Bull. Chem. Soc. Jpn., 55, 2588—2593 (1982) [Vol. 55, No. 8

The Temperature Dependence of the Peak Height of the Lead Ion in Square-wave Polarography

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(Received September 16, 1981)

The peak height of the square-wave (s.w.) polarogram of lead increased markedly upon the addition of anions forming insoluble compounds with lead, and the temperature coefficient of the peak height showed a negative value, different from the theoretical value in a diffusion-controlled or an electrode-reaction-rate-controlled process at the following concentrations of anions; $[\mathrm{Cl}^-]=1$ M†, $[\mathrm{Br}^-]=10^{-2}$ M, $[\mathrm{SCN}^-]=10^{-1}$ M for 10^{-4} M lead. In the case of the addition of iodide, the s.w. peak height of lead increased at concentrations of iodide above 10^{-4} M for 10^{-4} M lead but the temperature coefficient of the peak height was always positive. Moreover, another peak due to lead appeared superimposed on the oxidation peak of iodide at a more positive potential, and this peak had a negative temperature coefficient. It was found that these phenomena were attributable to a specific adsorption of lead on mercury electrodes, induced by the foremost adsorbed anions. However in the case of the addition of iodide or in that of a high concentration of bromide or thiocyanate, the reversibility of the electrode process decreased and the temperature coefficient varied to a positive value in spite of the increase in adsorbed depolarizers.

The influence of the temperature on polarographic currents has not been much reported on since the theoretical consideration by Ilkovič[1] and the experimental report by Nejedlý[2] using direct-current (d.c.) polarography.

The temperature coefficient of d.c., alternating current (a.c.), s.w., and other polarographic currents has generally been accepted as positive in a reversible or an irreversible process, for it depends on the temperature dependence of the diffusion coefficient of a depolarizer and that of the rate constant of the electrode reaction, too, in an irreversible process.

We reported in a previous paper[3] that, when a chloride ion coexisted as a supporting electrolyte, the temperature coefficient of the s.w. polarographic peak height of lead showed a negative value, different from the theoretical temperature coefficient in a reversible or an irreversible process, on the other hand, the temperature coefficient of the d.c. polarographic wave height agreeded well with the theoretical value in a reversible process.

In this paper, the temperature dependence of the s.w. peak height of lead was studied in the presence of a chloride, bromide, thiocyanate, or iodide ion, as it is known that these anions are adsorbed on dropping mercury electrodes[4] and then give various influences on the electrode reaction.[5–7]

Theoretical

In d.c. polarography, the temperature coefficient of a diffusion-controlled current, $(1/I_{\mathrm{d.c.}})\mathrm{d}I_{\mathrm{d.c.}}/\mathrm{d}T$, can be expressed theoretically[1] thus;

$$(1/I_{\mathrm{d.c.}})\mathrm{d}I_{\mathrm{d.c.}}/\mathrm{d}T=(1/2D)\mathrm{d}D/\mathrm{d}T-(1/2\eta_{\mathrm{Hg}})\mathrm{d}\eta_{\mathrm{Hg}}/\mathrm{d}T, \quad (1)$$

in which D is the diffusion coefficient of the depolarizer and η_{Hg} is the viscosity of mercury.

In s.w. polarography, $(1/I_{\mathrm{s.w}})\mathrm{d}I_{\mathrm{s.w.}}/\mathrm{d}T$ at the reversible half-wave potential $(E=E_{1/2})$ in the case of a diffusion-controlled process can be expressed theoretically as;

$$(1/I_{\mathrm{s.w.}})\mathrm{d}I_{\mathrm{s.w}}/\mathrm{d}T=(1/2D)\mathrm{d}D/\mathrm{d}T-1/T, \quad (2)$$

because $I_{\mathrm{s.w.}}$ can be expressed as follows, as reported by Barker,[8]

$$I_{\mathrm{s.w.}}=k\,\Delta E\,n^2 A\,c\,D^{1/2}T^{-1}P/(1+P)^2, \quad (3)$$

where k=a constant varing with the apparatus, ΔE= the amplitude of the superimposed square-wave voltage, n= the number of electrons in an electrode reaction, c= the concentration of a depolarizer, A= the electrode area, $P=\exp[(E-E_{1/2})nF/RT]$, and $P=1$ when $E=E_{1/2}$.

