Tensammetric Waves in Oscillographic Square-wave Polarography*

By Koichi OKAMOTO

(Received October 10, 1963)

In previous papers[1-5] the oscillographic square-wave polarographic behavior of some reducible or oxidizable depolarizers has been reported on. Since the oscillographic square-wave polarograph can selectively eliminate the charging current by means of the gating and the positive feed-back techniques, as described in a previous paper,[1] the reduction or the oxidation waves obtained by this method may contain none of the charging current. On the contrary, the changes of the electric double layer at the electrode surface, according to the adsorption or desorption of surface-active substances, can be observed as tensammetric waves by this polarograph. This work will study the possibility of the observation of tensammetric waves by means of this polarograph and will compare the properties of the waves with those obtained by a conventional a. c. polarograph.

There are two experimental methods used in order to obtain the tensammetric waves by this equipment. One of them is the suitable regulation of the amount of the positive feed-back of an electrolytic current. Another method is the removal of the gating circuit from the electric circuit of the polarograph. In the present study the measurements were carried out under the optimum positive feed-back conditions.

In this paper the behavior of such surface-active substances as aliphatic alcohols and several synthesized surface active substances will be presented in relation to their behavior in the pen-recording sine wave a. c. polarograph. Moreover, the measuring method of the critical micelle concentrations of the synthetic surface-active substances will also be presented.

Experimental and Results

Apparatus.—The oscillographic square-wave polarograph reported on in a previous paper[1] was used. A pen-recording a. c. polarograph (Yanagimoto Model PA-102; frequency$=50$ c. p. s., amplitude$=15\ \mathrm{mV_{p-p}}$) was also used. The characteristics of the DME used were $m=0.529$ mg. sec^{-1}, $t=6.26$ sec. (open circuit) in a 1 N sodium sulfate solution.

The measurements were carried out at 25 ± 0.5°C unless otherwise stated, and the potentials were referred to the external SCE, which was connected to the mercury pool anode through a 200 μF condenser. The dissolved air was removed by nitrogen gas. The degree of the positive feed-back of the electrolytic current was fixed at the optimum point for the base solution so as to completely eliminate its charging current, and then the studies with the sample solutions were carried out.

The Behavior of Aliphatic Alcohols.—In the oscillographic square-wave polarograph, the wave which appears at the potentials more positive than zero can not be observed because of the large charging current of the dissolution of the Hg-cathode, so only the waves appearing between 0 and -2 V. vs. SCE were studied.

The Summit Potentials and Currents.—Most of the aliphatic alcohols studied gave clear tensammetric waves, as is shown in Figs. 1—3; their summit potentials and currents are shown in Table I.

Generally speaking, the weakly surface-active alcohols, such as *n*- and isopropyl alcohols and *n*-butyl alcohol, show the broad waves, while the strongly surface-active alcohols, such as *t*-amyl alcohol and *n*-octyl alcohol, show the sharp waves.

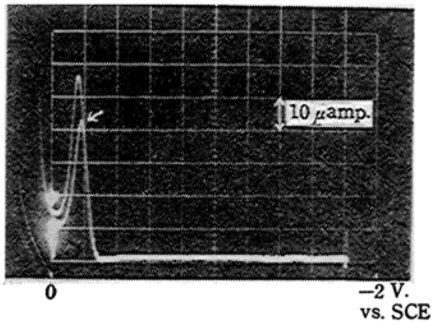

Fig. 1. 1 mol./l. isopropyl alcohol in 1 N Na_2SO_4, air free, 25°C. The wave in the cathodic sweep process is indicated by an arrow.

---

* Oscillographic Square Wave Polarography. Part VI.

[1] Y. Saitō and K. Okamoto, *Rev. Polarography*, **10**, 227 (1962).

[2]-[4] K. Okamoto, ibid., in press.

[5] K. Okamoto, This Bulletin, **36**, 1381 (1963).

