T. Yoshida, This Bulletin, **46**, 1320 (1973).

6) Molecular formula:



7) Molecular formula: $HO(CH_2CH_2O)_nH$

8) Molecular formula:



9) J. Koryta, *Collect. Czech. Chem. Commun.*, **18**, 206 (1953).

prepared by the reaction of *t*-octylphenol with ethylene oxide.

Experimental

The test electrodes were a platinum plate (1.870 cm^2), a platinum disk (0.071 cm^2) and platinum wire (0.160 cm^2). The counter electrode was a platinum plate having sufficiently large surface area, and the potentials were determined in reference to the saturated calomel electrode (SCE). Experiments were carried out in 1 N sulfuric acid at 30°C in an atmosphere of purified nitrogen. Solutions were prepared with chemical grade reagents and triply-distilled water. PVP (BASF), PEG (Sanyo Chemical Industry), and Triton X (Rohm and Haas) were used without further purification: their mean molecular weight ($\bar{M}$) were 750000, 37000, and 10000 for PVP, 8400, 1000, and 600 for PEG and 2000 (X-405), 1100 (X-205), and 650 (X-100) for Triton X. Potentiostat (Nichia Keiki) and function generator (Nichia Keiki) were used for potential scanning. The test electrode, cleaned with concentrated nitric acid, was pretreated by cyclic scanning at a rate of 10 V/s in 1 N sulfuric acid in order to obtain reproducible results. The cyclic scanning curve between −0.20 and 1.25 V was then recorded at a scanning rate of 0.1 V/s by means of a high response X-Y recorder (Toa Electronics). The differential capacity at 1 kHz was determined 5 min after setting the electrode potential by means of a universal bridge (Yokogawa).

Results and Discussion

During the anodic scanning (Fig. 1), adsorbed hydrogen is removed in the potential range −0.2—0.1 V, and an oxygen monolayer is formed in the range 0.55—1.25 V.[10–12] The potential range 0.1—0.55 is the so-called double layer charging region where platinum can be regarded as an ideally polarizable electrode. During the cathodic scanning, the peak at 0.5 V is caused by the reduction of adsorbed oxygen and two peaks between 0.1 and −0.2 V are caused by the electrosorption of hydrogen. The inhibition effect of polymer on the electrosorption can be examined from the decreasing amount of charge of adsorbed hydrogen or oxygen obtained by suitable integration. However, it will be discussed mainly by comparison of the current values at a certain potential, since the content of charge obtained by integrating the region extended over the wide potential range is too complicated due to the oxidation or reduction of adsorbates.

Adsorption of PVP. Figure 1 shows the potentiostatic *i-E* curves inhibited by PVP of $\bar{M}=10000$ whose inhibition effect is the most marked of the three kinds of PVP. During the course of anodic scanning, the two peaks due to the weakly and strongly adsorbed hydrogen become one peak having a constant current independent of the increase of PVP concentration. In the adsorbed oxygen region, the inhibition effect is revealed at the potentials 0.6—1.0, while the anodic current increases in the range 1.0—1.25 V with the addition of PVP. Such an increase may be ascribed to either the growth of oxygen layer for the saturated electrosorption at a more positive potential depressed in the range 0.6—1.0 V, or to the oxidation of adsorbed PVP. Since the reduction peak of adsorbed oxygen decreases with increasing PVP concentration (*i.e.*, the amount of adsorbed oxygen decreases with the addition of PVP), the oxidation of PVP may cause the current increase in the anodic range 1.0—1.25 V. During the course of cathodic scanning, the current in the double layer region increases with the addition of PVP. This might result from the reduction of adsorbed PVP since the peak height of cathodic current increases with increasing content of PVP in the adsorbed hydrogen region in spite of the decrease of anodic peak current in this region.