It has been reported that the temperature coefficient of the d.c. wave height was in the range of 1.3—2.3%,[2] while that of the a.c. peak height, which should be the same as that of the s.w. peak height, was experimentally found in the range of 0.4—1.6%.[9]

It was reported by Imai and Adachi[10] that, in the case of a reaction-rate-controlled process, the temperature coefficient of the a.c. peak height was much higher than that of a diffusion-controlled process. Kambara and Kunimatsu[11] showed that, in the case of a redox system of a fairly low reversibility, the temperature coefficient decreased with an increase in the temperature, and that when the rate of the electrode process has become fast enough at higher temperatures, the coefficient approached that of the completely reversible system.

Experimental

Square-wave polarographic curves were recorded by a Yanagimoto high-frequency polarograph, Model PF-500, using a mercury pool at the bottom of an electrolysis cell as an anode.

Experiments were carried out under the following conditions; the span voltage =2 V, the gate range=2 to 7, the time constant=5.5.

Direct-current polarographic curves were recorded by a Yanagimoto voltammetric analyzer, P-1000 type, using a spiral platinum wire electrode as an anode and a saturated calomel electrode as a reference electrode.

The electrolysis cell was held in a Tajiri electronic thermo-water bath, ECW-108 type, with an accuracy of ±0.2 °C.

All the chemicals used were guaranteed-grade reagents. As the standard solution of lead, lead nitrate was used. For the addition of anions, potassium chloride, sodium chloride,

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† 1 M=1 mol dm^{-3}.

sodium bromide, sodium thiocyanate, and sodium iodide were used.

Results and Discussion

Increased Sensitivity and Negative Temperature Coefficient. The peak height of the s.w. polarogram of lead increased markedly upon the addition of a smaller amount of iodide, bromide or thiocyanate than that of chloride, as is shown in Figs. 1—4. This increase was remarkable at lower temperatures, therefore, the temperature coefficient of the s.w. peak height of lead began to decrease from the theoretical value with an increase in the concentration of anions, except in the case of iodide, and was negative in the presence of the following concentrations, varing with each anion; $[Cl^-]=1$ M, $[Br^-]=10^{-2}$ M, $[SCN^-]=10^{-1}$ M. However, with still more increasing anions, the coefficient changed again to a positive value larger than the theoretical value.

Concerning the influence of the addition of anions

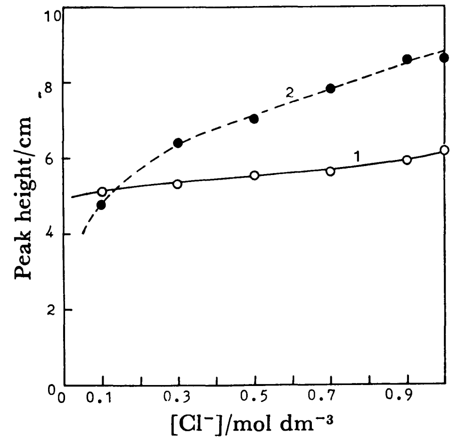

Fig. 1. Influence of the concentration of KCl on the peak height of 10^{-4} M Pb^{2+} in the s. w. polarogram. (HNO_3 acidic, pH 3—4).
1: 25.0 °C, 2: 1.0 °C, ΔE: 5 mV, sens.: 1/20, 0.200 μA/mm.

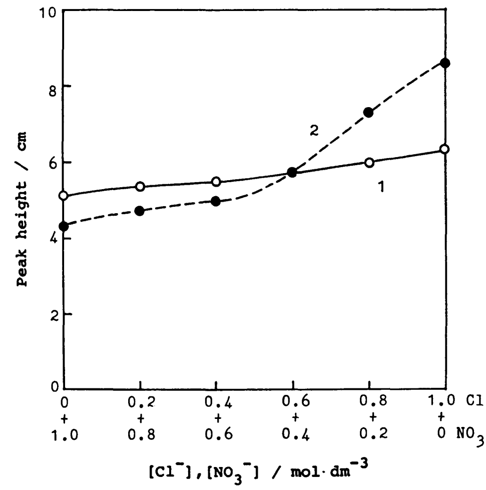

Fig. 2. Influence of the concentration of KCl summed with KNO_3 to 1.0 M on the peak height of 10^{-4} M Pb^{2+} in the s. w. polarogram. (HNO_3 acidic, pH 3—4)
1: 25.0 °C, 2: 0.8 °C, ΔE: 5 mV, sens.: 1/20, 0.200 μA/mm.

