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Polarographic Studies of Dispersed Dyes Solubilized in Surfactant Solutions. I. Kinetics of Orange OT Solubilized in Surfactant Solutions

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Orange OT (1-*o*-tolyl-azo-2-naphthol) dissolved in an aqueous ethanol solution and solubilized in various surfactant solutions, containing a citric acid-disodium hydrogen phosphate buffer, showed well-defined irreversible polarographic waves. The anionic, cationic, and nonionic surfactants used were sodium dodecyl sulfate (SDS) and sodium dodecylbenzenesulfonate (SDBS), dodecyltrimethylammonium chloride (DTMAC), and polyoxyethylene nonylphenyl ether (NP-10) respectively. The values multiplying the transfer coefficient by the number of electrons involved in the activation step, (αn_a), were calculated from the semilogarithmic plot of the wave. The plots of αn_a against the half-wave potential of Orange OT for each solution showed that a marked surfactant electric-charge dependence of αn_a was observed with a variety of surfactant solutions; *i.e.*, the electric-charges of the surfactant molecules or micelles remarkably affected the electrode kinetics of the solubilized Orange OT. No matter what Orange OT is an uncharged species, Orange OT solubilized in the anionic surfactant solutions seemed to behave in the electrode process as if it were an anionic species, and when solubilized in the cationic and nonionic surfactant solutions it seemed to behave as a cationic species.

The electrochemistry of dispersed dyes solubilized in several surfactant solutions has been described in previous papers,[1–3] mainly with regard to the mass-transfer of the micelle. Many electrochemical studies[4–6] of surfactant solutions have been published, but in most of them the surfactant concentration has usually been below the critical micelle concentration (CMC); few papers have reported concentrations above the CMC.[1–3,7] The surfactant solution may be regarded as a new solvent taking the place of aqueous and nonaqueous solvents in the sense that it has characteristics of both in electrochemistry. The solubilized system in actuality is heterogeneous, in spite of its homogeneous appearance. An electrode process of a surfactant solution, however, involves many problems: 1) the adsorption state and equilibrium of surfactant molecules or micelles on an electrode; 2) the diffusion of an electroactive substance through bulk and adsorption phases at the electrode;[8,9] 3) an electroactive species adsorbing or not adsorbing in the adsorption phase; 4) the charge in the electric double layer affecting the electrode processes; 5) the electric-charge of a surfactant affecting the double layer, *etc.* The present paper will deal with experimental results on a few of the above problems and will discuss various possible interpretations.

The reason for using Orange OT is that this dye is water-insoluble[10] and electroactive.

Determination of αn_a, *m, and* $k^0_{\mathrm{f,h}}$. Generally, the reaction occurring at the electrode for a totally irreversible wave may be described by the equation:

$$\mathrm{O} + ne \longrightarrow \mathrm{R} \tag{1}$$

where O and R are the oxidized and reduced forms of a substance respectively. The cathodic current, i, that results from the reduction of O at any potential is described by the equation:

$$i = nFAC_{\mathrm{o}}{}^0 k^0_{\mathrm{f,h}} \exp\left[-\alpha nF(E-E^0)/RT\right] \tag{2}$$

where n is the number of electrons involved in the overall reaction; F, the Faraday constant; A, the area of the electrode; $C_{\mathrm{o}}{}^0$, the concentration of O at the surface of the electrode; $k^0_{\mathrm{f,h}}$, the heterogeneous rate constant at 0 V *vs.* N.H.E.; α, the transfer coefficient; E, the electrode potential reffered to the S.C.E.; E^0, the formal potential; R, the gas constant; and T, the absolute temperature. For couples whose formal potentials are unknown or even unmeasurable (as is the case with many totally irreversible couples), however, a convenient and interpretable potential instead of the formal potential is 0 V *vs.* N.H.E. (−0.246 V *vs.* S.C.E. at 25 °C).

