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Original Scientific Paper

On the Adsorption of Lead Iodide on the Mercury Electrode

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The adsorption of lead iodide on the mercury electrode was studied by the potential-sweep chronoamperometric method, by recording of polarographic current-time curves and by the measurement of the differential capacity of the electric double-layer. From the dependence of height and potential of the adsorption peak on the concentration of iodide the solubility product of PbI_2 was calculated ($K_S = 1.3 \times 10^{-8}$). From polarographic current-time curves it could be concluded that the adsorption process is controlled by diffusion and the surface excess was calculated $\Gamma_S = 4.3 \times 10^{-10}$ mole/cm^2). The kinetics of the adsorption process is potential dependent. The measurements of the differential capacity have shown that the adsoprtion of lead occurs after previous adsorption of iodide ion and that in solutions of high iodide concentration the compact adsorption layer is destroyed.

The adsorption of lead in iodide solutions on a dropping mercury electrode was first noticed by V. Klemenčić and I. Filipović[1]. With lead solutions (0.4 m*M* Pb^{2+}) containing 0.01—1.5 *M* sodium iodide the polarogram consisted of two waves and from the electrocapillary curves it was evident that the two waves occur as a result of the formation of adsorption layer on the surface of the dropping mercury electrode[1]. V. S. Srinivasan and A. K. Sundaram[2] made detailed d. c. and a. c. polarographic studies of the behaviour of lead in 1 *M* sodium iodide solution on the dropping mercury electrode. They have shown that the second d. c. polarographic wave is an adsorption wave resulting from the adsorption of lead iodide complexes on the dropping mercury electrode. In the a. c. polarographic study three peaks are obtained. The first peak is due to a differential process of the first d. c. wave. The second peak corresponds to the desorption of the adsorbed species, and the third peak appears to be due to the reduction of the desorbed species. Hence, the second and the third peak correspond to the second d. c. polarographic wave. R. W. Murray and D. J. Gross[3] performed chronopotentiometric, chronocoulometric, and polarographic measurements of the adsorption of lead in 1 *F* NaI at mercury electrodes. The lead surface excess was measured, and the comparisons of calculated coverages for various lead iodide species with experimental caverages suggest an adsorption with a 1/1 or 1/2 lead to iodide ratio. One probably has to deal with the presence of -Pb-I-Pb-I- surface chains or linear I-Pb-I units with the bond axis perpendicular to the surface. The surface packing is of a relatively high density, so that the adsorbed lead iodide exhibits severe blocking effects on the electrode reactions of corresponding mercury (II) and bismuth complexes.

Investigations of lead adsorption on mercury electrodes, performed as yet, have been made mainly in 1 *M* sodium iodide solutions[2,3] although this phenomenon has been observed in solutions of iodide with a concentration below 20 m*M* as well[1]. To obtain a more complete insight in the behaviour of lead in iodide solutions this paper gives the results of investigations comprising a wide concentration range from 0 to 3 *M* NaI. Adsorption phenomena were investigated: (1) by the measurement of the double-layer differential capacity of the hanging mercury drop electrode, (2) by recording potential-sweep chronoamperograms, and (3) by recording polarographic current-time curves.

EXPERIMENTAL

The differential capacity of the double-layer and the capacity component of the electrode reaction (Grahame's pseudo-capacity)[4] were recorded continuously and automatically by the polarograph Polariter PO-4 with a supplementary device after Kowalski and Srzednicki[5] and Valeriot and Barradas[6].

Potential-sweep chronoamperograms and d. c. polarograms were recorded with the same polarograph Polariter PO-4.

The hanging mercury drop electrode was employed in capacity measurements and to obtain chronoamperograms. The hanging mercury drop electrode was prepared after Kowalski and Srzednicki[5] with necessary modifications, to achieve a greater exactness in reproducing the surface of the mercury drop. The surface of the mercury drop was 2.36 mm^2.

Polarographic current-time curves were obtained by means of a Hewlett-Packard Oscilloscope, Model 130C. Photographs of oscillograms were taken with a camera Exacta Varex IIA having a Flektogon wide-angle lens. A dropping capillary was used for these measurements ($m = 1.692$ mg/sec. and $t = 5.50$ sec. in 0.1 *M* KCl, measured at open circuit at $h = 26$ cm). Current-time curves were recorded with the »first drop« applying the equipment described by L. Nemec and I. Smoler[7].

The polarographic cell and other equipment did not differ from that described in a previous paper[8]. The circuit impedance was made small for a. c. measurements by shunting the mercury pool and the reference cell with a condenser[2]. All potentials are given with respect to the calomel electrode with a saturated solution of sodium chloride. All measurements were carried out under constant temperature of 25 ± 0.1^0 C.