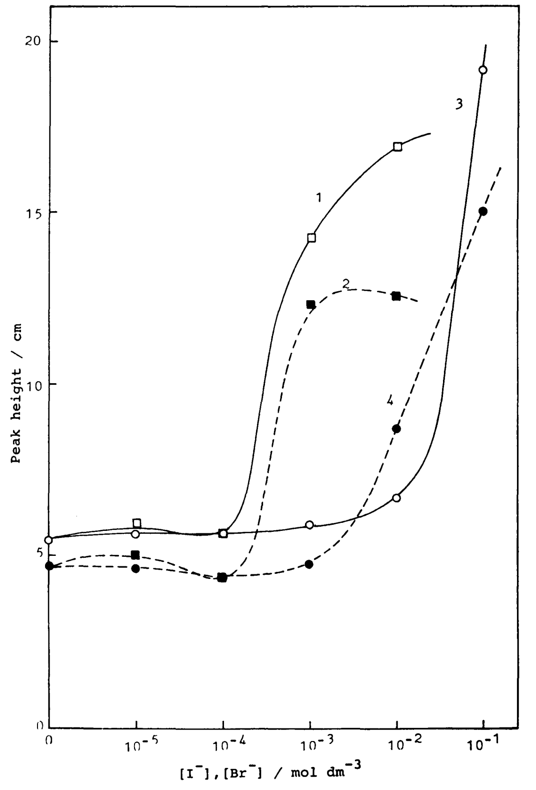

Fig. 3. Influence of I^- (1, 2) or Br^- (3, 4) concentration on the peak height of 10^{-4} M Pb^{2+} in 0.1 M $HClO_4$ in the s. w. polarogram.
1, 3: 25.0 °C, 2, 4: 0.2 °C, ΔE: 5 mV, sens.: 1/20, 0.200 μA/mm.

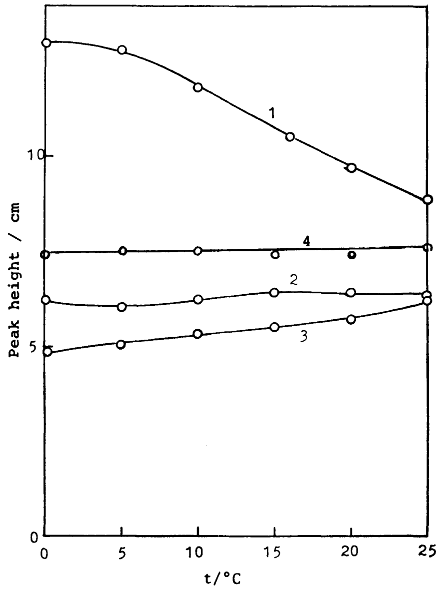

Fig. 4. Temperature dependence of the peak height in the s. w. polarograms of 10^{-4} M Pb^{2+} in 0.1 M $HClO_4$ with 10^{-1} M SCN^- (1), 10^{-2} M SCN^- (2), 10^{-3} M SCN^- (3), and 0.01 M $HClO_4$ with 1.0 M SCN^- (4). ΔE: 5 mV, sens.: 1/20, 0.200 μA/mm.

on the d.c. polarogram, the wave height of lead was constant, and the temperature coefficient coincided with the theoretical value, regardless of the addition of anions, unlike as in the case of the s.w. polarogram.

These experimental results seem to suggest the adsorption of the depolarizer.

In d.c. polarography, in which the mean current in a drop life is measured, a small quantity of adsorbed depolarizer has hardly any influence on the wave height, as the current occasioned by the reduction of an adsorbed depolarizer decreases with the growth of a drop in proportion to $t^{-1/3}$, where t is the time from the beginning of the drop.

