

**ADSORPTION OF ANTIMONY(III) IONS AT MERCURY  
IN ACID CHLORIDE SOLUTIONS**Angelika KRUMBEIN<sup>a</sup>, Ladislav NOVOTNY<sup>b,\*</sup> and Utz RETTER<sup>a</sup><sup>a</sup> *Bundesanstalt für Metallforschung,**OE-10.23, Rudowerschause 5, Haus 9.9, 2299 Berlin-Adlershof, Germany*<sup>b</sup> *The J. Heyrovsky Institute of Physical Chemistry,**UNESCO Laboratory of Environmental Electrochemistry,**Academy of Sciences of the Czech Republic, 182 23 Prague 8, The Czech Republic*

Received January 3, 1994

Accepted March 12, 1994

Interfacial tensions at concentrations of Sb(III) ranging from  $2 \cdot 10^{-6}$  to  $5 \cdot 10^{-4}$  mol l<sup>-1</sup> in 0.1 M HCl and 2.9 M HClO<sub>4</sub> mixture on the Hg-electrode were measured using the drop-time technique with long drop-times and a controlled convection of the solution. The dependence of the surface excess on concentration was determined. The adsorption was found to obey Langmuir isotherm. From the calculated surface area of antimony of 20 nm<sup>2</sup> it was concluded, that complexes of antimony with chloride are the adsorbing species.

Antimony Sb(III) ions undergo an irreversible charge transfer reaction at polarizable mercury electrodes in weakly complexing media like H<sub>2</sub>SO<sub>4</sub> and HClO<sub>4</sub>. Under these conditions polarographic techniques provide a relatively small analytical signal<sup>1,2</sup>. The measured signal is significantly higher in acid chloride solutions<sup>3,4</sup>, what was interpreted as largely due to a complexation process<sup>5-7</sup>. The role of adsorption was considered to be of minor importance in this effect. However, the occurrence of adsorption was proved by double potential step chronocoulometry<sup>8</sup>.

The determination of Sb(III) ions in pure materials for electronic industry is of considerable practical importance. The differential pulse anodic stripping voltammetry DPASV in 2.9 M HClO<sub>4</sub> + 0.4 M HCl was successfully applied for this purpose<sup>9</sup>, whereby the sensitivity of the method increased proportionally with the concentration of HCl up to 0.4 mol l<sup>-1</sup>.

The interfacial activity of other electroactive species has been indirectly observed in a series of cases in DC polarography, faradaic impedance measurements, various relaxation techniques and chronocoulometry. A relative surface excess  $\Gamma$  of inorganic com-

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plexes was taken into account in<sup>10-16</sup> in order to describe the reduction of metall cations Pb(II), Tl(I), Cd(II), In(III), Co(II), Ni(II), Cu(II) in presence of halide ions. For example, in case of Pb(II) the values of  $\Gamma$  estimated indirectly by the impedance technique, were of the order of  $10^{-12}$  to  $10^{-11}$  mol cm<sup>-2</sup>, depending on the potential applied and on the halide concentration<sup>13</sup>. Unfortunately, the direct adsorption (electrocapillary) data of electroactive inorganic reactants are rare in the literature in general, and are not available in the case of chloride complex of Sb(III), owing to the insufficient sensitivity and reproducibility of classical electrocapillary techniques at a very low concentrations of studied substances.

The aim of the present work is to provide direct quantitative information about the adsorption of Sb(III) in the mixture of 2.9 M HClO<sub>4</sub> and 0.4 M HCl beyond the potential region of electroreduction.

## EXPERIMENTAL

The surface tension of mercury  $\gamma$  was measured using the modified drop-time technique<sup>17</sup> under the controlled convection consisting in stirring of the solution during the drop growth until about 10 s before its detachment. The laboratory-made spindle capillary<sup>18</sup>, yielded natural drop time  $t \approx 47$  s in 0.1 M HCl at the zero charge potential  $E_{PZC} = -0.53$  V (SCE). In this way the attainment of adsorption equilibrium was ensured even at the lowest concentration of Sb(III).

All the drop-time data  $t$  were converted to surface tension values according to the Eq. (1),

$$\gamma = \frac{t}{t_{\text{ref}}} \gamma_{\text{ref}}, \quad (1)$$

where  $\gamma_{\text{ref}} = 426.2$  mN m<sup>-1</sup> was the value<sup>19</sup> ascribed to mercury in 0.1 M HCl at the zero charge potential and temperature of 293 K. The reproducibility of the measured surface tension values was better than  $\pm 0.2$  mN m<sup>-1</sup>.

The experimental set-up included the laboratory-made digital counter for the drop-time measurements and a LP 9 polarograph (Laboratorni pristroje k.p., Prague) in the two-electrode DC mode as the polarizing voltage source. The potential of the DME was controlled by means of digital voltmeter NR 50 (Metra, Blansko) with a precision of  $\pm 1$  mV and referred to SCE with the salt bridge containing 0.5 M Na<sub>2</sub>SO<sub>4</sub>. The data analysis was partly carried out on a personal computer. All solutions were prepared from analytical grade chemicals and double distilled water. Before measurements the solutions were deoxygenated by nitrogen, which was passed above the solution during measurements. The mixture of 2.9 M HClO<sub>4</sub> and 0.4 M HCl was chosen as the blank solution, like in the case of the corresponding pulse-polarographic measurements<sup>9</sup>. The Sb(III) concentration was varied in the range of  $2 \cdot 10^{-6}$  to  $5 \cdot 10^{-4}$  mol l<sup>-1</sup>.

