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# Polarographic Determination of Surfactants

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**Synopsis.** The suppression of the polarographic oxygen maximum current and the decrease of the differential capacity at a potential of zero charge by surfactants are proportional to the concentration of the surfactants in a dilute solution. Constants representing the abilities for suppressing the maximum current and decreasing the capacity were obtained concerning some thirty surfactants.

Nowadays, surfactants are widely utilized not only as detergent powders and as liquid cleaners, but, also in the preparation of insecticides, polish and cosmetics. The development of a convenient method for the determination of surfactants seems to be very significant. After the separation of a test solution into surfactant solutions by means of a chromatographic method, a determination of surfactants is carried out mainly by the spectrophotometric method, which generally includes many complicated processes.[1] Measurements of the suppression of the polarographic maximum current and of the nonfaradaic admittance based on the adsorption of surfactants to the mercury electrode are very expedient and have been adopted for the determination of surfactants.[2,3] However, up to the present the fundamentals for the determination were not strictly explicated.

This paper tries to describe basic facts regarding the suppression of the oxygen maximum current and the decrease of the differential capacity by some thirty surfactants and to present a convenient method for a determination of surfactants.

## Experimental

**Chemicals.** Reagent-grade chemicals purchased from Nakarai Chemical Co. and Tokyo Kasei Co. were used without further purifications. The water distilled for high-performance liquid chromatography made by Katayama Kagaku Co. was used to prepare the base solution. To prepare an oxygenated test solution this base solution was equilibrated with air by leaving it in air one day or longer.

**Instruments.** Dc, normal pulse (NP) and phase sensitive ac (psac) polarograms were recorded with a Yanagimoto Polarographic Analyzer P1100, a Watanabe XY recorder WX4401 and an NF auto-lock-in amplifier LI572B. The amplitude of the superimposed alternating voltage was adjusted to 10 mV (peak to peak) and the frequency to 50 Hz. The open-circuit mercury flow rate at a dropping mercury electrode (DME) was 1.33 mg/s in distilled water at 65 cm of mercury. Usually, the dropping time of DME, $t_d$, was adjusted to 3 s.

**Electrochemical Measurements.** Measurements of the oxygen maximum current were carried out at 25 °C in a 10 mM (M=mol dm$^{-3}$) KCl solution and measurements of the differential capacity were at 20 °C in a 100 mM KCl solution. Potentials were referred to the saturated calomel electrode. To prepare the test solution, aliquots of a surfactant solution, usually containing 1 mg cm$^{-3}$ of surfactant, was injected into 10 cm$^3$ of the base solution in an H-type cell.

## Results

**1. Suppression of Oxygen Maximum Current by Surfactant.** In the reduction of oxygen dissolved in a KCl solution with a concentration ranging from 1 to 150 mM, a pronounced increase in the current above a limiting value was observed in the potential range between −0.2 and −0.4—−0.6 V on dc, NP, and linear potential sweep polarograms and was considered to be caused by increased transport of oxygen toward the electrode due to streaming motion of the solution.[4] The oxygen maximum current varied with the concentration of KCl and had a maximum value at the concentration of 10 mM. Dc polarograms of the reduction of oxygen in the presence of 0 to 2.5 μg cm$^{-3}$ of sodium dodecyl sulfate (SDS) in 10 mM KCl solution are shown in Fig. 1 and NP polarograms in the presence of 0 to 6 μg cm$^{-3}$ of SDS in Fig. 2. Heights of maximum current obtained by dc method($I$) and NP method($I_p$) decreased with increasing SDS concentration. These suppressions were proved to be proportional to the amount of surfactant adsorbed on

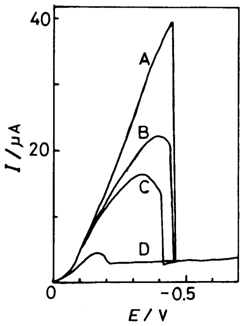

Fig. 1. Dc polarograms of reduction of oxygen in 10 mM KCl in the presence of 0 (A), 0.3 (B), 0.5 (C), and 2.5 (D) μg cm$^{-3}$ of SDS.