For the preparation of solutions analytical-grade chemicals (NaI, $NaNO_3$, $Pb(NO_3)_2$, $HClO_4$) were used. The concentration of sodium iodide was varied from 0 to 3 *M*. The ionic strength of the solution was maintained at the constant value 2 (except in NaI solution of a concentration higher than 2 *M*) by adding the corresponding quantity of sodium nitrate. The concentration of lead was varied from 0.1 to 1.2 m*M*. In order to prevent the hydrolysis of the lead ion, supporting electrolyte solutions contained 10 m*M* perchloric acid[3]. When solutions contained gelatine its quantity amounted to 0.006$^0/_0$[2].

RESULTS AND DISCUSSION

Potential-sweep Chronoamperometry

Figs. 1—3 represent characteristic potential-sweep chronoamperograms for 0.1, 0.4, and 0.8 m*M* lead in sodium iodide solutions of increasing concentration up to 3 *M* according to the solubility of PbI_2. The whole concentration range from 0 to 3 *M* was comprised by solutions of 0.1 m*M* lead. At certain minimum concentrations of sodium iodide a sharp adsorption-controlled peak appears at first on the potential-sweep chronoamperograms, this being followed by a rounded diffusion-controlled peak.[3] With the increase of concentration of iodide the height of the adsorption peak increases, it is shifted to more negative

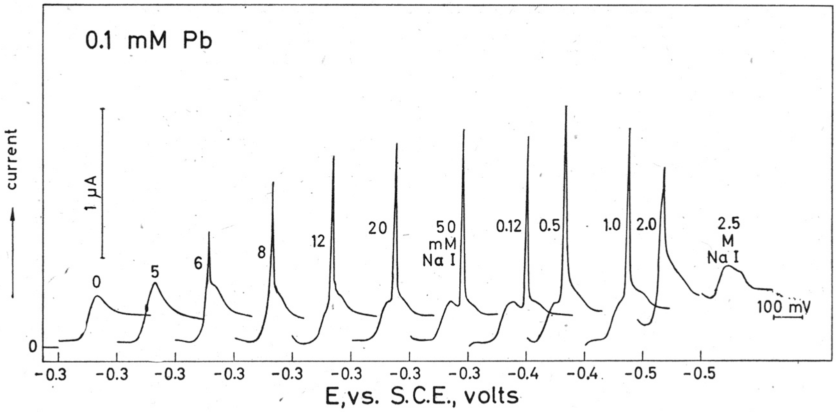


Fig. 1. Potential-sweep chronoamperograms for 0.1 mM lead. Scan rate = 0.0033 v./sec.

potentials, this shift being, at first, stronger than that of the diffusion peak, so that finally the sharp adsorption peak follows the rounded diffusion peak. At very high concentrations of iodide (> 1.5 *M*) a more or less significant mergence

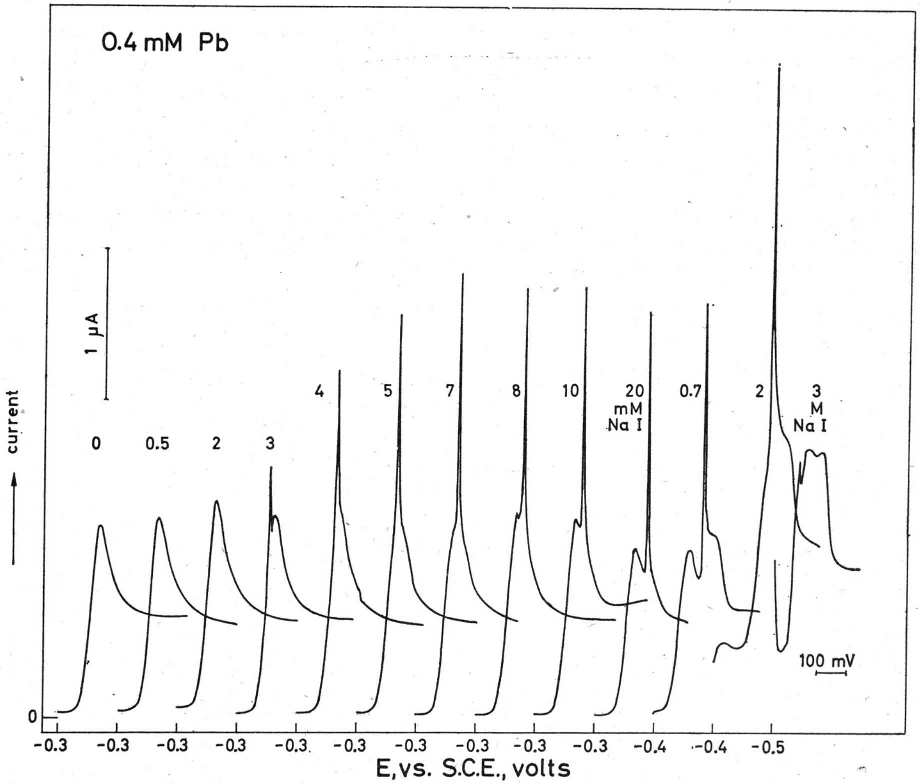


Fig. 2. Potential-sweep chronoamperograms for 0.4 mM lead. Scan rate = 0.0033 v./sec.