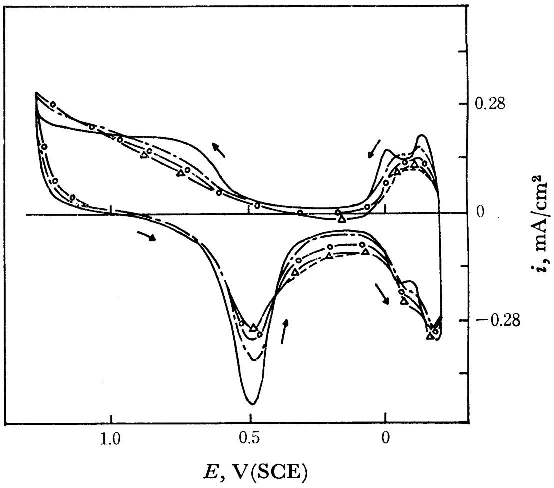


Fig. 1. Potentiostatic *i-E* curves on platinum electrode in the solution of 1 N sulfuric acid + PVP, $M=10000$.
30 °C, 0.1 V/s, concentration of PVP (—: 0 mg/l PVP, —·—: 10 mg/l, -○-: 50 mg/l, -△-: 150 mg/l, ---: 200 and 300 mg/l).

If adsorption or desorption of PVP takes place within the scanning range, the diffusion of adsorbates may influence the adsorption behavior in a similar way to that on a mercury electrode.[1,2,4,5] The dependence of current value on the scanning rate shows a linear relation, which implies that the diffusion of adsorbates has no influence on the adsorption behavior and that PVP always establishes the adsorption equilibrium. Such a dependence of current value is also revealed in the cases of PEG and Triton X.

The anodic peak of the weakly adsorbed hydrogen (P_H) and the cathodic peak of the adsorbed oxygen (P_0) are markedly depressed by the addition of PVP. The dependence of inhibition effect on PVP content is examined in these two regions as shown in Fig. 2. The degree of inhibition is given by $(i_b-i)/i_b$ or $(Q_b-Q)/Q_b$, where i_b or Q_b is the current or charge in solution without adsorbates.

For the oxidation of weakly adsorbed hydrogen (P_H), the degree of inhibition increases sharply until 30 mg/l of PVP and then it increases slowly with increasing PVP concentration (Fig. 2-(a)). The shapes of curves obtained from the peak currents agree approximately with those obtained from the charges. The order of inhibition effect is $\bar{M}=10000>\bar{M}=750000>\bar{M}=37000$

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10) M. W. Breiter, *Electrochim. Acta*, **7**, 25 (1962); *Annals New York Acad. Sci.*, **101**, 709 (1963); *J. Phys. Chem.*, **68**, 2249 (1964).

11) F. G. Will, *J. Electrochem. Soc.*, **112**, 451 (1965).

12) H. A. Laitinen and C. G. Enke, *ibid.*, **107**, 773 (1960); K. J. Vetter and J. W. Schultze, *J. Electroanal. Chem.*, **34**, 141 (1972).

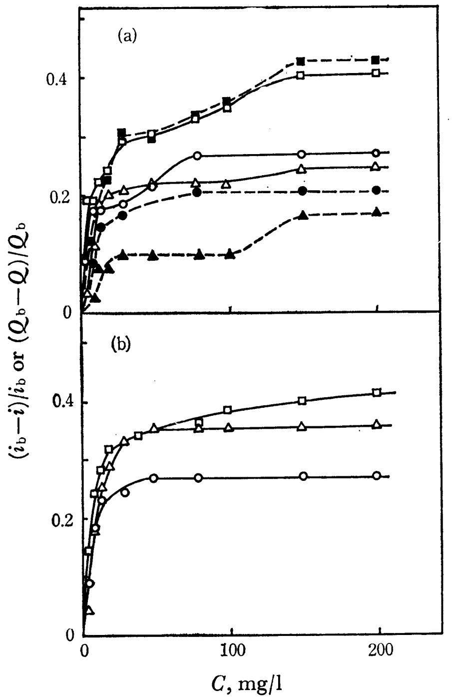

Fig. 2. Concentration dependence of the degree of inhibition on platinum electrode in the solution of 1N sulfuric acid +PVP.
30 °C, 0.1 V/s, solid lines: results from $(i_b-i)/i_b$, broken lines: results from $(Q_b-Q)/Q_b$, (a) the inhibition effect on the anodic peak due to electrosorption of hydrogen, □,■: $\bar{M}$=10000, △,▲: $\bar{M}$=37000, ○,●: M=750000, (b) the inhibition effect on the cathodic peak due to electrosorption of oxygen, □: $\bar{M}$=10000, △: $\bar{M}$=37000, ○: M=750000.