Taking into account the variation in the $C_{\mathrm{o}}{}^0$ with the current, Koutecký *et al.*[11] calculated the values of the $F(\chi)$ for the mean current:[12]

$$\bar{i}_{\mathrm{irrev}} = \bar{i}_{\mathrm{rev}}\bar{F}(\chi) \tag{3}$$

where

$$\chi = (12/7)^{1/2}k_{\mathrm{f,h}}t^{1/2}/D_{\mathrm{o}}{}^{1/2}, \tag{4}$$

where $k_{\mathrm{f,h}}$ varies with the electrode potential given by:

$$k_{\mathrm{f,h}} = k^0_{\mathrm{f,h}} \exp\left[-\alpha n_a F(E+0.246)/RT\right] \tag{5}$$

and where i is the mean current; t, the drop time; D_{o}, the diffusion coefficient of the oxidized form, and n_a, the number of electrons involved in the activation step. For a totally irreversible process, $\bar{i}_{\mathrm{rev}}$ may be said to be equal to the mean diffusion current.

The mean current was measured instead of the instantaneous maximum current because the concentration of the solubilizable dye was very low.

Many organic compounds can generally be reduced as;[12–14]

$$\mathrm{O} + \mathrm{mH^+} \rightleftharpoons \mathrm{O'} \quad \text{(fast)} \tag{6a}$$

$$\mathrm{O'} + n_a\mathrm{e} \longrightarrow \mathrm{I} \quad \text{(rate-determining)} \tag{6b}$$

$$\mathrm{I} + (n-n_a)\mathrm{e} \longrightarrow \mathrm{R} \quad \text{(fast)} \tag{6c}$$

where m is the number of hydrogen ions, and I, the intermediate. To describe the cathodic mean current, $\bar{i}$, resulting from the above reaction, one writes this equation:

$$\bar{i} = nF\bar{A}C^0_{\mathrm{o'}}k^0_{\mathrm{f,h}} \exp\left[-\alpha n_a F(E+0.246)/RT\right] \tag{7}$$

where A is the mean surface area of the dropping mercury electrode. If the solution is well buffered, the combination of Eq. (7) with

$$K = C^0_{o'}/C^0_o C^m_{H^+} \tag{8}$$

for the equilibrium constant, K, of Eq. (6a) yields:

$$\bar{i} = nF\bar{A}C^0_o k^0_{f,h} K C^m_{H^+} \exp\left[-\alpha n_a F(E+0.246)/RT\right] \tag{9}$$

where C_{H^+} is the concentration of hydrogen ions at the electrode surface; the $k^0_{f,h}$ in Eq. (9) is the one for a first-order reaction. The essential equations, as solved by Koutecký15) for the whole rising portion of the wave, are:

$$E = -0.246 + \frac{RT}{\alpha n_a F}\ln\frac{0.886k^0_{f,h}Kt^{1/2}}{D_o{}^{1/2}}C^m_{H^+} - \frac{RT}{\alpha n_a F}\ln\frac{\bar{i}}{\bar{i}_d - \bar{i}} \tag{10}$$

$$E_{1/2} = -0.246 + \frac{RT}{\alpha n_a F}\ln\frac{0.886k^0_{f,h}Kt^{1/2}}{D_o{}^{1/2}} - \frac{2.303RT}{\alpha n_a F}m(\mathrm{pH}) \tag{11}$$

$$E^0_{1/2} = -0.246 + \frac{RT}{\alpha n_a F}\ln\frac{0.886k^0_{f,h}K}{D_o{}^{1/2}} - \frac{2.303RT}{\alpha n_a F}m(\mathrm{pH}) \tag{12}$$

Hence,

$$\frac{dE^0_{1/2}}{d(\mathrm{pH})} = -\frac{2.303RT}{\alpha n_a F}m \tag{13}$$

is obtained from Eq. (12) for the estimation of m and $k^0_{f,h}$ at a constant value of αn_a. αn_a and m are calculated from Eqs. (10) and (13) respectively. $k_{f,h}$ is evaluated from Eq. (11) or (12) if the K value is known.

αn_a and $k^0_{f,h}$ are evaluated by an alternative method. By multiplying both sides of Eq. (5) by $KC^m_{H^+}$, we obtain:

$$\log KC^m_{H^+}k_{f,h} = \frac{\alpha n_a F}{2.303RT}E + \log Kk^0_{f,h} - m(\mathrm{pH}) - \frac{0.246\alpha n_a F}{2.303RT} \tag{14}$$

for $KC_{H^+}{}^m k_{f,h}$ based on Eq. (4), Eq. (8), Ilkovič's equation, and the table of χ values calculated by Weber *et al.*11) Similarly, $Kk^0_{f,h}$ and αn_a are calculated from Eqs. (13) and (14).