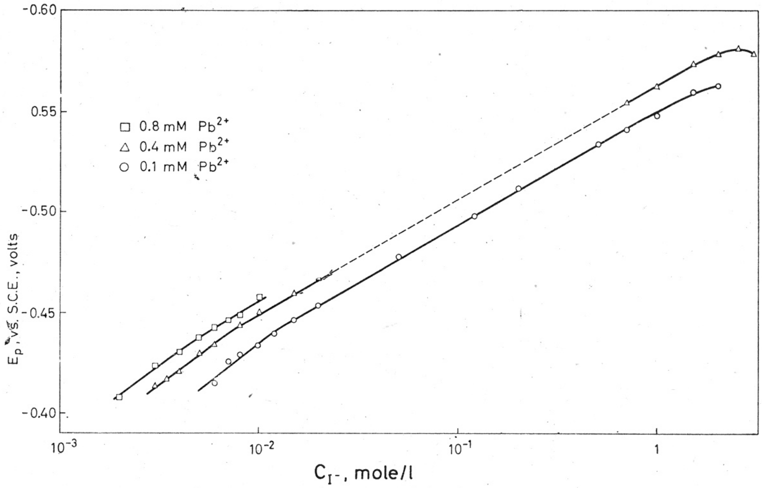


Fig. 5. Dependence of the potential of adsorption peak (E_p) on the concentration of iodide.

the height of the adsorption peak increases again, and then it decreases abruptly in highly concentrated solutions of sodium iodide.

It is, consequently, evident that the compactness of the adsorption layer at first increases with the increase of the concentration of iodide. At a certain concentration of iodide, which depends on the concentration of lead, the adsorption layer assumes a constant structure, which changes only in more highly concentrated solutions of sodium iodide. Then probably occurs at first the formation of a more compact structure which is, however, destroyed in highly concentrated solutions of sodium iodide.

According to Murray and Gross[3], the adsorption layer in 1 *M* solutions of sodium iodide consists of lead and iodide in a ratio of 1/1 or 1/2. The adsorption layer itself consists, most probably, of -Pb-I-Pb-I- surface chains or of linear I-Pb-I units with the bond axis perpendicular to the surface. However, the compact layer on the surface of the mercury electrode might be not only of adsorption character but also a solubility-determined PbI_2 surface film. In this case, from the diagram in Fig. 4 can be obtained equilibrium concentrations of iodide, corresponding to concentrations of lead (0.1, 0.4, and 0.8 m*M*) when the constant compactness of the adsorption layer of composition PbI_2 has been reached (the intersection of rising linear parts of curves with horizontal parts). If the compact adsorption layer consists of PbI_2, then from the obtained equilibrium concentrations of iodide and lead the solubility product of PbI_2 can be determined, amounting for the three quoted concentrations of lead to $K_s = 1.3 \times 10^{-8}$ (mean value), which is in good accordance with values given in literature[9].

The same value for the solubility product of PbI_2 can be obtained also by an analysis of the curves which gives the shift of the potential of adsorption peak (E_p) with the change of concentration of sodium iodide (Fig. 5) and with the change of concentration of lead (Fig. 6). The slope of the plot of E_p *vs.* $\log C_I$ in the concentration range where a compact adsorption layer exists (0.01 to 1 *M* NaI) amounts to 57 mV. The slope of the plot of E_p *vs.*

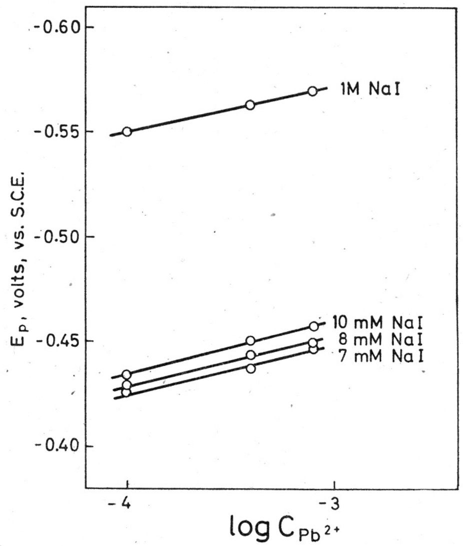


Fig. 6. Dependence of the potential of adsorption peak (E_p) on the concentration of lead.