In s.w. polarography, in which the electrode potential changes with the frequency of 200 Hz, even a small quantity of adsorbed depolarizer results in an increase in the peak height. The peak height is then increased by this approximate factor;[7)]

$$1+\frac{(\gamma_{E_{1/2}})^2\sum_{m=0}^{\infty}(-1)^m(m+\beta)^{-3/2}}{8D_{\mathrm{e}}\tau\sum_{m=0}^{\infty}(-1)^m(m+\beta)^{-1/2}}, \tag{4}$$

where $\gamma_{\mathrm{E1/2}}$ is the adsorption coefficient, which refers to the half-wave potential, τ is the half-period of the square-wave, and $\beta=t/\tau$, t now being the time elapsed since the last sudden potential change. The current occasioned by the reduction of adsorbed depolarizers decreases more rapidly than that occasioned by the reduction of diffusing depolarizers with the elapsed time t. Nevertheless, the current occasioned by the reduction of adsorbed depolarizers is considerably retained, even at the latter half-period of each square pulse, as the τ of 1/400 s is very short.

A temperature coefficient of the adsorption quantity always has a negative value in a physical adsorption, and frequently in a chemical adsorption as well and so

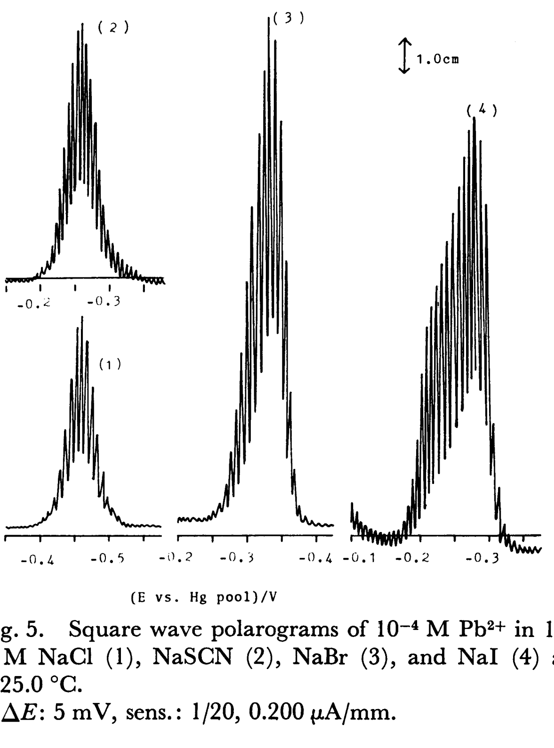

Fig. 5. Square wave polarograms of 10^{-4} M Pb^{2+} in 1.0 M NaCl (1), NaSCN (2), NaBr (3), and NaI (4) at 25.0 °C.
ΔE: 5 mV, sens.: 1/20, 0.200 μA/mm.

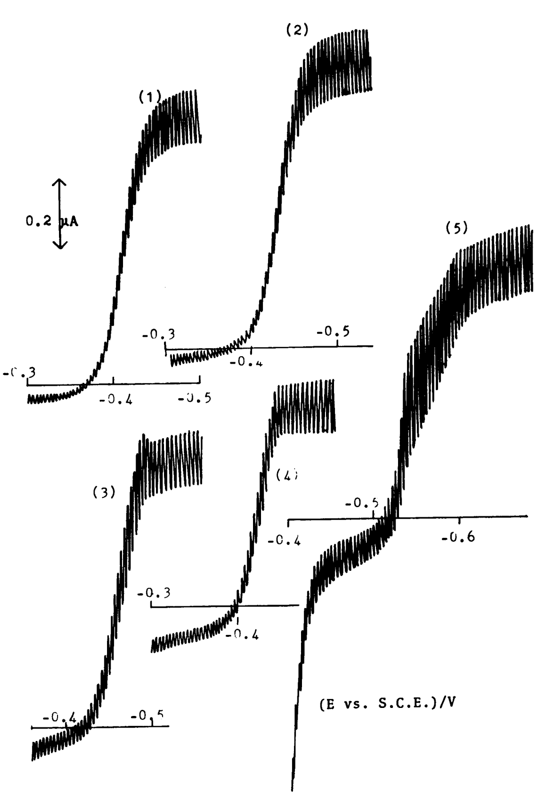

Fig. 6. Direct current polarograms of 10^{-4} M Pb^{2+} in 1.0 M NO_3^- (1), Cl^- (2), Br^- (3), SCN^- (4), and I^- (5) at 25.0 °C.