Experimental

Materials. 1-*o*-Tolyl-azo-2-naphthol (Orange OT) was recrystallized twice from ethanol. E.P.-grade sodium dodecyl sulfate (SDS) was purified by two recrystallizations from ethanol after extraction with ethyl ether for 50 hr. A sample of sodium dodecylbenzenesulfonate (SDBS; the CMC based on the polarographic method16) was 3.2×10^{-3} M at 30 °C), kindly supplied by Lion Oil and Fats Co. was recrystallized from petroleum ether. C.P.-grade dodecyltrimethylammonium chloride (DTMAC) was purified by recrystallization from acetone. A sample of polyoxyethylene nonylphenyl ether (NP-$\overline{10}$) was also obtained by courtesy of the Meisei Chemical Works. Ltd., and was used without further purification. Citric acid-disodium hydrogen phosphate buffers (McIlvaine's buffer solution) were prepared from G.R.-grade reagents without purification.

Solutions. Orange OT was dissolved in 6.8 M aqueous ethanol (about 40 vol%) and solubilized in anionic, cationic, and nonionic surfactant solutions, the concentrations of which were: 2×10^{-2} M SDS, 2×10^{-2} M SDBS, 5×10^{-2} M DTMAC, and 4×10^{-2} M NP-$\overline{10}$ respectively, buffered at various pH values. Also, the dye concentrations were 5×10^{-5} M in the aqueous ethanol, 5×10^{-5} M in the SDS, 2×10^{-5} M in the SDBS, 5×10^{-5} M in the DTMAC, and 1×10^{-4} M in the NP-$\overline{10}$ solution.

The solutions of the solubilized dye in the surfactant solutions were prepared with shaking and warming to a desired temperature for several days and were measured by polarography after the solubilization equilibrium.

The pH was measured with a Toa Dempa Model HM-5A pH meter. In the case of aqueous ethanol solutions, the apparent pH values were measured.

Polarography. Polarographic measurements were carried out by using a PAR Model 170 (Princeton Applied Research Co.). The characteristic σ value of the dropping mercury electrode was 1.74 mg s^{-1} (the height of the mercury column h=87.15 cm) in all solutions except the DTMAC solution, in which σ=1.72 mg s^{-1} (h=87.05 cm). The potential of a polarograph was recorded against the S.C.E. The solutions were deaerated by bubbling pure nitrogen gas through them for an hour and by then allowing its overflow to cover the surfaces of the solutions during measurement. The SDBS solutions were measured at 45±0.1 °C, while the other solutions were measured at 25±0.1 °C corresponding to their Krafft points.

Results

The polarographic behavior of Orange OT has already been mentioned3) in detail in surfactant solutions with a constant pH value. The present paper, however, will be concerned with solutions of various pH values. The relation of the limiting current to the square-root of the height of the mercury head in all the solutions shows a linear line. The lmiting current, therefore, is proved to be the diffusion-controlled current.

A maximum of the first kind in the aqueous ethanol solution containing dissolved Orange OT was appreciably observed in pH 2.78 and 5.30 solutions (it was not observed between pH 2.78 and 5.30), and it increased with an increase in the pH value.

Since the reduction wave of Orange OT solubilized in the SDS solution overlapped the reorientation wave of SDS molecules on the mercury electrode17) at pH 4.95 and 5.88, the current of the reduction wave was not analyzed.

The potential due to the reorientation of surfactant molecules shifted unwaveringly to a negative potential with an increase in the pH in the basic solution without Orange OT, while the reorientation potential-pH relation showed a curve with a minimum at pH 4.95 in

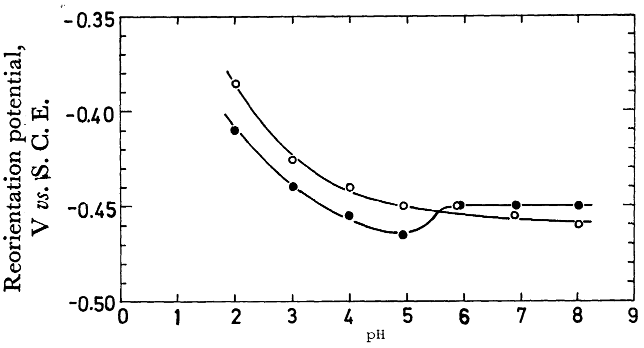

Fig. 1. Potential due to the reorientation of SDS molecules with pH: ○, SDS basic solution; ●, solution solubilizing Orange OT.

the solution solubilizing Orange OT (Fig. 1).