log C_{Pb} amounts to 24—26 mV. That would correspond to a lead to iodide ratio in the adsorption layer of 1/2. Hence the empiric relation:

$$E_p = K - 0.026 \log C_{Pb} - 0.057 \log C_I$$

where, according to the above said, $K = E_p^0 + 0.0295 \log K_s$. The E_p^0 potential corresponds to the concentration of iodide, when the height of the adsorption peak is equal to zero (*i. e.* in the absence of adsorbed PbI_2), which was easily obtained from the graph in Fig. 4, and then from the graph in Fig. 5 $E_p^0 = - 0.405$ V *vs.* S. C. E. was obtained. Value K corresponds to the potential of the adsorption peak when C_I and C_{Pb} are equal to 1, which is obtained from the graph (Fig. 6) giving the relation between E_p and log C_{Pb} in the solution of iodide of concentration 1 *M*. The value $K = 0.638 \pm 0.005$ V *vs.* S. C. E. was obtained by extrapolation to log $C_{Pb} = 0$. From this value the solubility product of PbI_2 was calculated and it amounts to $K_s = 1.4 \times 10^{-8}$, which is in good accordance with the value obtained directly from equilibrium concentrations of lead and iodide, as mentioned before.

According to the above said, the dependence of the height and potential of the adsorption peak on the concentration of iodide and lead indicates that the compact adsorption layer consists probably of PbI_2 units. It is interesting to mention, that Barker and Bolzan[10] recently found in pulse polarographic investigation of lead in $HClO_4$ solutions containing Br^- ion, that undissociated $PbBr_2$ may possibly also be adsorbed at the dropping mercury electrode. To enable a view into the kinetics of the formation of the adsorption layer as well as into its structure on the surface of the mercury electrode, recording of current-time curves was performed.

Polarographic Current-time Measurements

The recording of polarographic current-time (*i-t*) curves was performed in solutions of low (15 m*M*) and high (1 *M*) concentration of sodium iodide,

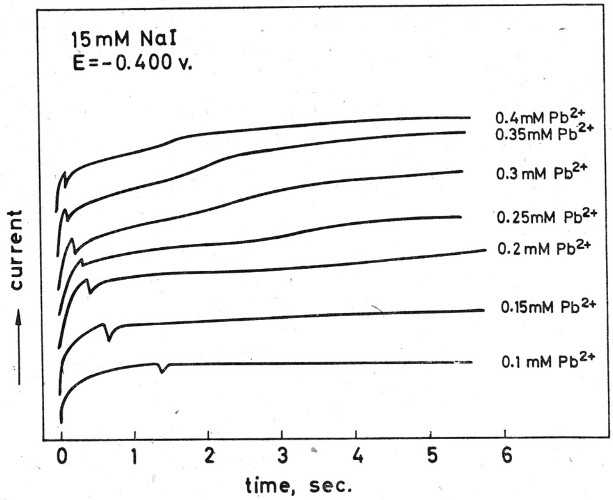


Fig. 7. Polarographic current-time curves at —0.400 v. vs. S. C. E. for lead with 15 mM NaI added.

without gelatine, varying the concentration of lead from 0.1 to 0.8 m*M*. The potential of the dropping mercury electrode was chosen in the range of the beginning of the rise of the »normal« lead wave (— 0.400 V, at 15 m*M* NaI and — 0.500 V at 1 *M* NaI). A part of the results of these measurements is represented in Figs. 7 and 8. It can ben seen, that at a certain time of the life of the

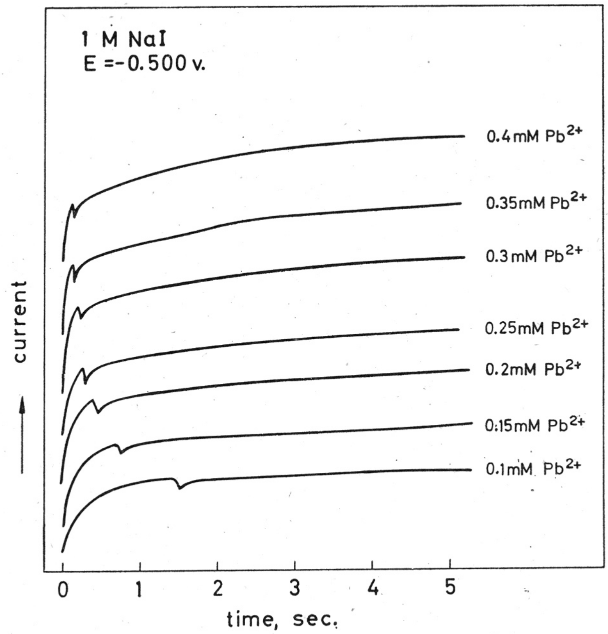


Fig. 8. Polarographic current-time curves at —0.500 v. vs. S. C. E. for lead with 1 M NaI added.