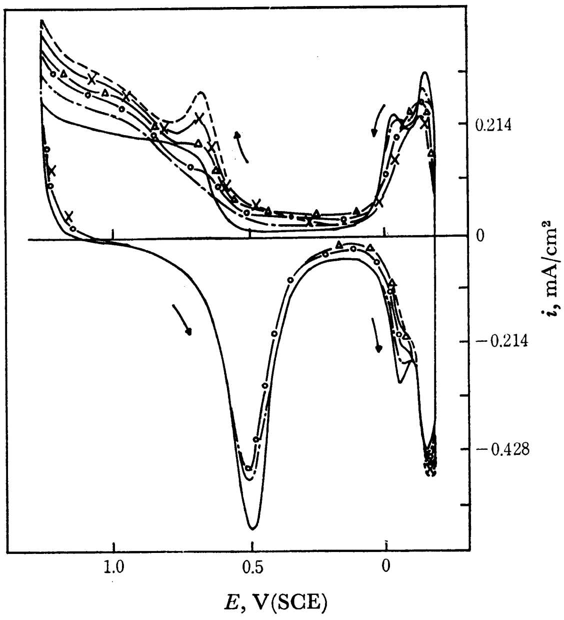

Fig. 3. Potentiostatic i-E curves on platinum electrode in the solution of 1N sulfuric acid + PEG, M=1000.
30 °C, 0.1 V/s, concentration of PEG (——: 0 mg/l PEG, —·—: 10 mg/l, -○-: 30 mg/l, -△-: 80 mg/l, -×-: 200 mg/l, ---: 1000 mg/l).

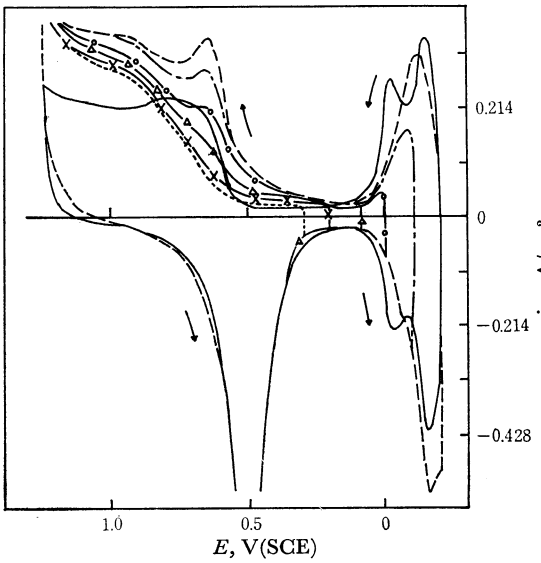

Fig. 4. Potentiostatic i—E curves on platinum electrode in the solution of 1N sulfuric acid + 1000 mg/l PEG, $\bar{M}$=600.
30 °C, 0.1 V/s, potential ranges (---: −0.2~1.25 V, —·—: −0.1~1.25, -○-: 0.0~1.25, -△-: 0.1~1.25, -×-: 0.2~1.25, ···: 0.3~1.25 V), solid line: i-E curve in the solution without adsorbates.

for the bulk concentration greater than 100 mg/l.

For the reduction of adsorbed oxygen (P_0), the degree of inhibition becomes also constant after the sharp increase, and the order of inhibition effect is $\bar{M}$=10000>$\bar{M}$=37000>$\bar{M}$=750000 (Fig. 2-(b)). Since the anodic peak in the adsorbed hydrogen region seems to be influenced by the reduction current of adsorbates, the degree of inhibition obtained from Fig. 2-(a) is somewhat doubtful. The order in Fig. 2-(b) is therefore more reliable than that in Fig. 2-(a). The inhibition effect seems to increase with the decrease in $\bar{M}$.