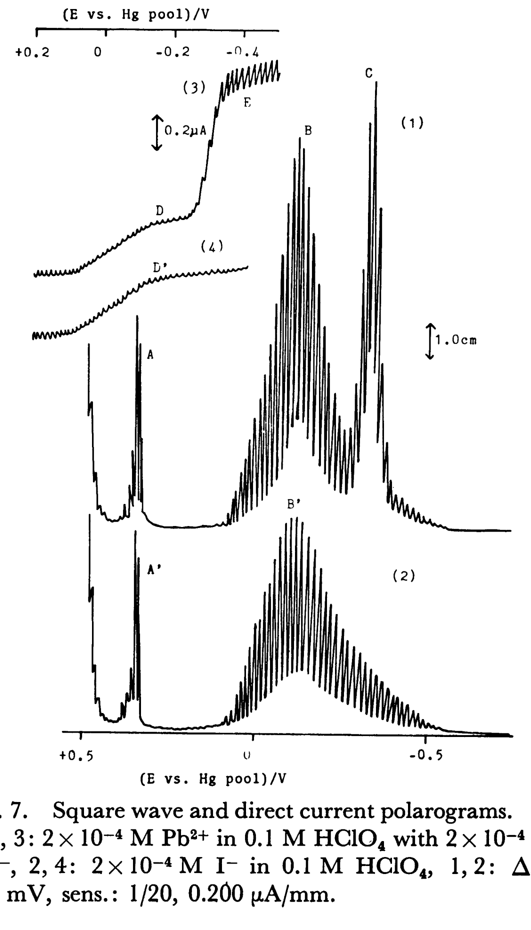

Fig. 7. Square wave and direct current polarograms.
1, 3: 2×10^{-4} M Pb^{2+} in 0.1 M $HClO_4$ with 2×10^{-4} M I^-, 2, 4: 2×10^{-4} M I^- in 0.1 M $HClO_4$, 1, 2: ΔE: 5 mV, sens.: 1/20, 0.200 μA/mm.

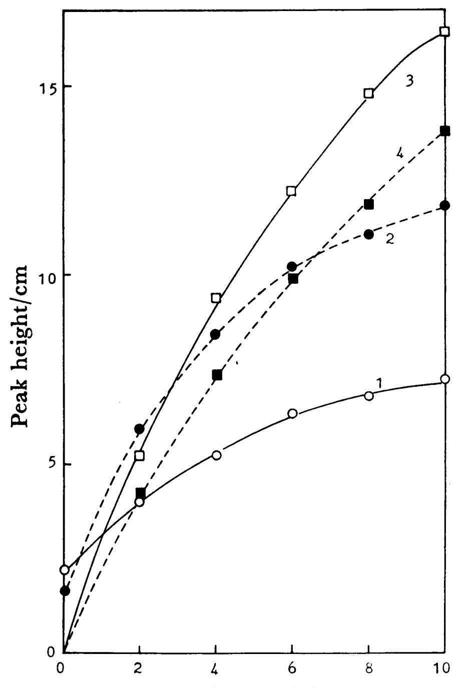

Fig. 8. Relation between the peak height of B, C, and Pb^{2+} concentration.
1: B, 25.0 °C, 2: B, 0.2 °C, 3: C, 25.0 °C, 4: C, 0.2 °C. ΔE: 5 mV, sens.: 1/50, 0.200 μA/mm.