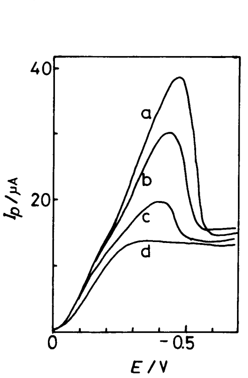

Fig. 2. NP polarograms of reduction of oxygen in 10 mM KCl in the presence of 0 (a), 0.5 (b), 2.5 (c), and 6 (d) μg cm$^{-3}$ of SDS.; initial potential was 0 V, sampling time was 16.6 ms.

the mercury electrode, $\Gamma$, by measurements of linear potential sweep polarograms.5) The net maximum current obtained by the dc method, $I^0-I^{\rm lim}$, was larger than that obtained by the NP method, $I_p^0-I_p^{\rm lim}$, in the absence of a surfactant. The degree of suppression of the net maximum current by the surfactant obtained by the dc method, $(I^0-I)/(I^0-I^{\rm lim})$, was larger than that by the NP method, $(I_p^0-I_p)/(I_p^0-I_p^{\rm lim})$, at a specific concentration of surfactant. Here $I^0$ and $I_p^0$ are the maximum currents in the absence of a surfactant and $I^{\rm lim}$ and $I_p^{\rm lim}$ are the limiting currents. In this NP method the initial potential is held at 0 V, where electrolysis scarcely occurs. Thus, streaming occurs intermittently and the supply of oxygen and surfactant to the electrode is reduced in comparison with the case of the dc method.

Figure 3 shows the dependence of the relative decrease of the oxygen maximum current measured at −0.3 V regarding the concentration of SDS(A, a) hexadecyltrimethylammonium bromide(CTAB)(B, b), and poly(oxyethylene)(20)sorbitan monolaurate-(Tween 20)(C, c) by the dc method(A, B, C) and the NP method(a, b, c). Roughly, linear relationships exist between the relative decrease of the current and the concentration of the surfactant in the range of $I/I^0$ and $I_p/I_p^0=2/3$ to 1 in the case of some thirty surfactants. Based on such a graph as shown in Fig. 3, the concentration of surfactant could be estimated.

**2. Decrease of the Differential Double Layer Capacity by Surfactant.** Figure 4 shows the differential capacity vs. potential, *C*–*E*, curves in the presence of 0 (A), 20 (B), and 50 (C) μg cm$^{-3}$ of SDS in 0.1 M KCl measured by the psac polarographic method. With the increase in the SDS concentration the differential capacity decreased in the potential range around the potential of zero charge, PZC, which in this case was −0.5 V. For an SDS concentration lower than 20 μg cm$^{-3}$ the relative decrease in capacity, $(C^0-C)/C^0$, was proportional to the square root of the dropping time of DME and the bulk concentration of SDS at −0.5 V, where $C^0$ is the capacity in the absence of a surfactant and $C$ in the presence of a surfactant.6)

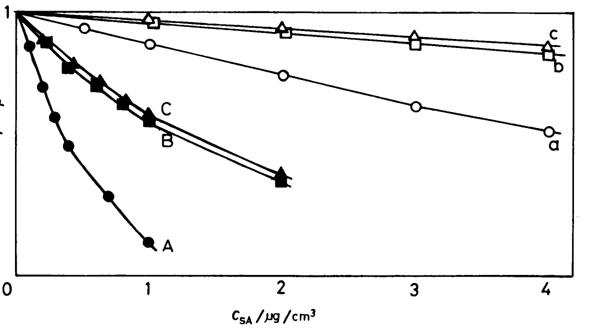

Fig. 3. Dependence of $I/I^0$ and/or $I_p/I_p^0$ at −0.3 V on the concn of SDS (A,a) ,CTAB (B,b) and Tween 20 (C,c) by dc (A,B,C) and NP (a,b,c) method.

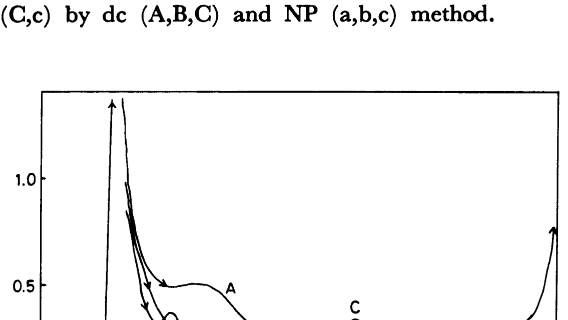

Fig. 4. *C–E* curves for 0 (A), 20 (B), and 50 (C) μg cm$^{-3}$ of SDS in 100 mM KCl.

Figure 5 shows the dependence of the relative decrease in the capacity at −0.5 V on the concentration of SDS (A), CTAB (B), and Tween 20 (C). At a lower surface coverage of the surfactant, an approximately linear relationship exists between the capacity and the bulk concentration of the surfactant. The adsorption of the surfactant at PZC is considered to be controlled by the diffusion, thus, $\Gamma$ is proportional to $t_d^{1/2}$ and $c$. For this reason the relative decrease in the capacity might be proportional to the degree of surface coverage of the surfactant, which has a lower dielectric constant than water. The differential capacity at $t_d=3$ s approached the minimum value, $C^m$, in the presence of 30 to 40 μg cm$^{-3}$ of water soluble surfactants and did not saturate even in the concentration of 100 μg cm$^{-3}$ of poorly soluble surfactants. The value of the differential capacity obtained in the presence of dissolved oxygen was the same as that obtained in the absence of oxygen at a potential more negative than −0.2 V.

