Polarization During the Recharging of Tin Ions

By *O. Essin* and *M. Loschkarew*[1]

1. Introduction

Processes concerned with the recharging of ions are used quite widely in electrochemical technology. The velocity of these processes and its dependence upon the value of the electrode potential, in other words the character of the electrode polarization which takes place in this case, have not only technical but also a certain theoretical interest. In contrast with the discharge of hydrogen and metallic ions, the number of stages responsible for the appearance of an overvoltage is quite limited here. Besides concentration polarization (and, in the special case of complex ions, retarded dissociation), during the recharging of ions one may assume apparently only a retarded discharge. In spite of this, the problem of the existence of chemical polarization in a number of cases remains doubtful and sometimes undecided. For example, in the simplest case of recharging of iron ions, only concentration polarization takes place according to Karaoglanoff's data[2], while acording to Le Blanc's data[3] there also occurs chemical polarization. In a later paper by Moll[4] much attention is paid to obtaining reproducible values for the polarization, and the author finally returns to Karaoglanoff's point of view.

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[1] Undergraduate student A. P. Lamanova and laboratory assistant K. N. Russanova participated in the experimental part of this investigation.

[2] Karaoglanoff, Z. Elektrochem., **11**, 489 (1905); **12**, 5 (1906).

[3] M. Le Blanc, Abh. Dtsch. Bunsen Ges., (1910).

[4] W. Moll, Z. physik. Chem., **175**, 353 (1936).

Although during processes of the recharging of ions some substantial difficulties disappear which are present in other cases, such as, *e. g.*, a peculiar change in the value of the electrode surface during the deposition of metals[5], yet the poor reproducibility of the experimental values points to the presence of additional factors which in one way or another influence the value and the character of the electrode surface. A number of investigators regard the appearance of a surface film on the electrode as one of these factors[6]. Thus, it is still not clear whether the polarization which is experimentally observed is caused only by the rate of diffusion of the ions and by additional difficulties which are due to the appearance of a surface film on the electrode, or whether the processes of the recharging of ions are accompanied by overvoltage.

One of the cases of the recharging of ions, where, according to the data given in the literature, there is a clearly expressed, considerable polarization, is the process of the cathodic reduction of stannic ions. According to Foerster and Yamasaki[7] who investigated this process using a platinum cathode, chemical polarization occurs in this case, which is caused by the retarded dissociation of complex anions of tin. In connection with this, however, they note an unsatisfactory reproducibility of experimental data.

Taking into account what has been mentioned above and taking measures which considerably reduce the effect of the surface film, we thought it would be of interest to find out whether there is chemical polarization in this case, and whether it is caused by retarded dissociation of complex anions, or by retarded discharge, or by both of these factors simultaneously.

2. Experimental procedure

Although in working with a solid cathode concentration polarization may be comparatively easily excluded in practice by the fast motion of the electrolyte in the neighbourhood of the cathode

[5] Erdey-Gruz a. Volmer, Z. physik. Chem., **157**, 165 (1931); Kohlschütter, Z. Elektrochem., **38**, 213 (1932).

[6] F. Foerster, Z. physik. Chem., **62**, 129 (1908); **146**, 8, 177 (1930); **151**, 321 (1930). E. Müller, Z. Elektrochem., **35**, 222 (1929). G. Grube, Z. Elektrochem., **18**, 189 (1912); **37**, 321 (1931); **38**, 117 (1932).

[7] F. Foerster a. Yamasaki, Z. Elektrochem., **17**, 362 (1911).

or by revolving the electrode itself, elimination of the difficulties caused by the formation of a film is in this case by no means an easy matter (see, for instance, Moll's work). It requires continuous renewal of the electrode surface and at the same time requires that the nature of the surface should remain constant all the time. In this respect the mercury jet electrode previously described by us[8] is the most suitable one. The linear velocity of flow of the mercury stream may be quite considerable, and this permits obtaining a continuously and rapidly renewed, constant electrode surface. Moreover, the use of a mercury jet electrode markedly lowers the effect of concentration polarization in the solution. As regards the concentration polarization in mercury, which we observed earlier[8] (during an investigation of the discharge of $Na^{\bullet}$, $K^{\bullet}$, and $NH_4^{\bullet}$ ions), it naturally drops off during an investigation of processes of the recharging of ions.