TABLE I. THE SUMMIT POTENTIALS AND CURRENTS OF ALIPHATIC ALCOHOLS
Base solution: 1 N Na_2SO_4, 25±0.5°C, air free

Alcohol	Concn.	Oscillographic				Pen-recording	
		$-E_s$, V. vs. SCE		i_s, μamp.		$-E_s$ V. vs. SCE	i_s μamp. r.m.s.
		Cathodic	Anodic	Cathodic	Anodic		
Isopropyl-	1 M	0.138 1.112	0.123 1.112	38.7 5.0	50.4 5.0	1.080	0.30
n-Butyl-	Satd.	1.335	1.317	39.9	43.0	1.334	0.69
t-Butyl-	1 M	0.069 1.456	0.048 1.456	24.8 1.1	42.0 1.1	0.035 1.281	2.25 0.59
n-Amyl-	Satd.	1.247	1.242	7.3	8.4	1.278	1.15
t-Amyl-	Satd.	1.335	1.315	72.0	74.8	1.349	1.11
Isoamyl-	Satd.	1.244	1.236	5.9	7.3	0.052 1.250	1.35 1.16
n-Hexyl-	Satd.	1.234	1.209	14.0	15.6	0.034 1.239	1.26 2.01
s-Hexyl-	Satd.	1.216	1.194	58.6	65.2	1.211	1.76
n-Heptyl-	Satd.	1.194 1.240	1.148 1.231	2.2 23.7	27.9 14.5	1.041 1.193	0.36 0.76
3-Heptyl-	Satd.	1.218	1.198	30.2	36.3	1.217	1.34
4-Heptyl-	Satd.	0.044 1.130	0.017 1.114	18.8 6.0	? 6.6	0.045 1.116	2.25 1.01
n-Octyl-	Satd.	0.053 1.126	0.032 1.116	21.0 99.2	5.0 130.6	1.134	1.19
2-Octyl-	Satd.	1.018	0.110	0.7	5.3	0.040 1.100	1.20 0.13
n-Nonyl-	Satd.	0.035 1.118	0.035 1.089	10.7 37.2	23.9 2.4	0.022 1.110	1.38 0.87
n-Decyl-	Satd.	1.069	0.050 1.060	16.6	25.0 0.9	0.039 1.070	1.60 1.18
n-Undecyl-	Satd.	0.087 0.060	0.063 0.096 1.053	21.6 13.2	29.7 7.6 6.3	0.026 1.073	1.04 0.40
Cyclohexyl-	Satd.	0.119 1.385	0.065 1.369	2.3 35.7	5.1 34.6	1.442 1.650	1.38 1.27

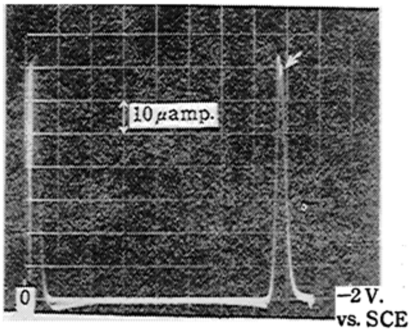

Fig. 2. *t*-Amyl alcohol satd. in 1 N Na_2SO_4, air free, 25°C.

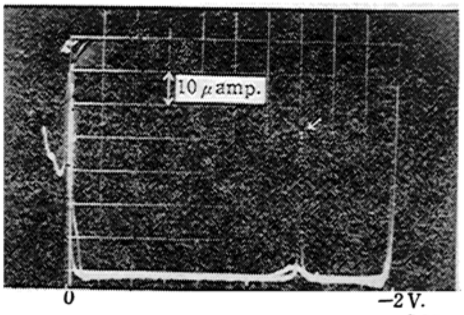

Fig. 3. 0.002 M *n*-octyl alcohol in 1 N Na_2SO_4, air free, 25°C.

With the oscillographic square-wave polarograph, the waves in the cathodic and the anodic sweep processes are very similar to each other, as is shown in Figs. 1 and 2. This is considered to correspond to the a. c. polarographic-reversible property of the adsorption-desorption reactions. Some exceptions were, however, observed, as in the case of *n*-octyl alcohol (Fig. 3). This may indicate an a. c. polarographic-irreversible property.

The Relation of the Concentrations to the Summit Potentials and Currents.—The findings on *t*-amyl alcohol are shown in Figs. 4 and 5. The summit potentials of their positive and negative tensammetric waves tend to approach each other as the concentration decreases, and the relationships between $(E_s^c - E_{ecm})^2$ or $(E_s^a - E_{ecm})^2$ and $\log C$ were linear, where

E_{ecm} is the electro-capillary maximum potential. In the present study, $E_{ecm}=-0.50$ V. vs. SCE was employed according to the electrocapillary curve. The summit currents increased to the limiting values as the concentration increased. However, the relation of $\log C$ to the summit current, $i_s{}^c$ or $i_s{}^a$, was not linear. This relation of $\log C$ to i_s values is not the same as the finding reported by Senda[8] on the a.c. waves of *t*-amyl alcohol obtained by by a pen-recording a.c. polarograph.