Adsorption of PEG. Figure 3 shows the adsorption behavior of PEG on a platinum electrode. The anodic peak P_H and the cathodic peak P_0 are depressed by the addition of PEG, while the anodic peak appears at *ca.* 0.7 V (P_{PEG}). The anodic current becomes larger than that in the solution without adsorbates in a range more positive than P_{PEG} and in the double layer charging region. The peak of P_{PEG} may result from the oxidation of adsorbed PEG in view of the depression of P_0 with increasing content of PEG. In a weakly adsorbed hydrogen region the cathodic peak height increases with increasing PEG concentration, which may be ascribed to the reduction of PEG. The degree of inhibition due to the adsorption of PEG can be hardly estimated from these results, as the reduction or oxidation of adsorbed PEG itself overlaps the inhibition effect.

For the purpose of examining the anodic peak at *ca.* 0.7 V (P_{PEG}), the cathodic limit of cyclic scanning was varied as shown in Fig. 4. The current growing at *ca.* 0.7 V begins to appear when the anodic scanning is started from 0.1 V, and a distinct peak is revealed at first by scanning from 0 V. Thus, adsorbates of the reduced type which cause the oxidaiton peak at 0.7 V seem to be produced at a more negative potential than 0.1 V, and the reduced type of adsorbates may increase as the potential becomes negative. It seems that the adsorbed amount of oxidized or reduced type of PEG depends on the electrode potential. However, the

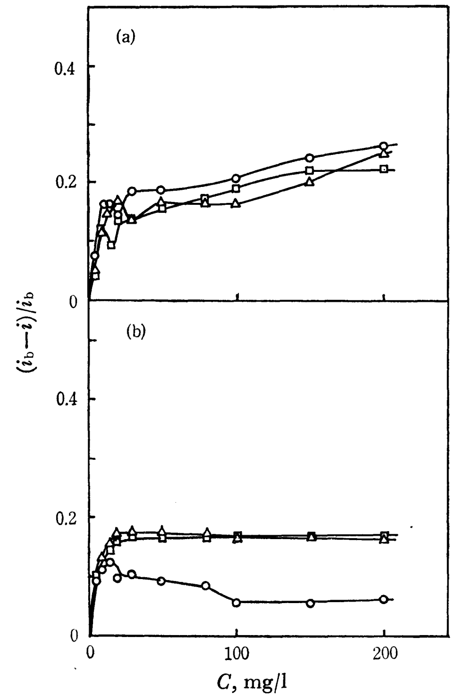

Fig. 5. Concentration dependence of the degree of inhibition on platinum electrode in the solution of 1N sulfuric acid + PEG.
30 °C, 0.1 V/s, (a) the inhibition effect on the anodic peak due to electrosorption of hydrogen, □: $\bar{M}=600$, △: $\bar{M}=1000$, ○: $\bar{M}=8400$, (b) the inhibition effect on the cathodic peak due to electrosorption of oxygen, □: $\bar{M}=600$, △: $\bar{M}=1000$, ○: $\bar{M}=8400$.

total amount of adsorbed PEG is expected to be independent of the potential from the results that the anodic peak at *ca.* 0.7 V (P_{PEG}) is not influenced by scanning after some interruption at −0.2 V and that the peak height increases linearly with the scanning rate.

The degrees of inhibition at P_{H} and P_0, estimated from the results in Fig. 3, are shown in Fig. 5. The degree of inhibition at P_{H} increases sharply until a bulk concentration of 10—20 mg/l, which may be influenced to some extent by the reduction of adsorbed PEG (Fig. 5-(a)). It decreases, however, to some extent with increasing PEG concentration just after the steep increase, after which it increases gradually. This may be ascribed to the increase of reduction current of PEG. Thus, the order of degree of inhibition (Fig. 5-(a)) is considered to be unreliable because of the overlapping of the reduction current of PEG and the oxidation current of adsorbed hydrogen.

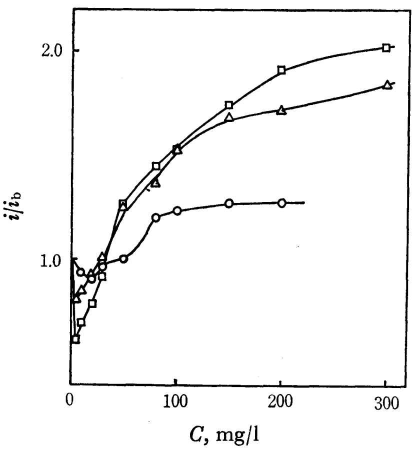

Fig. 6. Concentration dependence of the anodic peak at 0.7 V in the solution of 1N sulfuric acid + PEG.
30 °C, 0.1 V/s, □: solution of 1N sulfuric acid + PEG, $\bar{M}=600$, △: solution of sulfuric acid + PEG, $\bar{M}=1000$, ○: solution of sulfuric acid + PEG, $\bar{M}=8400$.