The construction of the electrolyzer and the experimental procedure were basically the same as in the previous studies[8]. A measurement of the polarization was carried out at room temperature using a saturated calomel electrode for comparison (Hg/Hg_2Cl_2, $KCl_{sat.}$) and electrolytes containing various concentrations of $SnCl_2$, $SnCl_4$ and HCl. We used stannous chloride for analysis and chemically pure hydrochloric acid to prepare the solutions. Stannic chloride was prepared by passing chlorine through a stannous chloride solution and subsequently driving off excess chlorine by boiling and by the addition of $SnCl_2$.

3. Discussion of results

The results of some of the most characteristic experiments are quoted in Table 1.

One may see from this Table that the polarization is quite considerable even for very small current densities. The data of experiment No. 1, which are typical for cathodic polarization, are plotted in Fig. 1 using the coordinates η *vs.* $\lg i$; they yield a curve which is, in its general appearance, analogous to the one obtained by

[8] O. Essin, M. Loschkarew a. K. Sofyiski, J. Phys. Chem. (Russ.), 10. 132 (1937); Acta Physicochimica URSS, 7. 433 (1937); M. Loschkarew a. O. Essin, J. General Chem. (Russ.), 8, 510 (1938).

Foerster and Yamasaki for a Pt-cathode. The slope of this curve ($d\eta / d \lg i$) at first increases continuously; then, in the neighbourhood of a value of the polarization equal to 340—350 mV (which corresponds to a value of the electrode potential equal to —0.13—0.14 V according to the hydrogen scale), the curve sharply changes its direction, and its slope on the average markedly decreases. As shown by an analysis of the cathodic mercury, from this moment onwards, there occurs the discharge of tin ions with formation of metallic tin; this process is accompanied by the formation of amalgam. On the other hand, the first part of the curve corresponds to the process of reduction of the tin from the stannic to the stannous form.

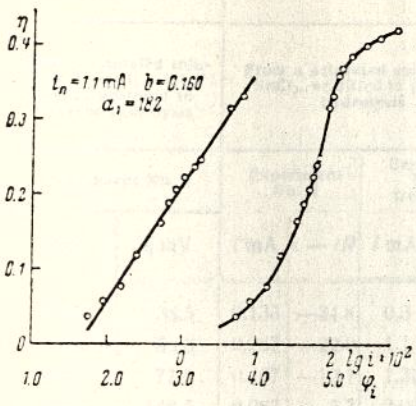

Fig. 1.
Cathodic polarization on a Hg-electrode.

(1) Limiting current density

The very small value of the current density at which the cathodic deposition of metallic tin starts (this density in what follows will be termed the limiting current density), may be explained, generally speaking, in two ways. As Foerster and Yamasaki point out, in similar solutions stannic ions form quite stable complexes which are different, moreover, in their composition. Further on, however, we shall speak, as a first approximation, of complex anions of the type $(SnX_nY_{6-n})''$ only, or even simply of $SnCl_6''$. The latter will be strictly correct only for very concentrated HCl solution. In the remaining cases it is evidently necessary also to take into account the oxygen-containing complex anions of tin. However, the following discussion remains basically the same in both cases.

If one assumes that the reduction of stannic to stannous tin proceeds by way of the direct discharge of complex ions, then very small values of the limiting current density for solutions with a high