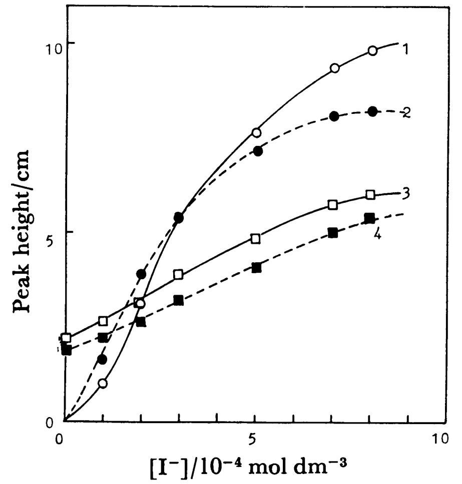

Fig. 9. Influence of I^- concentration on the peak heights of B and C.
1: B, 25.0 °C, 2: B, 0.8 °C, 3: C, 25.0 °C, 4: C, 0.8 °C. ΔE: 5 mV, sens.: 1/50, 0.200 μA/mm.

these experimental results may be considered reasonable.

Moreover, the following facts support adsorption of the depolarizer. In the presence of high concentrations of anions, s.w. polarograms of lead became noticeably asymmetric, as is shown in Fig. 5. In the presence of 1 M Br^-, a maximum which characterized the adsorption of the depolarizer appeared in the d.c. polarogram of 10^{-4} M lead. The surface-active substances, such as gelatin, Methyl Red, camphor, Eosin, thymol, and Alizarin S, changed the temperature coefficient of the peak height in the s.w. polarogram of lead from negative

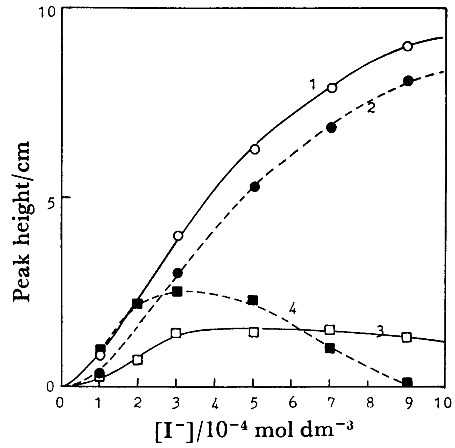

Fig. 10. Relation between I^- concentration and the peak height of B′ and B-B′.
1: B′, 25.0 °C, 2: B′, 1.0 °C, 3: B-B′, 25.0 °C, 4: B-B′, 0.2 °C. ΔE: 5 mV, sens.: 1/50, 0.200 μA/mm.

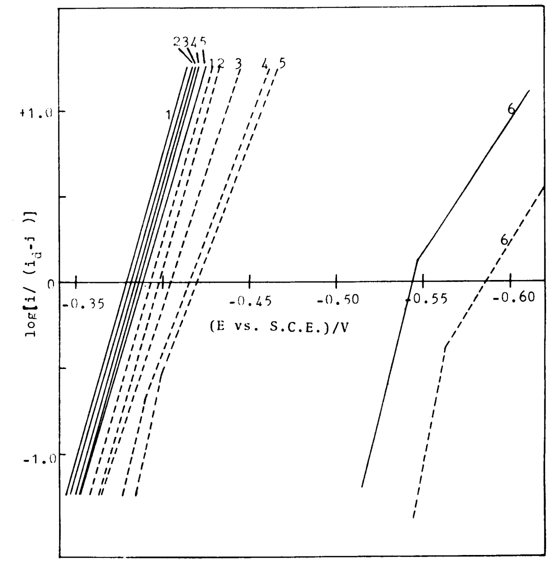

Fig. 11. Log plot analysis of the d. c. polarogram of 10^{-4} M Pb^{2+} in 0.1 M $HClO_4$.
Added I^-: 1) 0, 2) 2×10^{-4} M, 3) 4×10^{-4} M, 4) 6×10^{-4} M, 5) 8×10^{-4} M, 6) 1.0 M.
—— 25.0 °C, ------ 0 °C.

to positive, as has been shown in a previous paper.[3]

Increased Sensitivity and Positive Temperature Coefficient. Upon the addition of iodide, the temperature coefficient was always positive in spite of the increased peak height of lead in the s.w. polarogram caused by the adsorbed depolarizer, this was different from the cases of the addition of bromide, thiocyanate, and chloride.

However, it was found that another peak attributable to lead, which was superimposed on the oxidation peak of iodide, had a negative temperature coefficient.