The reduction wave of Orange OT solubilized in the SDBS solution overlapped the tensametric wave of SDBS at pH<3.00 and could not be analyzed. The polarograph, therefore, was measured in solutions at pH>3.00.

The fine reduction wave in the DTMAC solution solubilizing Orange OT was obtained over the range of pH 1.92 to 7.99.

Two waves in the NP-1̄0 solution solubilizing Orange OT were obtained in each pH solution. The first wave was the reduction wave of Orange OT, as the wave height linearly increased with the concentration of the dye; the second wave showed a maximum wave at −0.760 V. For a more basic solution, only the first wave shifted to the negative potential. The two waves overlapped at pH 5.88, and complicated waves were observed at pH 6.89 and 8.01 (Fig. 2).

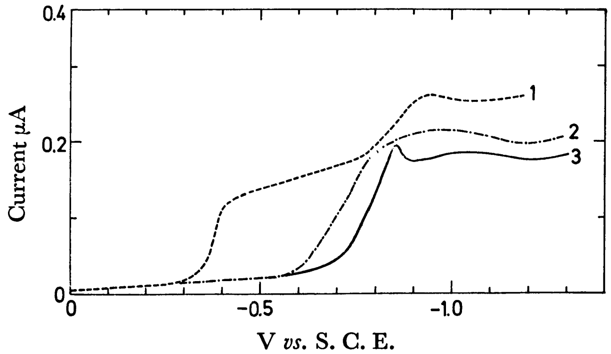

Fig. 2. Polarograms of solubilized Orange OT in NP-1̄0 solution: (1) ------, pH 3.00; (2) -·-·-, 5.88; (3) ——, 8.01.

Discussion

$E_{1/2}$—pH. The relation of the corrected half-wave potential to the pH value in each solution is shown in Fig. 3, in which the slope of each straight line is different. The equations calculated by the least-squares procedures of each relation are shown in Table 1. The slope of each straight line is different because m and αn_a are different in the variety of solutions, as will be described below. In the SDBS solution, two straight lines are obtained; they have not yet been explained.

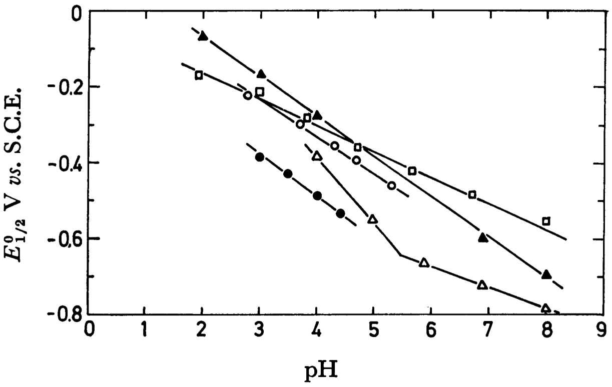

Fig. 3. $E^\circ_{1/2}$-pH plots: ○, aqueous ethanol; ▲, SDS, △, SDBS; □, DTMAC; and ●, NP-10 solutions.

Table 1. Relation of corrected half-wave potential against pH in each solution

Solution	Relation of $E^\circ_{1/2}$—pH
C_2H_5OH	$E^\circ_{1/2}=-0.094$ pH$+0.047$
SDS	$E^\circ_{1/2}=-0.107$ pH$+0.150$
SDBS	$E^\circ_{1/2}=-0.178$ pH$+0.329$[a] $E^\circ_{1/2}=-0.055$ pH-0.343[b]
DTMAC	$E^\circ_{1/2}=-0.066$ pH-0.036
NP-1̄0	$E^\circ_{1/2}=-0.108$ pH-0.055

a) Left branch b) Right branch

$E_{1/2}$—log t. According to Eq. (11), the half-wave potential shifts to less negative potentials in all the solutions with an increase in the drop time. It is found that Orange OT dissolved in an aqueous ethanol solution and solubilized in each surfactant solution is an irreversible species under the conditions investigated.

The slope of $E_{1/2}$—log t in the solution of each pH value is different, mainly because of the difference in αn_a; *e.g.*, in the DTMAC solution the slopes at the pH values of pH 3.83 and 4.70 smaller than the others, which is reasonable because the (αn_a)'s of the former are larger than those of the latter (Fig. 4).