Table 1

Mercury jet electrode with a surface of 0.15 cm.²								Pt-cathode with a surface of 1 cm.²	
Cathodic polarization		Anodic polarization						Cathodic polarization	
From a saturated solution of $SnCl_4$ + 0.1 *N* $SnCl_2$, acidified to prevent hydrolysis		From a saturated solution of $SnCl_2$, acidified to prevent hydrolysis				From a solution of 0.4 molal $SnCl_4$ + 0.1 molal $SnCl_2$ + 6 molal HCl		From the solution of exp. No. 1	
Experiment No. 1		Experiment No. 2		Experiment No. 3 (repeated)		Experiment No. 4		Experiment No. 5	
i mA	η mV	i mA	$\varepsilon - iR$	i mA	$\varepsilon - iR$	i mA	η mV	$i \cdot 10^3$ mA	ε mV
0.050	38.5	0.133	—34.8	0.3	—26.7	0.005	2.6	3.00	73.6
0.080	58.3	0.267	—22.0	1.1	—10.3	0.010	3.5	4.00	95.1
0.133	77.5	0.467	—12.1	1.33	— 0.89	0.020	3.9	5.3	109.7
0.200	119.5	0.667	— 5.7	2.00	+ 4.66	0.025	5.0	7.00	119.2
0.333	168.7	1.000	+ 2.7	3.33	+13.2	0.035	6.9	10.80	161.4
0.400	191.1	1.333	+ 7.4	4.70	+18.9	0.055	10.2	15.00	181.5
0.467	211.2	1.667	+11.2	6.00	+22.5	0.133	19.5	18.00	196.0
0.533	227.6	2.000	+14.6	8.00	+27.0	0.400	35.1	22.5	213.9
0.600	243.7	2.667	+19.8	10.00	+30.7	0.460	37.7	27.5	231.3
0.667	252.6	3.333	+24.0			0.600	41.9	32.2	262.3
0.867	321.7	4.000	+26.3			1.000	49.8	34.00	270.9
0.933	337.6	4.667	+29.8			1.666	58.4	40.00	298.9
1.000	350.0	5.33	+32.0			2.33	63.9	45.0	321.0
1.133	365.6	6.000	+34.0			3.00	69.8	51.3	343.0
1.267	375.8	7.000	+36.8			3.06	71.3	67.0	366.6
1.667	391.5	8.00	+39.1			4.33	73.7	73.0	367.6
2.667	405.8					6.33	79.8	133.0	387.5
4.000	415.5					8.66	85.1	200.0	394.6
6.670	433.6					10.00	87.2	333.0	406.7

tin concentration, using a rapidly flowing mercury electrode, may be explained only if one presumes the formation of a surface film. In this case, the latter should markedly decrease the actual electrode

surface and on account of this should impede the diffusion of $SnCl_6''$ to the cathode.

If, on the other hand, one assumes that on the jet electrode the continuous renewal of the mercury surface eliminates the formation of a film, then, to explain the insignificant value of the limiting current density, one must assume that the reduction of tin proceeds by way of the discharge of "free" $Sn^{\cdot\cdot\cdot\cdot}$ ions (not bound into a complex). Since the concentration of the latter may be taken to be comparatively small, the value of the limiting current density obtained is due either to the insufficient velocity of diffusion of $Sn^{\cdot\cdot\cdot\cdot}$ ions to the cathode, or, as Foerster and Yamasaki assume, to a retarded dissociation of the complex anion. It is doubtless, however, that in the given case both of these processes should be sufficiently slow, since they determine the concentration of $Sn^{\cdot\cdot\cdot\cdot}$ ions near the electrode. Indeed, if diffusion is retarded, while dissociation proceeds sufficiently fast, the deficiency of $Sn^{\cdot\cdot\cdot\cdot}$ ions will be made up by this dissociation, since the concentration of complex ions in the neighbourhood of the electrode is sufficiently high and practically constant (for the current densities used). On the contrary, if the dissociation is retarded, while, in spite of this, the diffusion proceeds sufficiently rapidly (*i. e.*, the equilibrium concentration of $Sn^{\cdot\cdot\cdot\cdot}$ ions in the solution is comparatively high), then there is no reason for the appearance of small limiting current densities.

Let us first analyze the experimental material on the basis of the second assumption, *i. e.*, let us assume that the surface film does not form, and the reduction of tin is accomplished by the discharge of $Sn^{\cdot\cdot\cdot\cdot}$. For the case of retarded dissociation of the complex anion $SnCl_6''$ and insufficient diffusion of $Sn^{\cdot\cdot\cdot\cdot}$ ions, the concentration of the latter near the cathode will be related to the current density in the following manner:

$$i = K_1 [SnCl_6''] - K_2 [Sn^{\cdot\cdot\cdot\cdot}]_k [Cl']^6 + \Delta \{[Sn^{\cdot\cdot\cdot\cdot}] - [Sn^{\cdot\cdot\cdot\cdot}]_k\} \quad (1)$$

or

$$[S^{\cdot\cdot\cdot\cdot}n]_k = [Sn^{\cdot\cdot\cdot\cdot}] \left\{1 - \frac{i}{i_{ng} + i_{nk}}\right\}. \quad (2)$$