When iodide was added to a 10^{-4} M Pb^{2+} solution of 0.1 M $HClO_4$, three peaks appeared in the s.w. polarogram, as is shown in Fig. 7. The first peak, A, at about +0.4 V (*vs.* Hg pool), apparently depends on the tensammetric process. The height of the second peak, B, which was, at first sight, thought to be the oxidation peak of iodide, was higher than the oxidation peak, B′, of iodide in the absence of lead, and increased progressively with an increase in the concentration of lead or iodide, as is shown in Figs. 8 and 9. The temperature coefficient of B was negative, whereas that of B′ was positive, as is shown in Fig. 10. By substracting the peak height of the oxidation of iodide, B′, from the peak height of B, the plot of (B-B′) against the concentration of iodide shown in Fig. 10 was obtained. At a low concentration of iodide, (B-B′) increased with an increase in the iodide concentration, and the temperature coefficient of (B-B′) was negative. On the other hand, at higher concentrations of iodide, (B-B′) decreased with an increase in the iodide concentration and the temperature coefficient of (B-B′) was positive.

In the d.c. polarogram, the D and D′ corresponding to B and B′ were equal in wave height, so both D and D′ were only the oxidation waves of the iodide ion.

Therefore, (B-B′), which was superimposed on the peak of the iodide oxidation, must be a peak attributable to the adsorbed lead ion, the same as the C peak.

Next, the plot of $E_{\mathrm{d.e.}}$ (a potential of a dropping mercury electrode) *vs.* log $[i/(i_{\mathrm{d}}-i)]$ in the d.c. polarogram of lead (E corresponding to Peak C in the s.w. polarogram) was analyzed; the results are shown in Fig. 11.

In a reversible process, a plot of $E_{\mathrm{d.e.}}$ *vs.* log $[i/(i_{\mathrm{d}}-i)]$ shows a straight line, with a slope equal to $0.0591/n$ V at 25.0 °C and $0.0550/n$ V at 0 °C.

The presence of 2×10^{-4}—8×10^{-4} M I^- at 25 °C did not influence the slope, but at 0 °C, with an increase in the concentration of iodide, the slope was larger than the theoretical value and the half-wave potential was more negative.

These results show that the process becomes irreversible with an increase in the concentration of iodide at low temperatures.

In s.w. polarography, which requires a faster electrode reaction than d.c. polarography for an electrode reaction to be reversible because of the frequent periodic change in the electrode potential, the electrode processes in this case should be far more irreversible than in d.c. polarography. In an irreversible process, the temperature coefficient of a Peak height should be positive and larger than in a diffusion-controlled process.

Therefore, in spite of the electrode process accompanied by the depolarizer adsorption, the temperature coefficient of the peak (C) height of lead in the addition of iodide in the s.w. polarogram was positive.

Moreover, the positive temperature coefficient in the presence of bromide or thiocyanate of a high concentration may be attributable to the same reason.

The accelerating effect of halide ions on the electrode reactions of bismuth,[12] copper,[12] and zinc[13] has been reported. Breyer *et al.* suggested that the presence of halide ions decreased the repulsion of the aqueous Bi^{3+} or Cu^{2+} from the positively charged electrode, either because of the formation of a halo-complex or because of the adsorption of negatively charged halide ions on the electrode. Therefore, similar accelerating effects of iodide on the electrode reaction may be expected in the case of lead. Nevertheless, a decreasing reversibility with an increase in the concentration of iodide was observed. It may be that this decreasing reversibility is related to the dissociation rate of the complex preceeding the electrode reaction. A more detailed investigation is, however, necessary to clarify the cause of the decreasing reversibility.

Complex Formation and Adsorption. The half-wave potential shifted to a more negative potential upon the addition of anions in the order of; SCN^-, Cl^-, Br^-, I^- at 25 °C, and in the order of; Cl^-, SCN^-, Br^-, I^- at 0 °C, as is shown in Fig. 12. This order of the shift of a half-wave potential to a negative potential shows a tendency to form complexes of the depolarizer with anions or a tendency to form insoluble compounds. This order coincided with the ability to adsorb lead found from the degree of the increase in the peak height in the s.w. polarogram and also approximately with the ability to adsorb anions on mercury electrodes which was calculated by Grahame[14] and which is shown in Table 1. Therefore, the ability to adsorb lead may depend on both the adsorbed ability of anions on mercury electrodes and the complex-forming ability of lead with anions.