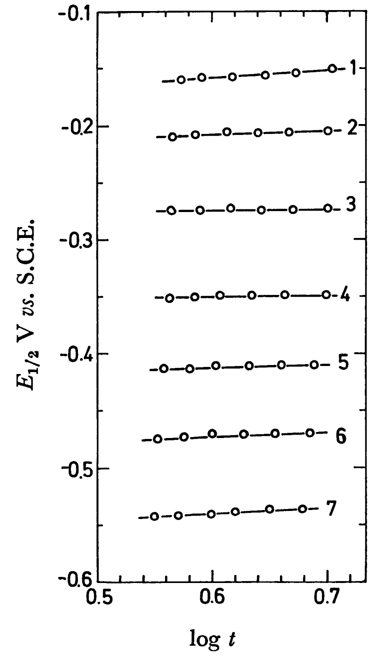

Fig. 4. $E_{1/2}$—log t plots in DTMAC solution: (1) pH 1.92; (2) 2.96; (3) 3.83; (4) 4.70; (5) 5.67; (6) 6.71; (7) 7.99.

αn_a—$E_{1/2}$. In discussing the electrode process, especially the effect of the double-layer structure on the electrode process,[18] the reaction of αn_a—$E_{1/2}$ is very important. However, the apparent value of $(\alpha n_a)_{app}$ found directly from the semilogarithmic plot of the wave, or that of the rate constant mentioned above, is markedly different from its true value.[19] The relationship between the observed value and the true value of αn_a is generally expressed by:[20,21]

$$(\alpha n_a)_{app} = \alpha n_a + (z-\alpha n_a)(\partial \Psi_1/\partial \phi)_{E_{1/2}} \qquad (15)$$

where z is the electric-charge on the reacting species; Ψ_1, the potential of the outer Helmholtz plane, and

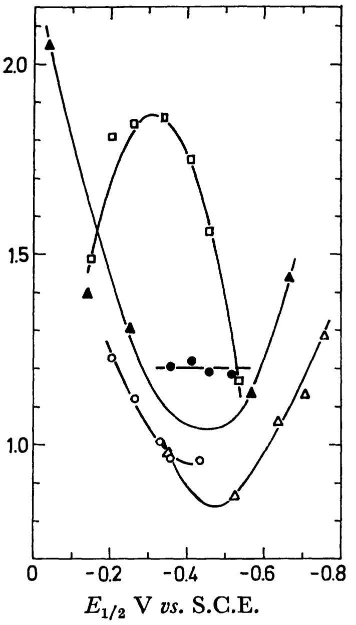

Fig. 5. Variation of $(\alpha n_a)_{app}$ with $E_{1/2}$ from semilogarithmic plot of wave: ○, aqueous ethanol; ▲, SDS; △, SDBS; □, DTMAC; and ●, NP-$\overline{1}$0 solutions.

ϕ, the potential difference between the electrode potential and the potential of the zero charge. However, most of the solutions are micellized solutions. The surfactant molecules strongly adsorb on the mercury electrode, so that the potential of zero charge can not be measured; *i.e.*, $(\partial\Psi_1/\partial\phi)_{E_{1/2}}$ can not be calculated, and the true value of αn_a can not be obtained. Therefore, only the apparent values of αn_a are shown here (Fig. 5).

In calculating $(\alpha n_a)_{app}$, the above two methods, *i.e.*, $\log i/(i_d-i)-E$ and $\log KC_{\mathrm{H}}^{m}+k_{\mathrm{f,h}}-E$, are applied. The difference between the values obtained by the two methods is very small.

The relation of $(\alpha n_a)_{app}$ to $E_{1/2}$ shows the curve passing through a minimum in the anionic surfactant solutions, and a maximum in the cationic surfactant solution. The $(\alpha n_a)_{app}$ in the nonionic surfactant and the aqueous ethanol solutions remains constant and decreases, respectively, with shift of the $E_{1/2}$ to the negative potential.

These results show that the electric-charge of the surfactant at the mercury electrode affects the electrode reaction of Orange OT. Though Orange OT itself is an uncharged species, when solubilized in ionic micelles it seems to behave in the electrode process as if it were an ionic species. In the cationic surfactant solution, $(z-\alpha n_a)$ becomes a positive value, judging from the fact that the plot of $\alpha n_a-E_{1/2}$ indicates a maximum; therefore, the electric-charge of the cationic surfactant micelle is not less than two.[22]

Most of the αn_a values obtained are larger than one, and the value of n_a seems to be 2 rather than one.