Here, according to what has been said above, the concentration of the $SnCl_6''$ and Cl' ions near the cathode is taken to be the same

as that throughout the whole body of the electrolyte. The quantities i_{ng} and i_{nk}, equal to

$$i_{ng} = k_1 [SnCl_6''],$$

and

$$i_{nk} = \Delta [Sn^{\cdots\cdot}] = \Delta \frac{K_1 [SnCl_6'']}{K_2 [Cl']^6} \quad (3)$$

are the limiting current densities for the processes of the dissociation of the complex ion and of the diffusion of $Sn^{\cdots\cdot}$ ions. As is evident from equation (2), the concentration of $Sn^{\cdots\cdot}$ ions near the cathode will be mainly determined by the process for which the quantity i_n is the largest. The ratio of the latter may be obtained from (3):

$$\frac{i_{ng}}{i_{nk}} = \frac{K_2 [Cl']^6}{\Delta}, \quad (4)$$

and, besides the association rate constant, coefficient of diffusion, and convection, depends markedly upon the concentration of Cl'-ions. Therefore, in HCl solutions of high concentrations it is apparently possible to assume that the value of the limiting current density is determined fundamentally by i_{ng} (retarded dissociation).

(2) Retarded discharge

Furthermore, if the observed polarization η were caused exclusively by the velocities of dissociation of $SnCl_6''$ ions and of diffusion of $Sn^{\cdots\cdot}$ ions, the relation between η and i would be determined by the equation:

$$\eta = \frac{RT}{2F} \ln \left(1 - \frac{i}{i_n}\right). \quad (5)$$

However, as calculation showed, the experiment data cannot be described by this equation. The shape of the experimental curves (η *vs.* $\lg i$) — namely, the presence, together with the limiting current density, of linear portions (see Figs. 1, 2, and 5) having a large slope of the order of 0.15 which is characteristic of a retarded discharge, — is quite similar to that of the curves obtained by a num-

ber of authors[9] during their investigation of the anodic solution of hydrogen.

What has been said above led us to the assumption that, in the recharging of tin ions, polarization is conditioned by the velocity of the following stages: (a) dissociation of the complex anion, *e. g.*, $SnCl_6''$, (b) diffusion of $Sn^{\cdot\cdot\cdot\cdot}$ ions, and (c) the discharge of the latter to $Sn^{\cdot\cdot}$ (*i. e.*, $Sn^{\cdot\cdot\cdot\cdot} + 2\,\ominus \rightarrow Sn$). In this case the connection between polarization and current density will be determined by the following equation[10] (the upper sign for the cathodic, and the under sign for the anodic processes):

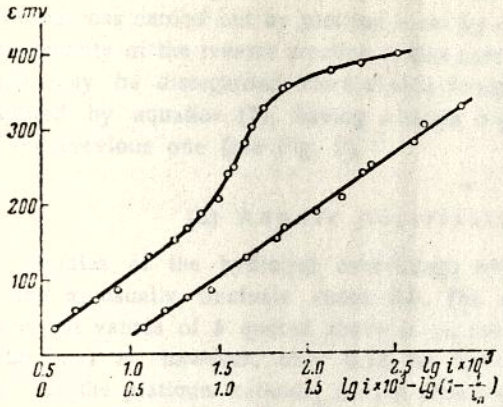

Fig. 2.
Cathodic polarization on a Pt-electrode.

$$\pm i = K_I\,[Sn^{\cdot\cdot\cdot\cdot}]\,(1 \mp i/i_n)\,\exp.\left\{-\frac{\alpha_1 2F\eta}{RT}\right\} - K_{II}\,[Sn^{\cdot\cdot}]\exp.\left\{\frac{\alpha_2 2F\eta}{RT}\right\} \quad (6)$$

Hence, the value of the cathodic polarization will be:

$$\eta = a - b\lg i + b\lg(1 - i/i_n - 10^{\eta/0.029}), \quad (7)$$

where

$$b = \frac{RT}{2F\alpha_1\,0.4343}.$$

A graphical test for the applicability of equation (7) to the data of experiment No. 1 (see Fig. 1), upon plotting η *vs.* $[\lg i - \lg(1 - i/i_n - 10^{\eta/0.029})]$

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[9] See, for example, Hammet, J. Amer. Chem. Soc., **46**, 7 (1924). M. Volmer a. H. Wick, Z. physik. Chem., **172**, 429 (1935). Roiter a. Polujan, J. Phys. Chem. (Russ.), **7**, 775 (1936).