## Discussion

Measurements of the oxygen maximum current and the differential capacity at a fixed potential are so simple and convenient to take that only one or two minutes are required to determine the concentration of any kind of surfactant ranging from 0.1 to 20 μg cm$^{-3}$. The presence of amino acids, sugars and non-surfactive fatty acids did not interfere with the measurements up to ten times the quantity of the surfactant. In the presence of any two kinds of surfactants, the total concentration of the two surfactants being lower than 20 μg cm$^{-3}$, their con-

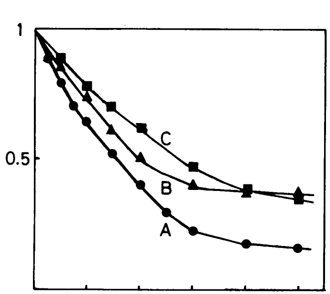

Fig. 5. Dependence of relative decrease of the differential capacity at −0.5 V on the concn of SDS (A), CTAB (B), and Tween 20 (C).

Table 1. Activity of Suppressing the Oxygen Maximum Current at $-0.3$ V, $k$, and of decreasing the Differential Capacity at $-0.5$ V, $K$

| Surfactant | mol mass<br>g mol$^{-1}$ | $k$<br>$\mu$g/cm$^3$ | $K$<br>$\mu$g/cm$^3$ |
|---|---|---|---|
| Na Octanate | 166 | 0.02 | 0.001 |
| Na Decanoate | 194 | 0.48 | 0.011 |
| Na Laurate | 222 | 1.70 | 0.030 |
| Na Myristate | 250 | 1.18 | 0.026 |
| Na Palmitate | 278 | 0.40 | 0.014 |
| Na Stearate | 306 | 0.29 | — |
| Na Oleate | 304 | 0.70 | 0.020 |
| Na Dodecyl sulfate | 288 | 1.40 | 0.036 |
| Na Hexadecyl sulfate | 345 | 0.60 | 0.008 |
| Na Dodecanesulfonate | 272 | 1.50 | 0.036 |
| Na Tetradecanesulfonate | 300 | 1.20 | 0.028 |
| Na Hexadecanesulfonate | 328 | 0.56 | 0.016 |
| Na Dodecylbenzenesulfonate | 348 | 1.20 | 0.025 |
| *N*-Dodecylpyridinium Cl$^-$ | 284 | 0.92 | 0.031 |
| *N*-Hexadecylpyridinium Cl$^-$ | 358 | 0.65 | 0.022 |
| Dodecyltrimethylammonium Cl$^-$ | 264 | 0.63 | 0.031 |
| Tetradecyltrimethylammonium Cl$^-$ | 292 | 0.61 | 0.030 |
| Hexadecyltrimethylammonium Br$^-$ | 365 | 0.60 | 0.023 |
| Hexylamine | 101 | 0.00 | 0.003 |
| Octylamine | 129 | 0.09 | 0.024 |
| Decylamine | 157 | 0.13 | 0.022 |
| Dodecylamine | 185 | 0.22 | 0.021 |
| Tetradecylamine | 213 | 0.07 | 0.006 |
| poly(oxyethylene)(n) *p*-*t*-octylphenyl ether | | | |
| Triton *x*-100 n=9.5 | 624 | 0.63 | 0.030 |
| Triton *x*-305 n=30 | 1526 | 0.42 | 0.018 |
| Triton *x*-405 n=40 | 1966 | 0.42 | 0.017 |
| poly(oxyethylene)(20) sorbitan monoalkanoate | | | |
| Tween 20, laurate | 1214 | 0.59 | 0.020 |
| Tween 40, palmitate | 1265 | 0.57 | 0.019 |
| Tween 60, stearate | 1293 | 0.54 | 0.017 |
| Tween 80, oleate | 1291 | 0.54 | 0.017 |
| Bovine serum albumin | 69000 | 0.11 | 0.005 |
| Horse cytochrom c | 13500 | 0.14 | 0.007 |

tribution in suppressing the maximum current and decreasing the capacity is independent. A rigid control of the temperature (20—30 °C) and the dropping time of DME (3—5 s), which influence the adsorption of surfactant, is desirable for a better analysis. Constants characteristic of the surfactant representing the ability to suppress the oxygen maximum current, $k$, and to decrease the differential capacity, $K$, were calculated while assuming that the following empirical equations are valid:

$$I/I^0 = 1 - kc \tag{1}$$

and

$$C/C^0 = 1 - Kc. \tag{2}$$

These concern some thirty surfactants and are summarized in Table 1. This table is useful in a polarographic determination of the surfactants.

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