In the case of cadmium, which forms an insoluble

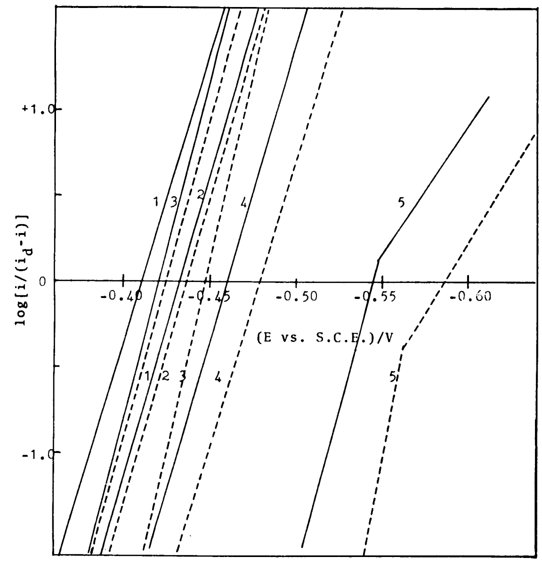

Fig. 12. Log plot analysis of the d. c. polarogram of 10^{-4} M Pb^{2+} in 1.0 M NO_3^- (1), Cl^- (2), SCN^- (3), Br^- (4), and I^- (5) with 0.01 M $HClO_4$.
—— 25.0 °C, ------ 0 °C.

Table 1. THE QUANTITIES OF THE ELECTROLYTES ADSORBED PER UNIT OF AREA OF THE MERCURY INTERFACE AT THE ELECTROCAPILLARY MAXIMUM[14]

Electrolyte	$\Gamma_{\mathrm{m}}/\mu\mathrm{C\ cm^{-2}}$
1 M NaCl	3.6
1 M KBr	10.6
1 M KI	15.2
1 M NaSCN	14.0
1 M KNO_3	5.5

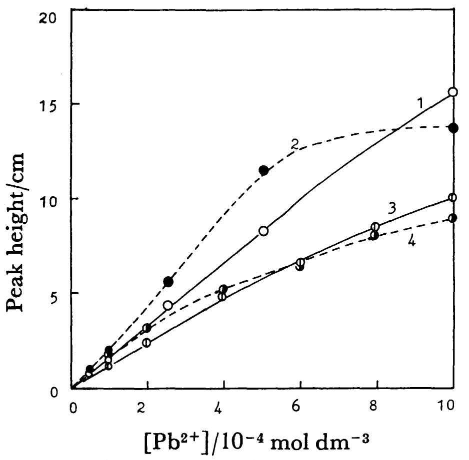

Fig. 13. Relation between the peak height in the s. w. polarogram and the concentration of lead in the presence of 1.0 M Cl$^-$ (1, 2) and 0.5 M Cl$^-$ (3, 4).
1, 3: 25.0 °C, 2, 4: 0 °C, ΔE: 5 mV, sens.: 1/100, 0.200 μA/mm.

compound with these anions only with difficulty, no adsorption of cadmium was found by means of s.w. polarography[3] in the presence of chloride, but it was reported in the presence of iodide on the basis of the experimental result from differential-pulse polarography.[15]

In the case of thallium, which forms an insoluble compound with chloride, the adsorption of thallium[16] was found by means of s.w. polarography[3] in the presence of chloride.

Moreover, the adsorption of lead decreased upon the addition of nitrate to chloride, as may be seen in Figs. 1 and 2. These results can be explained as follows; the adsorption of chloride on mercury was decreased by the nonspecific adsorption of nitrate, which did not induce so much adsorption of lead as chloride did.

These facts show that lead is induced by a covalent bonding force with adsorbed anions and adsorbed on mercury electrodes; in other words, lead adsorption is a specific adsorption induced by the foremost adsorbed anions. Therefore, upon the increase in the depolarizer over the inducing ability of anions, the temperature coefficient of the peak height of the depolarizer approached the theoretical value in a diffusion-controlled process, as is shown in Fig. 13.

The auther wishes to express her thanks to Professor Toyokichi Kitagawa of Osaka City University for his continuous encouragement and for his kind guidance in this work.

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