[10] Equation (6) may be derived in a manner similar to that developed in the paper by M. Loschkarew a. O. Essin, J. Phys. Chem. (Russ.), **11**, 410 (1938); Acta Physicochimica URSS, **8**, 189 (1938).

yielded a straight line required by the equation, with a slope $b = 0.16$. Similar data obtained for the Pt-cathode (experiment No. 5) and shown in Fig. 2 were also used for testing equation (7). In connection with this, it is necessary to point out that the values of η showed poorer reproducibility than for the case of the mercury jet electrode. The test was carried out by plotting η *vs.* $[\lg i - \lg (1 - i/i_n)]$, since the velocity of the reverse reaction in this case (η is sufficiently negative) may be disregarded. Here also a straight line was obtained, required by equation (7), having a slope $b = 0.14$ which is close to the previous one (see Fig. 2).

(3) Anodic polarization

Studies of the hydrogen overvoltage show that the values of α_1 and α_2 usually fluctuate about 0.5. The value of α_1 calculated using the values of b quoted above (*i. e.*, for the process $Sn^{\cdot\cdot\cdot\cdot} + + 2\theta \; Sn^{\cdot\cdot}$) is, however, only 0.18 for the mercury cathode and 0.20 for the platinum cathode, *i. e.*, it differs considerably from 0.5. In connection with this it was of interest to study the anodic polarization for the recharging of tin ions for the purpose of checking the applicability of equation (6) to this case also, and, moreover, to compare the value of α_2 with α_1 found for the cathodic process. Equation (6) in this case gives:

$$\eta = a + b \lg i - b \lg [1 - (1 + i/i_n) \cdot 10^{-\eta/0.029}]. \qquad (8)$$

To simplify the analysis of the experimental data, the measurements of the anodic polarization were carried out, however, chiefly in the region of high current densities, at which the velocity of the reverse reaction already does not play a considerable rôle; and equation (6) simplifies to:

$$\varepsilon = a + b \lg i. \qquad (9)$$

Such measurements were found to be possible inasmuch as the limiting current density, in contrast with the cathodic process, is here absent (over a sufficiently wide range of current strengths). The measurements were carried out using a mercury jet anode only, since the values of the potential obtained with a Pt-anode were extremely unsteady and not reproducible.

However, in the region of high current densities, it is already necessary to take into account the value of the ohmic voltage drop which is caused by the syphon-tube not being located sufficiently close to the jet electrode, and to introduce a corresponding correction into the value of the potential measured. To determine this correction we used the results of an investigation carried out in parallel with the present one[11] and dealing with the polarization in the process of deposition of metallic tin ($Sn^{\cdot\cdot} + 2\theta \rightarrow Sn$) from solutions of $SnCl_2$ and $SnSO_4$. As was established in this investigation, chemical polarization for the process $Sn^{\cdot\cdot} + 2\theta \rightarrow Sn$ is absent, and the equation connecting ε with i for the mercury jet electrode has the form:

$$\varepsilon - iR = 0.029 \lg i + \text{const.} \qquad (10)$$

With the help of the above relation, the value of R, necessary for an analysis of the anodic polarization during the recharging of tin ions, was determined. Using the solution intended for the study of the process $Sn^{\cdot\cdot} - 2\theta \rightarrow Sn^{\cdot\cdot\cdot\cdot}$, a section of the curve ε *vs.* i corresponding to the deposition of metallic tin ($Sn^{\cdot\cdot} + 2\theta \rightarrow Sn$) was obtained with the help of the Hg-cathode. The data obtained, when plotted using the coordinates ($\varepsilon - 29$ lg. i) *vs.* i, yielded a straight line whose slope represents the resistance R sought for (see equation 10). The value of R thus found was multiplied by the corresponding value of i, and the iR product was subtracted from the values of the anodic potential measured for the process $Sn^{\cdot\cdot} - 2\theta \rightarrow Sn^{\cdot\cdot\cdot\cdot}$. In Fig. 3, using the coordinates ε *vs.* $\lg i$ and ($\varepsilon - 29 \lg i$) *vs.* i the results are shown of such a determination of R for the solutions of experiment No. 2 (curves *a*). The value of R here equals 1.05. Using this value of R, in Fig. 4 were represented the results of an analysis of the data obtained in experiment No. 2 (anodic polarization for the recharging), plotting ($\varepsilon - iR$) *vs.* $\lg i$. Here a straight line a', required by equation (9), is obtained, whose slope b is equal to 0.039. To illustrate the reproducibility of the experimental data using a jet electrode, in Fig. 3 (curves *b*) and in Fig. 4 (straight line b') there are presented the results of a paral-