The degree of inhibition becomes constant (Fig. 5-(b)) for the peak of P_0 at *ca.* 20 mg/l.[13] The order of inhibition is $\bar{M}=600>\bar{M}=1000>\bar{M}=8400$, namely, the degree of inhibition increases with the decrease of $\bar{M}$.

The peak of P_{PEG}, which may result from the oxidation of PEG, is examined from the concentration dependence of i/i_b at 0.7 V (Fig. 6). In a low concentration range, the value of i/i_b is less than unity and shows a minimum indicating inhibition of the electrosorption of oxygen, but it becomes larger than unity in the concentration range greater than 30—50 mg/l. In the case of PEG of $\bar{M}=600$ and 1000 which reveal P_{PEG}, i/i_b increases with the addition of PEG, while for PEG of $\bar{M}=8400$ which reveals no P_{PEG}, it remains constant in the concentration range greater than 100 mg/l. In the i/i_b plots at 1.0 V (not shown), PEG of $\bar{M}=600$ and 1000 reveal constant i/i_b (*ca.* 1.4) in the range greater than 100 mg/l, while PEG of $\bar{M}=8400$ shows nearly constant values somewhat larger than those of the above. Thus, PEG of high $\bar{M}$ may be more difficult to be oxidized as compared with that of low $\bar{M}$.

The differential capacity at the platinum/solution interface was determined 5 min after setting the electrode potential which was scanned from negative to

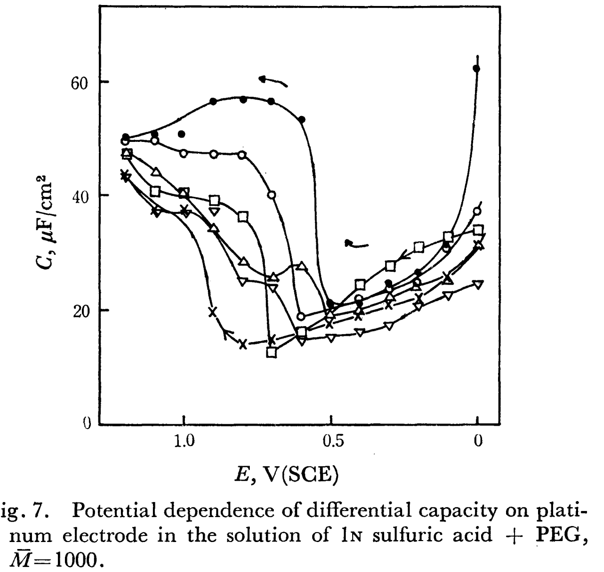

Fig. 7. Potential dependence of differential capacity on platinum electrode in the solution of 1N sulfuric acid + PEG, $\bar{M}=1000$.
30 °C, capacity was determined at 5 min after setting the electrode potential, concentration of PEG, $\bar{M}=1000$ (●: 0 mg/l PEG, ○: 10 mg/l, △: 20 mg/l, □: 50 mg/l, × : 100 mg/l, ▽: 200 mg/l).

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[13] In the case of $\bar{M}=8400$, it is peculiar that the degree of inhibition decreases gradually with PEG concentration after the appearance of a peak at *ca.* 20 mg/l. This remains to be explained.

positive (Fig. 7). In the potential range between hydrogen and oxygen evolution, there are three distinct regions for the platinum electrode. In solutions having no adsorbates, the pseudocapacity due to adsorbed hydrogen is revealed between −0.2 and 0.1 V. Hydrogen or oxygen is hardly adsorbed in the so-called double layer region 0.1—0.55 V, while the pseudocapacity due to adsorbed oxygen appears between 0.55 and 1.25 V.