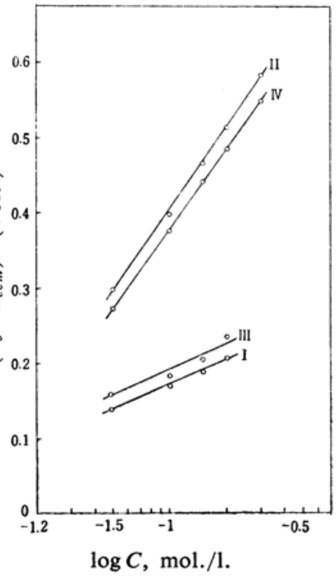

Fig. 4. Relation of $(E_s-E_{ecm})^2$ to $\log C$.

t-Amyl alcohol in 1 N Na_2SO_4, 25°C, air free
I, II: Positive and negative waves in cathodic process respectively
III, IV: Positive and negative waves in anodic process respectively

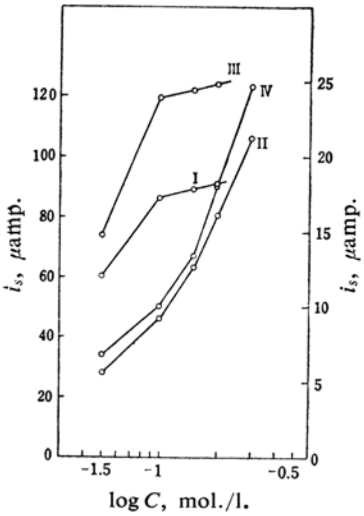

Fig. 5. Relation of i_s to $\log C$.

t-Amyl alcohol in 1 N Na_2SO_4, 25°C, air free
I, II: Positive and negative waves in cathodic process respectively
III, IV: Positive and negative waves in anodic process respectively

Temperature Effects.—As Fig. 6 shows, the summit currents of *t*-amyl alcohol decreased with the rise in temperature, while the summit potential scarcely changed. These results may show the typical properties of the adsorption waves.

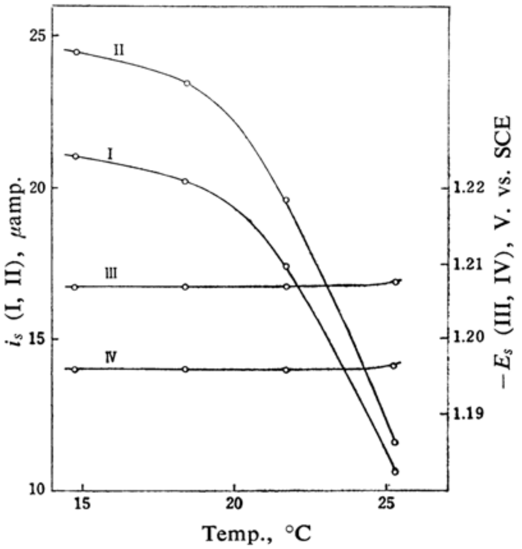

Fig. 6. Relations of i_s and E_s to temperature.

0.15 mol./l. *t*-amyl alcohol in 1 N Na_2SO_4, air free
I, III: Negative wave in cathodic process
II, IV: Positive wave in anodic process

The Behavior of the Mixtures of Alcohols.—When the pen-recording a.c. polarograph is used the solution containing two or more surface-active substances gives the tensammetric wave of only one component which has the strongest surface activity.[6]

The polarographic behavior of the binary mixtures shown in Table II was studied.

The system of isopropyl alcohol - *n*-butyl alcohol showed waves similar to those of *n*-butyl alcohol. No wave of isopropyl alcohol could be observed. The summit potentials, however, of the mixture were slightly more negative than those of *t*-butyl alcohol, and the summit currents were not equal to those of *t*-butyl alcohol. A similar result was also obtained with an isopropyl alcohol - *t*-amyl alcohol system. The mixture of *t*-amyl alcohol and *n*-

---

[6] M. Maruyama et al., *Kagaku-no Ryōiki, Extra Ed.*, **50**, 124 (1962).