[11] M. Loschkarew, O. Essin a. V. Sotnikova, J. Genera Chem., (in press).

lel experiment (No. 3) with an anode possessing a different surface and a different distance between the end of the syphon-tube and the stream of Hg. The value of R in this experiment was 0.67 (see Fig. 3, *b*). As is evident from Fig. 4, the straight lines a' and b' possess the same slope and are displaced with respect to each other by $\lg i = 0.2$ owing to a 1.5-fold change in the surface of the stream. In Fig. 4 (curve *c*) the results are also shown relating to experiment No. 4. The value of iR may here be discarded, since the specific conductance of the solution was considerable (6 molal HCl). An examination of this curve reveals that the relation between η and $\lg i$ becomes linear starting with values of the order of 20 mV. Evidently, from here on, the velocity of the reverse reaction already does not play any significant rôle. The slope of the linear portion, $b = 0.036$, is close to the previous values (0.039).

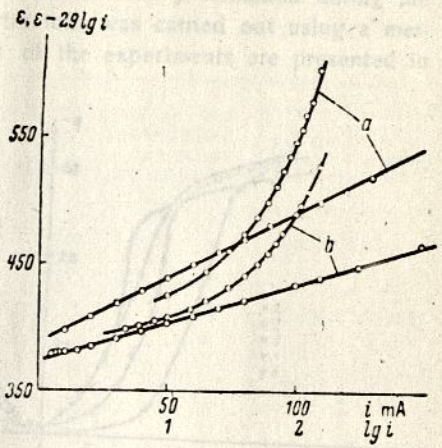

Fig. 3.
A determination of the ohmic resistance between the end of the syphon-tube and the jet of mercury.

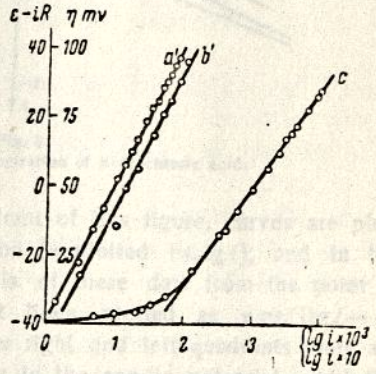

Fig. 4.
Anodic polarization on a Hg-electrode.

Thus, the dependence of the cathodic and anodic polarization upon the current density for the process of the recharging of tin ions in acidified solutions of its chlorides is satisfactorily described by equation (6). It is also necessary to note that the sum of the values of α_1 (0.18—0.2) and α_2 (0.75—0.8) is in this case close to unity.

(4) The effect of the HCl concentration

Besides the experiments already described, another series of measurements of the cathodic and anodic polarization during the process of the recharging of tin ions was carried out using a mercury jet electrode. The data of the experiments are presented in

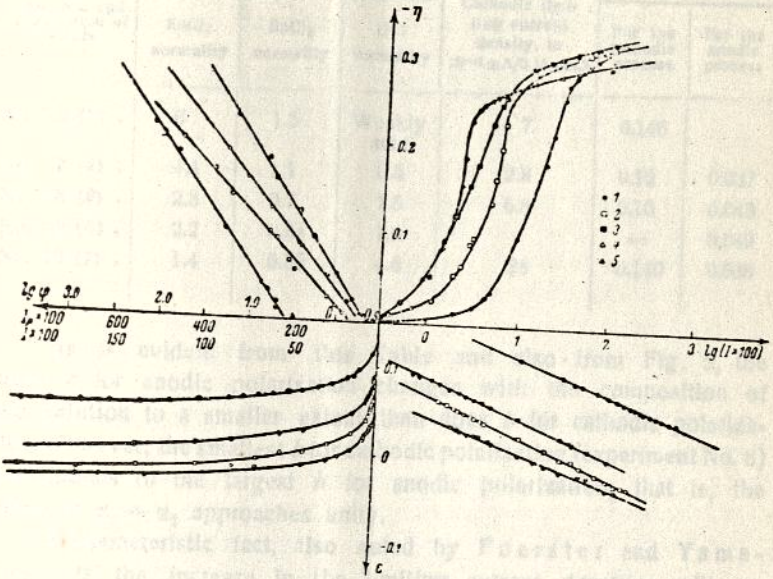

Fig. 5.
The effect of the concentration of hydrochloric acid.