In the case of the aqueous ethanol and ionic surfactant solutions, the value of m is not obtained because αn_a varies with the half-wave potential and $k^0_{\mathrm{f,h}}$ can not be calculated.

Table 2. Heterogeneous rate constant of Orange OT solubilized in NP–$\overline{1}$0 solution

pH	$(Kk^0_{\mathrm{f,h}})^{a)}$ (cm l^2 mol^{-2} s^{-1})	$(Kk^0_{\mathrm{f,h}})^{b)}$ (cm l^2 mol^{-2} s^{-1})
3.00	3.4	4.3
3.49	5.7	3.3
4.00	3.7	3.0
4.40	2.2	1.8

a) From Eq. (11). b) From Eq. (14).

m and $Kk^0_{\mathrm{f,h}}$ of Orange OT Solubilized in an NP-$\overline{1}$0 Solution. In the case of Orange OT solubilized in NP-$\overline{1}$0, αn_a does not vary with the half-wave potential in the potential range. The value of m from Eq. (13) is calculated to be 2; this value is reasonable. $Kk^0_{\mathrm{f,h}}$ is calculated from Eq. (10) or (14) as the values of αn_a and m are obtained, but K is not known. The values of $Kk^0_{\mathrm{f,h}}$ are tabulated in Table 2.

$(z-\alpha n_a)$ in Eq. (15) becomes zero because the value of αn_a is constant in a variety of half-wave potentials. Orange OT, which is essentially an uncharged species, seems to behave as the ionic species of the unit electric-charge, because the value of αn_a is nearly equal to one.

References

1) S. Hayano and N. Shinozuka, This Bulletin, **42**, 1469 (1969).
2) S. Hayano and N. Shinozuka, *ibid.*, **43**, 2083 (1970).
3) S. Hayano and N. Shinozuka, *ibid.*, **44**, 1503 (1971).
4) R. W. Schmid and C. N. Reilley, *J. Amer. Chem. Soc.*, **80**, 2087 (1958).
5) R. G. Barradas and F. M. Kimmerle, *J. Electroanal. Chem.*, **11**, 128 (1966).
6) M. Jhring and A. Weiß, *Tenside*, **6**, 251 (1969).
7) P. G. Westmoreland, R. A. Day, and A. L. Underwood *Anal. Chem.*, **44**, 737 (1972).
8) I. R. Miller, *J. Phys. Chem.*, **69**, 2740 (1965).
9) Y. F. Frei and I. R. Miller, *ibid.*, **69**, 3018 (1965).
10) H. Schott, *ibid.*, **68**, 3612 (1964).
11) J. Weber and J. Koutecký, *Coll. Czech. Chem. Commun.*, **20**, 980 (1955).
12) J. Heyrovsky and J. Kůta, "Principles of Polarography," Academic Press, New York, (1966), Chap. 14.
13) L. Meites, "Polarographic Techniques," Interscience, New York, (1965), Chap. 4.
14) A. A. Humffray, "Modern Aspects of Electrochemistry," vol. 8, ed. by Bockris and Conway, Plenum Press, New York (1972), Chap. 3.
15) J. Koutecký, *Coll. Czech. Chem. Commun.*, **18**, 597 (1953).
16) N. Shinozuka, H. Suzuki, and S. Hayano, *Kolloid-Z. Z. Polym.*, **248**, 959 (1971).
17) K. Eda, *Nippon Kagaku Zasshi*, **80**, 349 (1959).
18) W. H. Reinmuth, L. B. Rogers, and L. E. I. Hummelstedt, *J. Amer. Chem. Soc.*, **81**, 2947 (1959).
19) R. Parsons, "Advance in Electrochemistry and Electrochemical Engineering," Vol. 1, ed. by P. Delahay, Interscience, New York, (1961), Chap. 1.
20) P. Delahay, "Double Layer and Electrode Kinetics," Interscience, New York, (1966).
21) S. G. Miranovskii, "Progress in Polarography," Vol. 3, ed. Zuman, Meites and Kolthoff, Wiley-Interscience, (1972), Chap. 5.
22) R. D. Geer, E. H. Eylar, and E. W. Anacker, *J. Phys. Chem.*, **75**, 369 (1971).