TABLE II. THE SUMMIT POTENTIALS AND CURRENTS OF THE MIXTURES OF ALCOHOLS

Base solution: 1 N Na_2SO_4, 25°C, air free

Alcohol	Concn. M	Oscillographic $-E_s$, V. vs. SCE Cathodic	Oscillographic $-E_s$, V. vs. SCE Anodic	Oscillographic i_s, μamp. Cathodic	Oscillographic i_s, μamp. Anodic	Pen-recording $-E_s$ V. vs. SCE	Pen-recording i_s μamp. r.m.s.
Isopropyl-	0.5	0.201 1.112	0.214 1.112	17.8 3.5	30.0 3.5	1.080	0.30
n-Butyl-	0.5	1.337	1.306	19.3	29.4	1.294	0.33
t-Amyl-	0.5	1.337	1.317	29.3	40.9	1.268	0.49
n-Octyl-	0.002	1.152	1.137	44.4	3.5	1.062	0.07
Isopropyl- +*n*-butyl-	0.5 0.5	1.372	1.335	20.5	28.1	1.323	0.53
Isopropyl- +*t*-amyl-	0.5 0.5	1.341	1.335	45.1	69.2	1.239	0.83
n-Butyl- +*t*-amyl-	0.5 0.5	1.275	1.256	20.5	30.5	1.314	0.38
t-Amyl- +*n*-octyl-	0.5 0.002	1.344	1.324	29.4	39.2	1.286	0.17

TABLE III. THE SUMMIT POTENTIALS AND CURRENTS OF SYNTHETIC SURFACE ACTIVE SUBSTANCES.

Base solution: 0.5 M KCl, 25°C, air free

Compound	Concn. M	$-E_s$, V. vs. SCE Cathodic	$-E_s$, V. vs. SCE Anodic	i_s, μamp. Cathodic	i_s, μamp. Anodic
CTACl*1	10^{-2}	0.069	—	27.6	—
SLS*2	10^{-3}	1.209	1.168	24.0	1.2
NaCap.*3	10^{-2}	0.074 1.069	0.048 1.069	14.8 2.0	13.7 2.0
SPEG-19*4	$5\cdot10^{-3}$	ca. 0.14 1.757	0.144 1.746	ca. 2 50.1	13.7 23.3
SPEG-30*5	$5\cdot10^{-3}$	ca. 0.12 ca. 1.78	0.111 1.749	ca. 2 55.2	ca. 4 40.0
SPEG-40*6	5.10^{-3}	ca. 0.11 1.784	ca. 1.1 1.753	ca. 2 58.6	ca. 2 51.2
LPEG-8*7	10^{-2}	1.761	1.760	68.8	17.1
OPEG-10*8	10^{-2}	1.784	1.783	66.5	25.6
OPEG-12*9	10^{-2}	1.780	1.773	45.5	31.8
NPPEG-10.5*10	10^{-2}	1.746	1.747	71.0	7.4
NPPEG-12*11	10^{-2}	1.787	1.786	48.9	36.4

*1 Cetyltrimethylammonium chloride
*2 Sodium lauryl sulfate, base solution = 0.5 N Na_2SO_4
*3 Sodium caprate
*4 Stearylpolyethyleneglycol ether ($n=19$)
*5 $n=30$
*6 $n=40$
*7 Laurylpolyethyleneglycol ether ($n=8$)
*8 Oleylpolyethyleneglycol ether ($n=10$)
*9 $n=12$
*10 Nonylphenylpolyethyleneglycol ether ($n=10.5$)
*11 $n=12$

octyl alcohol showed quite the same waves as those of *t*-amyl alcohol. However, the mixture of *n*-butyl alcohol and *t*-amyl alcohol gave a wave with a more positive summit potential and a higher summit current than those of the individual components.

The tensammetric wave of a mixed alcohol solution may correspond to the wave of the alcohol, the negative tensammetric wave of which appears at more negative potentials than that of the other alcohol. When the summit potentials of the alcohols in a mixture are, however, almost identical, a new wave appears as is observed in a *n*-butyl alcohol-*t*-amyl alcohol mixture.