Fig. 5. In the upper right quadrant of this figure, curves are plotted for the cathodic polarization (η plotted *vs.* $\lg i$); and in the upper left quadrant, an analysis of these data from the point of view of equation (7) (straight lines plotted as η *vs.* $[\lg i - \lg (1 - i/i_n - 10^{\eta/0.029})]$. In the lower right and left quadrants there are given the corresponding changes in the anodic potential ε with the current strength i and the dependence of ε upon $\lg i$ for large η. In the cases in which the cathodic and anodic polarizations were studied for the same solution, the points on the curves are designated in the same manner (squares, triangles, etc.). The values of

the cathodic limiting current densities and the slopes b for various compositions of the electrolyte are given in Table 2.

Table 2

Exp. No. and designation of points	Composition of electrolyte			Cathodic limiting current density, in 10^{-2} mA/0.15 cm.^{2}	Slope b	
	$SnCl_4$ normality	$SnCl_2$ normality	HCl normality		For the cathodic process	For the anodic process
No. 6 (3) .	6	1.5	Weakly acid	7	0.146	
No. 7 (4) .	4.4	1.1	0.5	2.8	0.12	0.037
No. 8 (2) .	2.8	0.7	1.5	6.8	0.10	0.043
No. 9 (5) .	2.2	0.54	1.0		—	0.042
No. 10 (1) .	1.4	0.35	4.6	28	0.140	0.038

As is evident from this Table and also from Fig. 5, the slope b for anodic polarization changes with the composition of the solution to a smaller extent than does b for cathodic polarization. However, the smallest b for cathodic polarization (experiment No. 8) corresponds to the largest b for anodic polarization; that is, the value of $\alpha_1 + \alpha_2$ approaches unity.

A characteristic fact, also noted by Foerster and Yamasaki, is the increase in the limiting current densities with an increase in the HCl content, notwithstanding the decrease in the $SnCl_4$ content. It seems difficult to explain this relation on the basis of the existence of only one type of complex ion. Indeed, the decrease in the $SnCl_4$ concentration at a sufficiently high HCl content leads to a decrease in the concentration and the degree of dissociation of $SnCl_6''$ ions, *i. e.*, as follows from equation (3), to a simultaneous decrease in i_{nk} and i_{ng}, and, consequently, in their sum i_n. Apparently it is necessary to assume, together with Foerster and Yamasaki, that there exist oxygen-containing complex anions of quadrivalent tin which are more stable and less dissociated than anions of the type of $SnCl_6''$. In this case the transition from weakly acid, concentrated solutions, which mainly contain

oxygen-containing complex ions, to strongly acid and less concentrated solutions of $SnCl_4$, leads first to a decrease in i_n (see Table 2) due to the general decrease in the concentration of the complex ion, and then to an increase in i_n due to the transition from more stable oxygen-containing complex ions to anions of the $SnCl_6''$ type.

(5) The discharge of complex ions

Let us now consider the other possible explanation for the small values of the cathodic limiting current density — namely, the supposition of the existence of a surface film on the electrode. As has already been pointed out above, here there is no necessity to assume that the reduction of tin ions must pass through the stage of the formation of free $Sn^{\cdots\cdot}$. In this case it may be considered as the result of the direct discharge of complex anions — for instance, of the type of $SnCl_6''$. The magnitude of the concentration polarization may in connection with this be very considerable[12] and change markedly with the current density, since it will be conditioned not only by the large decrease in the $SnCl_6''$ concentration in the pores of the film, but also by the significant increase in the concentration of the products of the discharge, *i. e.*, Cl' and $Sn^{\cdot\cdot}$ ions, in these pores. Actually, in this case the value of the electrode potential, upon taking into account only concentration polarization, will be equal to:

$$\varepsilon = \varepsilon_0 + \frac{RT}{2F} \ln \frac{[Sn\,Cl_6'']_{k_1 A}}{[Sn^{\cdot\cdot}]_{k_1 A}\,[Cl']^6} = a + \frac{RT}{2F} \ln (1 \mp K_1 i) - \frac{RT}{2F} \ln (1 \pm K_2 i) - 6\frac{RT}{2F} \ln (1 \pm K_3 i); \tag{11}$$

(the upper sign refers to the cathodic process and the under sign to the anodic process). But this supposition may explain the cathodic polarization observed only if one assumes that $K_3 \gg K_1$ and

[12] O. Essin a. A. Matantzev, Z. physik. Chem., A **174**, 384 (1935); O. Essin a. E. Alfimova, J. Phys. Chem. (USSR), **8**, 137 (1936). J. Gen. Chem. (USSR), **7**, 2030 (1937); O. Essin a. T. Beklemysheva, J. Phys. Chem. (USSR), **10**, 145 (1937).