mercury drop it is covered with an adsorbed layer of lead iodide, and that this time decreases with the increase of the concentration of iodide. On the covered surface the process of reduction of unadsorbed lead ions is continuing, but this process is inhibited by the adsorbed layer. From the shapes of *i-t* curves at 15 m*M* and 1 *M* NaI it can be concluded that the process of covering of the surface with adsorption layer as well as the process of discharge of lead on the covered surface are in both cases the same. As the time necessary for the covering of electrode surface with the adsorbed layer decreases with the increase of the concentration of lead, it is evident that the rate of formation of the adsorption layer is controlled by the diffusion of lead to the surface of the electrode. In this case the well-known Koryta equation[11] is valid:

$$\vartheta = 1.85 \times 10^6 \, \Gamma_s^2 / C^2 D$$

where ϑ is the time necessary for a complete covering of the surface with the adsorption layer, Γ_s is the surface excess at complete coverage, C is the concentration of the surface active substance (in the given case the lead concentration), and D is its diffusion coefficient (for lead iodide $D = 1.6 \times 10^{-5}$ cm^2/sec)[3]. Accordingly, if the rate of surface covering of mercury electrode with the adsorption of lead iodide is controlled by the process of diffusion, a linear plot of ϑ *vs.* $1/C_{Pb}^2$ with zero intercept must be obtained. Fig. 9 gives such a plot of t_{max}, t_{min}, and t_o *vs.* $1/C_{Pb}^2$, where t_{max} is the time corresponding to the maximum on *i—t* curve (the beginning of coverage), t_{min} is the time corresponding to the analogous minimum on *i—t* curve, and t_o

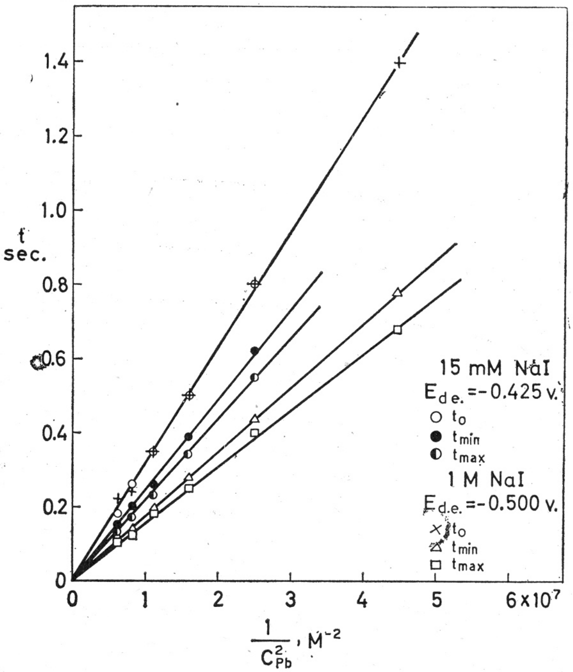


Fig. 9. Plot of t versus $1/C_{Pb}^2$

is time extrapolated to zero, which corresponds approximately to time ϑ. It can be seen that there is a linear plot with zero intercept. The slope of the plot of t_0 *vs.* $1/C^2_{Pb}$ is the same for both concentrations of iodide. However, this is not the case with analogous plots of t_{max} and t_{min} *vs.* $1/C^2_{Pb}$. As surface excess Γ is obtained from these plots, it might be concluded, that Γ, during surface covering, depends on the concentration of iodide, but at completely covered surface (t_0) Γ_s is not dependent on the concentration of iodide, as can be seen from the diagram. In other words, the structure of the adsorption layer of a completely covered surface is independent of the concentration of iodide in the concentration range from 15 m*M* to 1 *M*. Using the t_0 *vs.* $1/C^2_{Pb}$ plot, its slope yields a surface excess, Γ_s, of 4.3×10^{-10} mole/cm². This value is lower than that obtained by Murray and Gross[3] by another method (8.4×10^{-10} mole/cm²), or than the value obtained from the polarographic adsorption wave by Srinivasan and Sundaram[2] (6.5×10^{-10} mole/cm²). Though the method of Murray and Gross is considerably more exact than that using *i—t* curves (because of very difficult extrapolation to the zero current), it is still interesting to note that, assuming an adsorption layer consisting of linear PbI_2 species with bond axis parallel to the surface theoretically Γ_s should amount[3] to 4.6×10^{-10} mole/cm², which agrees very well with the obtained Γ_s of 4.3×10^{-10} mole/cm². That would be in accordance with results of measurements obtained by the mentioned potential-sweep chronoamperometric method. Figs. 10 and 11 represent *i-t* curves recorded at different