The adsorbed hydrogen and oxygen regions shift to somewhat negative and positive sides, respectively, with the addition of PEG of $\bar{M}=1000$ (Fig. 7). It is certain from the capacity depression that the adsorption of PEG always occurs in these regions. In the adsorbed oxygen region, the capacity depression with increasing content of PEG is complicated. It is too difficult to discuss the capacity behavior in the adsorbed oxygen region from only the results shown in Figs. 3 and 7, though it is doubtless influenced by the oxidation of adsorbed PEG.

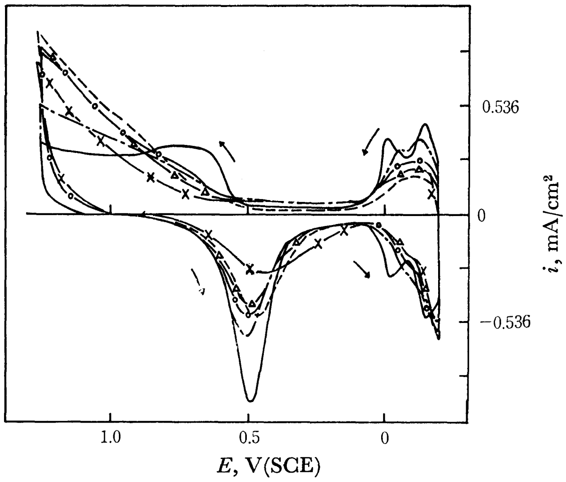

Fig. 8. Potentiostatic $i-E$ curves on platinum electrode in the solution of 1N sulfuric acid + Triton X-205, $\bar{M}=1100$. 30 °C, 0.1 V/s, concentration of Triton X (——: 0 mg/l Triton X, - - -: 30 mg/l, -○-: 100 mg/l, -△-: 200 mg/l, -×-: 400 mg/l, ---: 1000 mg/l).

Adsorption of Triton X. Figure 8 shows the i-E curves in 1N sulfuric acid containing Triton X of $\bar{M}=1100$. The degree of inhibition at P_H and P_0 and the increase of anodic current in the region $E \geq 0.9$ V are distinctly larger than those for PVP and PEG. The increase of anodic current in the region $E \geq 0.9$ V may be attributed to the oxidation of adsorbed Triton X because the peak of P_0 is depressed by the addition of Triton X. The reduction of oxidized Triton X may occur since the cathodic current increases at the potential of *ca.* 0.4—−0.2 V in the cathodic scanning. In the case of Triton X, it is characteristic that the concentration dependence of current is complicated in the potential regions $E \geq 0.9$ V and P_0. Triton X can form micelles,[14] and the above behavior can be ascribed to the formation of multilayer.

Figure 9 shows the relation between the degree of inhibition and the bulk concentration in P_H and P_0 regions. For P_H region, the degree of inhibition increases sharply until 100 mg/l and then becomes nearly constant (Fig. 9-(a)). The order of degree of inhibition is as follows: $\bar{M}=650$ (X-100)$>\bar{M}=1100$ (X-205)$>\bar{M}=2000$ (X-405). For P_0 region, the degree of inhibition *vs.* concentration curve reveals a maximum whose position seems to move to higher concentration range with increasing $\bar{M}$ (Fig. 9-(b)). In general,