$K_2 \gg K_1$, while K_1 is sufficiently large ($K_1 i \simeq 1$). Indeed, equation (11) in this case may be written in the form:

$$\varepsilon = a_1 + \frac{RT}{2F} \ln(1 - K_1 i) - \frac{7RT}{2F} \ln i. \qquad (12)$$

The large value of K_1 ($= 1/i_n$) explains the appearance of small limiting current densities, and the simple logarithmic dependence of ε upon i with a large slope (0.16), observed experimentally, directly follows from the last term of equation (12), which at room temperature is equal to 0.21 $\left(= \frac{7RT}{2F\,0.4343}\right)$.

From these necessary assumptions ($K_3 \gg K_1$ and $K_2 \gg K_1$), however, it follows that (for comparable concentrations of $SnCl_4$, $SnCl_2$ and HCl) during the anodic process there should also exist a limiting current density whose magnitude should be considerably smaller than, or at least of the same order as during the cathodic process. As is seen from the experimental data quoted, even the highest cathodic limiting current density, $i_n = 28 \times 10^{-2}$ (experiment No. 10), is many times smaller than the current densities $i = 1000 \times 10^{-2}$ at which, for the anodic polarization, there is not observed any noticeable effect of the possible i_{nA}. In other words, if the anodic polarization also possesses a limiting current density, it considerably surpasses (more than 30 times) the cathodic one, *i. e.*, $K_3 \ll K_1$ and $K_2 \ll K_1$. Thus, the supposition of the direct discharge of $SnCl_6''$, whose diffusion to the cathode is hindered by a surface film, is not borne out by the experimental data.

The absence of a small i_n for the anodic process necessarily leads to the condition that there takes place a small change in the concentration of Cl' and $Sn^{\cdot\cdot}$ ions near the electrode. This requires the same condition for the concentration of $SnCl_6''$. For the same reasons one must discard the supposition of the direct discharge of complex anions, with polarization conditioned simultaneously both by retarded discharge and by reatrded diffusion (film) of these ions. In the same fashion, the mutual discharge of complex and "free" ions of tin is hardly probable. In any case, owing to the small concentration of $Sn^{\cdot\cdot\cdot\cdot}$ ions, the latter will not determine the magnitude of the electrode polarization.

Thus, what has been stated above indicates that the reduction of quadrivalent tin to bivalent in the solutions investigated proceeds,

apparently, by way of the recharging of simple ions ($Sn^{\cdot\cdot\cdot\cdot}$ and $Sn^{\cdot\cdot}$). The eventual presence of a surface film on the electrode during this process does not change this circumstance, *i. e.*, does not lead to the direct discharge of complex anions, but may make the reproducibility of the experimental data worse or even hamper the measurements (for instance, in the case of the Pt-electrode).

Summary

1. Measurements of cathodic and anodic polarization for the process of the recharging of tin ions in solutions containing various concentrations of $SnCl_4$, $SnCl_2$, and HCl were carried out. In connection with this, in order to eliminate difficulties connected with the supposed formation of a surface film, the measurements were carried out mainly with a mercury jet electrode.

2. On the basis of an analysis of the data obtained, a conclusion was drawn that the process of the recharging of tin ions proceeds via the direct discharge of simple ions ($Sn^{\cdot\cdot\cdot\cdot}$, $Sn^{\cdot\cdot}$) and is accompanied by polarization, apparently caused by the retarded dissociation of complex anions of quadrivalent tin, by the diffusion of $Sn^{\cdot\cdot\cdot\cdot}$ ions, and by the retarded discharge of simple ions.

3. It was found that the equation derived on the basis of these assumptions (*i. e.*, for the small but comparable velocity constants of the three stages mentioned above) is in accordance with the experimental data.

Industrial Institute of the Urals,
Laboratory of Theoretical Electrochemistry,
Sverdlovsk.

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