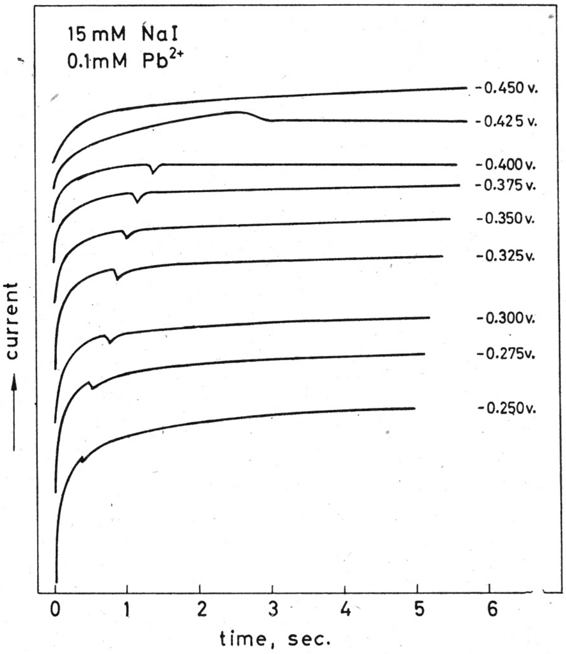


Fig. 10. Polarographic current-time curves for 0.1 mM lead with 15 mM NaI added, recorded at different potentials (—0.250 to —0.450 v. vs. S. C. E.)

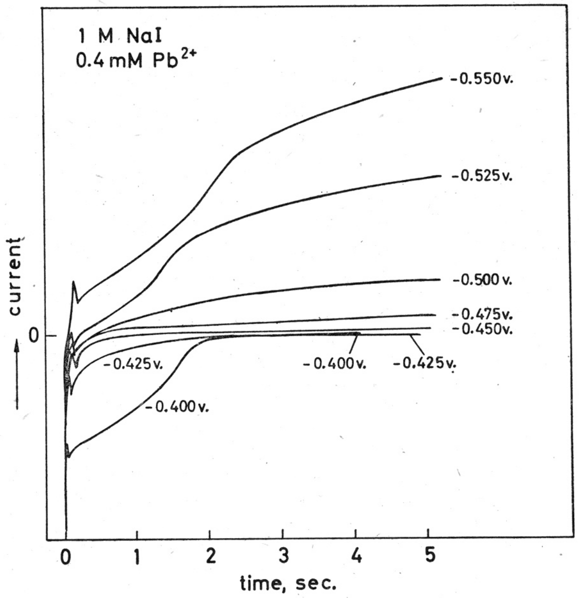


Fig. 11. Polarographic current-time curves for 0.4 mM lead with 1 M NaI added, recorded at different potentials (—0.450 to —0.550 v. vs. S. C. E.)

potentials within the range of the »normal« polarographic lead wave. It is seen that the time necessary for the covering the surface with an adsorption layer of lead, increases with the shift of the electrode potential to more negative values. This phenomenon is probably in connection with the simultaneous progression of the adsorption process and the process of discharge of lead on the covered surface, at which the rate of discharge increases with the shift of the potential to more negative values, and less lead is at disposal for the coverage of the electrode surface with the adsorbed layer of lead iodide.

Differential Capacity Measurements

Differential capacity (C_D) of the electric double-layer of the electrode is sensitive to the adsorption of surface active substances on the electrode surface. Therefore, differential capacity measurements offer a means of obtaining an insight into the adsorption process, especially with regard to the dependence of the adsorption on the electrode potential. Srinivasan and Sundaram[2] investigated the change of differential capacity of the mercury dropping electrode (applying the a. c. polarographic method, as $i \sim C_D$) with the change of the electrode potential in 1 *M* solutions of NaI at different concentrations of lead. In the solutions which gave a polarographic adsorption wave besides a »normal« polarographic wave, they obtained three peaks on a. c. polarograms. From their forms and positions on the potential scale, as well as from the behaviour of these a. c. peaks at different frequencies of the alternating voltage and at different temperatures, they concluded, that the first and the third peak are diffusion-controlled and the second sharp peak corresponds to the dessorption of the adsorbed species. As a. c. peak was, in the presence of lead, lower than that of the supporting electrolyte at potentials more positive than the peak potentials, they concluded, that this was due to the lowering of the double layer capacity arising from the adsorption of oxidized species. Our measurements under the same conditions agree with these published results.

Therefore, here will be given the results of differential capacity measurements obtained with the hanging mercury drop in solutions containing 0.1 and 0.4 m*M* Pb, the concentration of NaI being varied from 0 to 2.5 *M*. As potentials-sweep chronoamperograms were also recorded in the same solutions, this will enable us to get an insight into the process of formation of the sharp peaks at low concentrations of NaI, as well as their decrease or disappearance, in very concentrated solutions of NaI.