The Synthetic Surface-active Agents. — A cationic agent (cetyltrimethylammonium chloride (CTACl)), and anionic agents (sodium caprate (SC) and sodium laurylsulfate (SLS)) of the reagent grade were studied. Non-ionic agents (oleylpolyethyleneglycol ethers ($n=10$ and 12, OPEG), stearylpolyethyleneglycol ethers ($n=19$, 30 and 40, SPEG), laurylpolyethyleneglycol ether ($n=8$, LPEG) and nonylphenylpolyethyleneglycol ethers ($n=10.5$ and 12, NPPEG)) which had been synthesized in this laboratory were also studied.

The Summit Potentials and Currents. — The samples studied, except SLS, gave the waves at the potentials near to 0 and −2 V., as Fig. 7 shows. The numerical data are listed in Table III. The shape of the waves is very sharp, and their heights in the cathodic and the anodic processes were not generally equal.

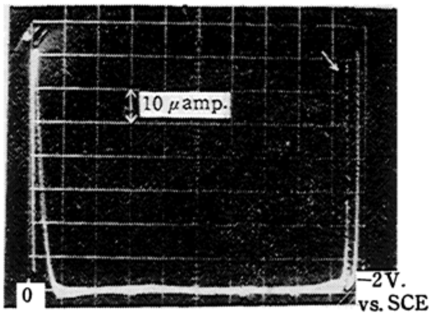

Fig. 7. 10^{-2} mol./l. oleylpolyethyleneglycol ether ($n=10$) in 0.5 M KCl, air free, 25°C.

The Relation of the Concentrations to the Summit Potentials and Currents.—The effect of the concentration change upon the cathodic waves of the non-ionic agent OPEG is shown in Fig. 8. The summit current increases to the limiting value as the concentration increases, and the potentials began to shift to more negative values at concentrations lower than ca. 2×10^{-4} mol./l.

The Influence of the Micelle Formation upon the Polarographic Waves of Some Metallic Ions. —In order to obtain the relation of critical micelle concentration (CMC) to the polarographic data, the values of the CMC of several agents were measured beforehand by the usual spectrophotometric method, using the color change of a dye.⁷⁾ The results are listed in Table IV.

The obscure negative shift of the summit potential of OPEG at the concentration of ca. 2×10^{-4} mol./l. (Fig. 8) was thought to correspond nearly to the CMC of OPEG, but the waves at such low concentrations can not be measured well. Therefore, the detection of the CMC from the concentration $-E_s$ or i_s curves is not a suitable method.

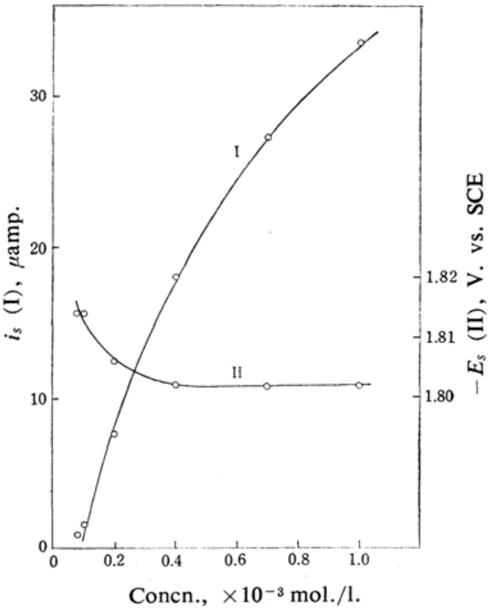

Fig. 8. Relation of i_s and E_s to concentration. Oleylpolyethyleneglycol ether ($n=10$) in 0.5 N Na_2SO_4, 25°C, air free

The d. c. polarographic wave of a metallic cation is considerably affected by the addition of a surface-active agent, so the CMC of the agent can be detected by the change in the wave height or the half-wave potential of the metallic cation.⁷⁾ This change may mean a decrease in the reversibility of the electrode reaction of a metallic cation. The a. c. polarographic method is more sensitive than the d. c. method with respect to the response to the change in the reversibility of the electrode reaction. Therefore, the author's oscillographic method was also considered to be suitable for this purpose. Moreover, with this polarograph, since the cathodic and the anodic waves can be observed continuously, the change of the wave form can be observed more precisely than with the conventional pen-recording method.