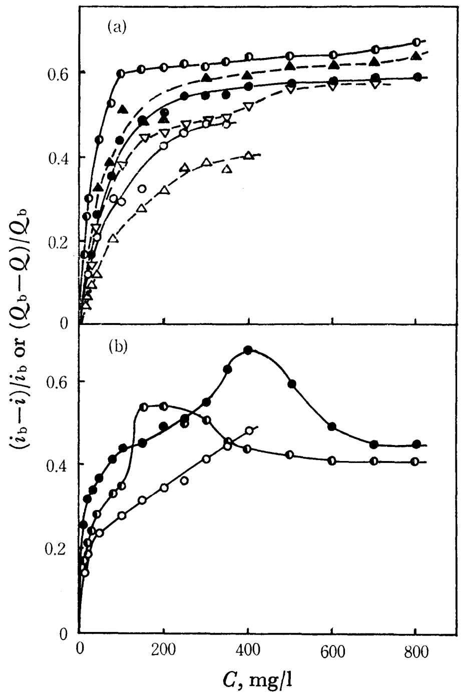

Fig. 9. Concentration dependence of the degree of inhibition on platinum electrode in the solution of 1N sulfuric acid + Triton X.
30 °C, 0.1 V/s, solid lines: results from $(i_b-i)/i_b$, broken lines: results from $(Q_b-Q)/Q_b$, (a) the inhibition effect on the anodic peak due to electrosorption of hydrogen, ◐,▲: X-100, $\bar{M}=650$, ●,▽: X-250, $\bar{M}=1100$, ○,△: X-405, $\bar{M}=2000$. (b) the inhibition effect on the cathodic peak due to the electrosorption of oxygen, ◐: X-100, $\bar{M}=650$, ●: X-205, $\bar{M}=1100$, ○: X-405, $\bar{M}=2000$.

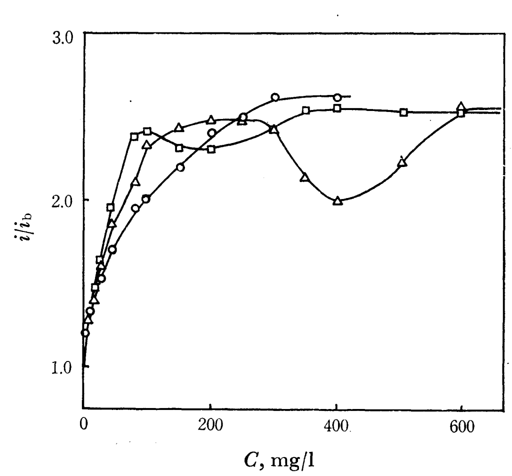

Fig. 10. Concentration dependence of anodic current at 1.2 V in the solution of 1N sulfuric acid + Triton X.
30 °C, 0.1 V/s, □: 1N sulfuric acid + Triton X-100, $\bar{M}=650$, △: 1N sulfuric acid + Triton X-205, $\bar{M}=1100$, ○: 1N sulfuric acid + Triton X-405, $\bar{M}=2000$.

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[14] R. G. Barradas and F. M. Kimmerle, *J. Electroanal. Chem.*, **11**, 128 (1966).

critical micelle concentration (CMC)[15)] of Triton X is *ca.* $10^{-2}\%$ or 100 mg/l, and the adsorption of Triton X on mercury electrode shows unusual phenomenon owing to the formation of multilayer.[5,14)] The maximum peak in Fig. 9-(b) seems to be related to the formation of multilayer.

Figure 10 shows the concentration dependence of i/i_b at 1.2 V, where the ratio of anodic current (i/i_b) is considered to be approximately proportional to the amount of oxidized Triton X on platinum. After the sharp increase, i/i_b at 1.2 V shows a minimum and then shows a nearly constant value of *ca.* 2.5. The minimum may be ascribed to the formation of a multilayer which prevents Triton X from being oxidized. However, it remains also unknown why the oxidation current increases again with the increase of Triton X content after the appearance of the minimum. It is interesting that the maximum positions in Fig. 9-(b) are nearly in agreement with the minimum positions in Fig. 10.

The inhibition effect of these polymers on the electrosorption of hydrogen or oxygen on platinum is small even in a relatively concentrated solution of adsorbate sufficient to form the monolayer. Such a small inhibition effect upon the process on a platinum electrode may be attributed to the roughness of a solid electrode, where the adsorbed layer of each polymer is considered to be irregular or porous.

Radacanu and Lorenz[16)] have examined the process on a solid electrode, which is inhibited by β-naphthoquinoline or dibenzylsulfoxide. The inhibitors are oxidized or reduced by the addition or separation of proton, which may have some connection with hydrogen evolution. Such an analysis might be useful, though the reaction of polymer on platinum is too complicated (*e.g.*, local oxidation or reduction of polymer).

The authors are grateful to Mr. Yasuyuki Konoshima for his kind assistance.

[15)] CMC: bulk concentration required to form micelle in solution, *cf.*, catalogue of Triton X by Rohm and Haas Co.

[16)] I. C. Radacanu and W. J. Lorenz, *Electrochim. Acta*, **16**, 995 (1971).