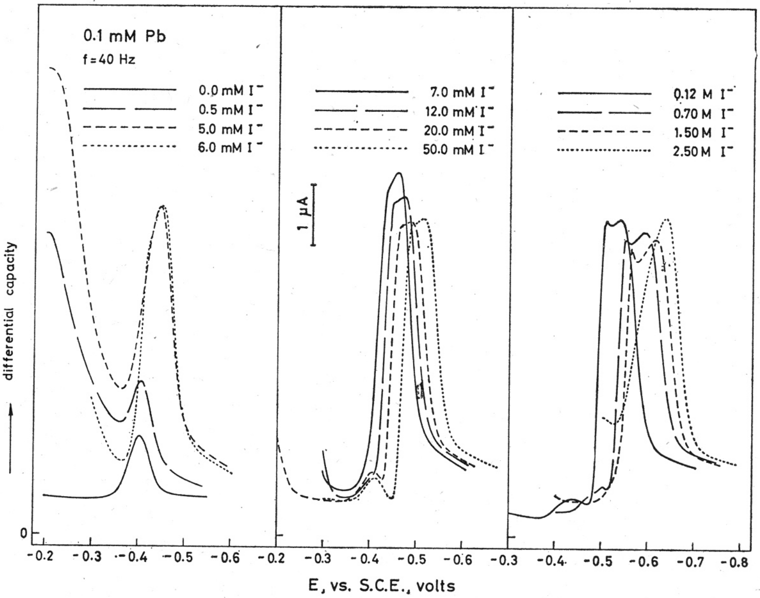
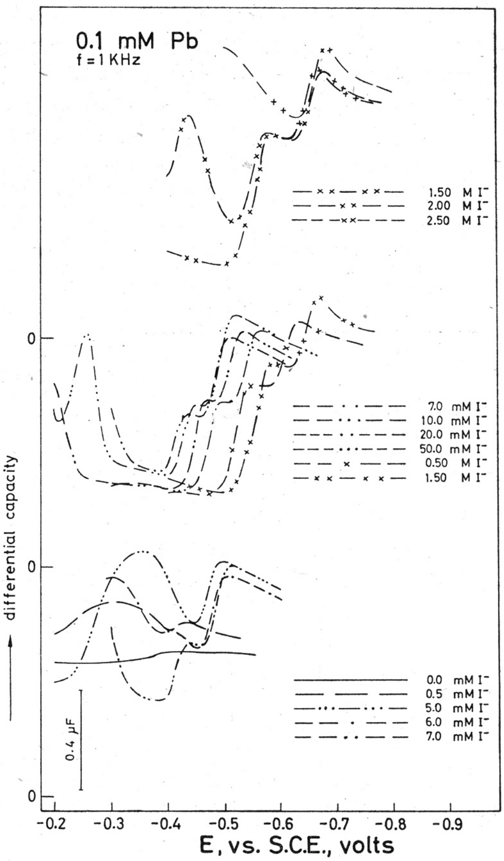


Fig. 12 Differential capacity curves at 40 Hz for 0.1 mM lead with different concentrations of NaI. Scan rate = 0.0067 v./sec.

Figs. 12, 13, and 14 represent the results of these measurements. Measurements of differential capacity were performed at low (40 Hz) and high (1 kHZ) frequency (the superimposed alternating voltage was 7 mV).

At a frequency of 40 Hz (Fig. 12) in the potential range where the first rounded diffusion peak appears on the potential-sweep chronoamperograms a diffusion-controlled »pseudo-capacity« peak[4] is formed. With the increase of iodide concentration to 5 m*M* the pseudo-capacity peak is shifted to higher values of C_D due to iodide adsorption. In that concentration range no sharp adsorption peak (Fig. 1) appears on the potential-sweep chronoamperogram. However, a transition of the pseudo-capacity peak into a considerably higher and wider peak occurs at 5 m*M* NaI. With a further increase of the iodide concentration a sharp adsorption peak (Fig. 1) appears on the potential-sweep chronoamperogram, while C_D—E curves (Fig. 12) are shifted to lower values



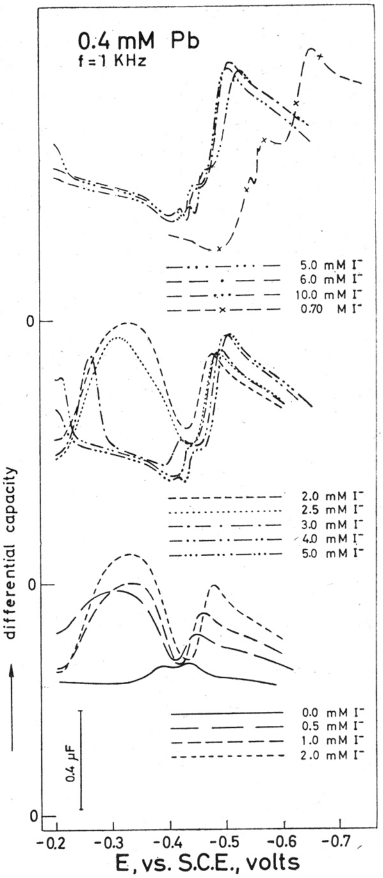


Fig. 13. Differential capacity curves at 1 KHz for 0.1 mM lead with different concentrations of NaI. Scan rate = 0.0067 v./sec.