The metallic ions used were lead(II) and zinc(II), which give a reversible and a quasi-reversible wave respectively. The surface-active agents used were CTACl, SLS, OPEG and NPPEG. The measurements were carried out in a deoxygenated 0.5 N sodium sulfate aqueous solution containing a constant amount of the metallic ions (2.5×10^{-4} mol./l. in lead(II) or 10^{-3} mol./l. in zinc(II)) and also various amounts of the surface-active agents. The degree of the positive feed-back of the electrolytic current was fixed at the optimum point for the solution of 0.5 N sodium sulfate containing only the metallic ions.

---

7) T. Nakagawa, *Shionogi's Ann. Rep.*, **8**, 31 (1958).

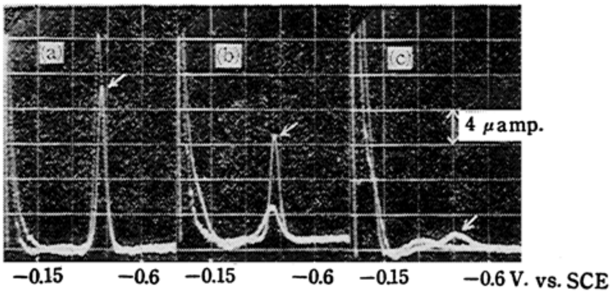

Fig. 9. 0.25×10^{-3} mol./l. Pb(II) + OPEG (n=10) ; (a) 0.01×10^{-3}, (b) 0.10×10^{-3}, (c) 0.20×10^{-3} mol./l., in 0.5 M KCl, air free, 25°C.

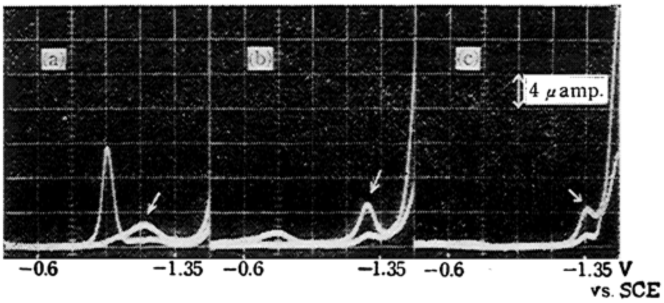

Fig. 10. 1.0×10^{-3} mol./l. Zn(II) + OPEG (n=10) ; (a) 0, (b) 0.10×10^{-3}, (c) 0.40×10^{-3} mol./l., in 0.5 N Na_2SO_4, air free, 25°C.

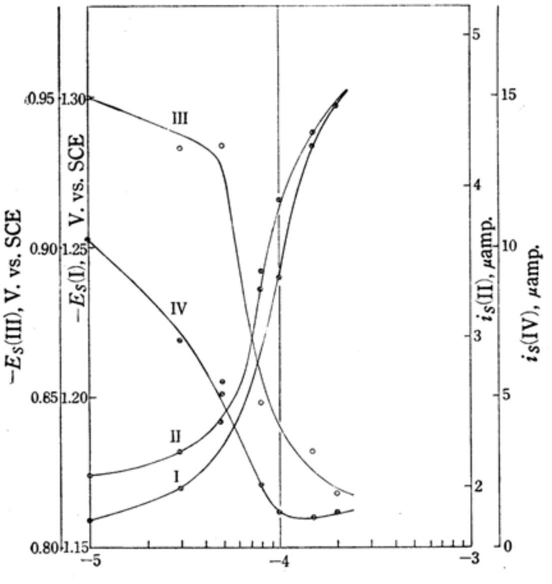

Fig. 11. Relations of i_s and E_s of waves of 1×10^{-3} mol./l. Zn(II) to concentration of CTACl, 25°C, air free, in 0.5 N Na_2SO_4.

I, II : Reduction wave
III, IV : Oxidation wave

TABLE IV. THE CMC VALUES

Solvent : 0.5 N Na_2SO_4, 25±0.5°C

Compound	By oscillographic square wave polarograph $\times10^{-4}$ mol./l.	By spectrophotometric method $\times10^{-4}$ mol./l.
CTACl	0.4∼1.8	2.0*1
SLS	2.0∼5.0	1.5*2
OPEG-10	0.5∼1.8	2.5*2
NPPEG-10.5	0.3∼1.1	1.5*2

*1 Obtained from the shift of λ_{max}^{516} and ε_{max}^{516} of eosin yellow

*2 Obtained from the shift of λ_{max}^{547} of pinacyanol chloride

Typical changes in the reduction and the oxidation waves of lead(II) and zinc(II) upon the addition of OPEG are shown in Figs. 9 and 10 respectively. In all the cases studied, the remarkable decrease in the summit currents and the shifts in the summit potentials were observed at the concentration near to the CMC. These relations are indicated in Fig. 11 in the case of the zinc(II)-CTACl system.