Fig. 14. Differential capacity curves at 1 KHz for 0.4 mM lead with different concentrations of NaI. Scan rate = 0.0067 v./sec.

of C_D at potentials more positive than the peak. Besides this, the wide peak splits gradually and increasingly into three peaks, the first and third of which are diffusion-controlled, and the second is a sharp adsorption peak, as follows from their behaviour towards the increase of frequency (see later). Consequently, the peaks are analogous to those obtained using the dropping mercury electrode and, accordingly, they should correspond to analogous mechanisms[2].

Accordingly, at very low concentrations of iodide the adsorption of iodide ions on the mercury electrode surface prevails, and C_D corresponds to that obtained in iodide solutions without lead. Only when the electrode surface is covered with iodide ions to a certain extent, the adsorption of lead ions and the formation of a lead iodide film of relatively high density occur, which results in a large decrease of differential capacity. Besides this, the adsorption of lead takes place at potentials which become more positive with increasing iodide concentration. The potentials of the sharp second peak on the C_D—E curves agree with the potentials of the sharp second adsorption peak on the potential-sweep chronoamperograms, and both are undoubtedly due to the desorption of lead iodide film. The third rounded peak on C_D—E curves corresponds to the reduction of the desorbed lead iodide, as can be also concluded from the fact that it has an approximately constant value in the same concentration range as the adsorption peak on the potential-sweep chronoamperograms. It is interesting, that the desorption process and the process of the discharge of the desorbed species are represented by only one peak on potential-sweep chronoamperograms, while on C_D—E curves two peaks appear, which are the more separated, the higher the concentration of iodide. However, the first sharp peak on C_D—E curves appears at the same potential as the sharp peak on potential-sweep chronoamperograms. At very high (> 2 *M*) iodide concentrations (Fig. 12) the three peaks merge again into, one, and the differential capacity increases at potentials more positive than the peak. It is evident, consequently, that at these iodide concentrations the adsorption of lead iodide decreases, or the adsorption film is destroyed, this being indicated also by potential-sweep chronoamperograms (Fig. 1).

The same conclusions can be drawn from the analysis of C_D—E curves at a frequency of 1 kHz (Figs. 13 and 14). C_D—E curves at this frequency show distinctly a change of C_D with the change of iodide concentration at potentials more positive than the potential of electro-reduction of lead. At a high frequency the first and third diffusion-controlled pseudo-capacity peaks disappear, and a recess on the C_D—E curves occurs in their place. The sharp adsorption peak is still there, though it is rather small. C_D—E curves of 0.1 (Fig. 13) and 0.4 m*M* Pb^{2+} (Fig. 14) do not differ qualitatively, which indicates analogous adsorption processes in both cases. The appearance of the sharp adsorption peak on the potential-sweep chronoamperograms at 3 m*M* NaI in the presence of 0.4 m*M* Pb^{2+} (Fig. 2) is connected with the decrease of C_D (Fig. 14), while at lower concentration of NaI C_D increases with the increase of iodide concentration. The decrease of adsorption of lead iodide at iodide concentrations higher than 1.5 *M* is distinctly seen in Fig. 13, as C_D increases with the increase of iodide concentration. The morphology of the C_D—E curves was not dependent on the scan rate employed (0.0033 and 0.0067 v./sec.).

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IZVOD

O adsorpciji plumbum-jodida na živinoj elektrodi

I. Filipović, M. Tkalčec, B. Mayer i I. Piljac

Proučavana je adsorpcija plumbum-jodida primjenom kronoamperometrijske metode, snimanjem polarografskih krivulja struja-vrijeme i mjerenjem diferencijalnoga kapaciteta. Izračunan je produkt topivosti plumbum-jodida ($K_S = 1.3 \times 10^{-8}$) iz ovisnosti visine i potencijala adsorpcijskog vrha kronoamperograma o koncentraciji jodida. Određen je površinski višak PbI_2 ($\Gamma_S = 4.3 \times 10^{-10}$ mol/cm^2). Iz rezultata mjerenja diferencijalnoga kapaciteta moglo se zaključiti da adsorpcija PbI_2 nastupa tek nakon stvaranja adsorpcijskoga sloja jodida i da se adsorpcijski sloj PbI_2 razara u otopinama visoke koncentracije jodida.

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