The nature of these changes can not be explained theoretically, but the inclusion of a metallic ion by the micelles or the increase in the thickness of the adsorption layer on the electrode surface upon the micelle formation may interfere with the electrode reaction of the metallic ions.

The concentration ranges where the summit potentials and currents of the metallic ions changed are summarized in Table IV. It appears that they represent the appoximate CMC values of the surface-active agents.

Discussion

The tensammetric waves of surface-active substances are said to correspond to the reversible wave in a pen-recording a. c. polarograph. This is also applicable to an oscillographic square-wave polarograph. As has been described in previous sections. the tensammetric wave could be observed very clearly and rapidly by means of the oscillographic method.

The values of the summit potentials of aliphatic alcohols obtained with the oscillographic method were almost always equivalent to those obtained with the pen-recording method as is shown in Table I. The summit current values, on the other hand, were found to be very much higher than those obtained by means of the pen-recording method. This may be mainly due to the difference between the frequencies of the a. c. potentials: the oscillographic method employs 3 kc./sec. and the pen-recording method employs 50 c.p.s. The sensitivity of the oscillographic square wave polarograph for the measurement of the adsorption-desorption wave is superior to that of the pen-recording polarograph.

The relation between the logarithm of the concentrations and the square of the summit potentials of *t*-amyl alcohol showed a linear relation similar to that in a pen-recording polarograph, as Fig. 4 shows.

When the concentration of a surface active substance is comparatively high, and when the concentrations at the electrode surface and in the bulk solution ($C_n{}^0$) can be thought to be equal, the relation of the summit potential to the bulk concentration may be expressed as $\ln C_n{}^0 \propto (E_s - E_{ecm})^2$, as was shown by Senda.[8] This relation seemed to be adaptable to the oscillographic polarographic waves of *t*-amyl alcohol.

The summit currents increased as the concentration increased, but the behavior of the positive tensammetric wave was not equal to that of the negative tensammetric wave (cf. Fig. 5). The relation between the $\log C$ and i_s of the negative wave is near to the linear relation.

The wave height in an anodic sweep process, as was observed on *n*-octyl alcohol (Fig. 3) and also on synthetic surface-active agents (Fig. 7), is not equal to that in a cathodic process. This may indicate the a. c. polarographically-irreversible property of their adsorption-desorption processes.

The critical micelle concentration of synthetic surface-active agents can be measured or detected by means of the measurement of the change, caused by the addition of the surface-active agents, in the summit potentials or the currents of such metallic ions as lead(II) and zinc(II). The mechanisms of the change in the form of the reduction or oxidation waves of the ions may possibly be studied by means of the author's polarograph.

Summary

The possibility of observing the tensammetric waves of surface-active agents by an oscillographic square wave polarograph has been investigated. Well-defined tensammetric waves of some aliphatic alcohols, as well as those of some synthetic surface-active agents, can be obtained both in the cathodic and anodic sweep processes. The summit potential values, measured by the oscillographic method and pen-recording method, are almost identical. The relations of the concentrations and temperature to the summit potentials obtained by the two methods are almost equivalent, also. However, the summit current observed by the oscillographic method is higher than that obtained by the pen-recording method, and also the relation of $\log C$ to i_s is not equivalent.

In order to measure the CMC of surface-active agents, the author had made use of the fact that, at the CMC of the agents, the form of the reduction or the oxidation wave of a metallic ion added to the solution of the agent changes remarkably. This method is thought to be superior to the conventional d. c. polarographic method, for the reduction and also the oxidation waves of a metallic ion can be observed, and the response to the change in the reversibility of the electrode reaction is much faster than with the d. c. method.

The author is much indebted to Professor Taichirō Fujinaga (Kyōto University) for his kind instruction and to Dr. Munetoshi Matsui and Dr. Akira Itō (both of this laboratory) for affording facilities for this investigation.

Research Laboratories of
Sankyo Co., Ltd.
Sinagawa-ku, Tokyo

---

[8] M. Senda and I. Tachi, *Rev. Polarography*, **10**, 79 (1962).