## RESULTS AND DISCUSSION

As can be seen from Table I, the presence of Sb(III) ions in solution results in surface tension changes in the whole actual potential range. The concentration of antimony has

been denoted as total analytical concentration regardless of the possible formation of chloride complexes.

From the polarographic studies follows that at the potential of about  $-0.21$  V (SCE) antimony ions undergo electroreduction. Hence at potentials more negative than  $-0.21$  V measurements are affected by the onset of the faradaic process. Under these conditions the electrocapillary data cannot give the desired thermodynamic quantities because of the coupling effects described in literature<sup>20</sup>. The direct adsorption data were evaluated at constant potentials of  $-0.17$  V,  $-0.18$  V,  $-0.19$  V,  $-0.20$  V and  $-0.21$  V. In this potential range the maximum interfacial activity occurred at  $-0.17$  V, as illustrated in Fig. 1. Thereby, at constant antimony concentration the surface pressure  $\pi$ , defined by Eq. (2),

$$\pi = \gamma_0 - \gamma, \quad E = \text{const.} \quad (2)$$

monotonously decreased with increasing negative potential. In Eq. (2)  $\gamma_0$ ,  $\gamma$  are surface tensions in the absence of antimony ions and at a given antimony concentration, respectively. In agreement with the  $\pi$ - $E$  and analogous  $\Gamma$ - $E$  dependences at constant antimony concentration and following Eq. (3), absolute values of  $|(\delta\gamma/\delta E)_c|$  slopes for  $\gamma$ - $E$  curves were slightly decreasing from  $-0.17$  V to  $-0.21$  V.

$$\left(\frac{\partial q}{\partial \ln c}\right)_E = RT \left(\frac{\partial \Gamma}{\partial E}\right)_c, \quad q = - \left(\frac{\partial \gamma}{\partial E}\right)_c \quad (3)$$

Here  $q$ ,  $\Gamma$ ,  $T$  and  $c$  denote the surface charge density, the relative surface excess, the absolute temperature and antimony concentration respectively.

The  $\gamma$ - $\log c$  curves plotted at constant potential  $E$  (Fig. 2) could be well superimposed by shifting along the ordinate, indicating a good congruence of isotherms with

TABLE I  
Data of surface tension (in  $\text{mN m}^{-1}$ ) of Sb(III) ions in 2.9 M  $\text{HClO}_4$  + 0.4 M HCl mixture at given potentials  $E$

$E$ , V	Concentration of Sb(III), $\text{mol l}^{-1}$								
	0	$2 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$1 \cdot 10^{-5}$	$2 \cdot 10^{-5}$	$5 \cdot 10^{-5}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$5 \cdot 10^{-4}$
-0.17	365.8	365.3	364.8	364.7	364.0	363.1	362.4	361.0	359.4
-0.18	368.0	367.5	367.0	366.7	366.1	365.3	364.3	363.0	361.6
-0.19	369.7	369.1	369.0	368.8	368.1	367.4	366.5	364.9	363.6
-0.20	371.7	371.4	371.0	370.6	369.9	369.1	368.3	366.9	365.5
-0.21	373.4	372.9	372.2	372.5	372.0	371.0	370.1	368.9	367.4

respect to potential  $E$ . From these data the adsorption isotherms (Fig. 3) were calculated using Eq. (4), (5)

$$d\gamma = -q dE - \Gamma RT d \ln c, \quad (4)$$

$$\Gamma = -\frac{1}{2.303 RT} \left( \frac{\partial \gamma}{\partial \log c} \right)_E. \quad (5)$$

The differentiation (5) of the  $\gamma$ - $\log c$  dependence was performed in the way when the experimental  $\gamma$ - $\log c$  dependence was fitted by the polynomial

$$\gamma = a_0 + a_1 x + a_2 x^2 + \dots + a_n x^n \quad \text{with } n = 7, \quad (6)$$

and then numerically differentiated.

The corresponding sets of adsorption isotherms are compared in Fig. 3. The small differences in  $\Gamma_m = \lim_{c \rightarrow \infty} \Gamma$  approaching  $0.15 \cdot 10^{-6} \text{ mol m}^{-2}$ , are not significant from the viewpoint of the discussed desirable information. The values of the adsorption coefficient and the maximum surface concentration  $\Gamma_m$  evaluated from the extrapolation of the plot  $c/\Gamma$  vs  $c$  for  $c \rightarrow 0$  and slope of the straight line at  $E = -0.17 \text{ V}$  (Fig. 4) amounted to  $\beta = 4.3 \cdot 10^4 \text{ mol}^{-1}$  and  $\Gamma_m = 0.84 \cdot 10^{-6} \text{ mol m}^{-2}$ . A well fitting lineari-

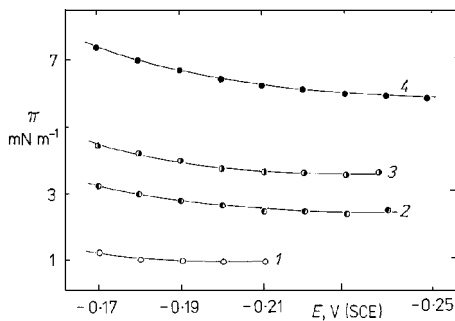


FIG. 1  
Dependence of the surface pressure  $\pi$  on potential  $E$ . Concentration of Sb(III) ions (in  $\text{mol l}^{-1}$ ):  
1  $1.5 \cdot 10^{-6}$ ; 2  $2.5 \cdot 10^{-5}$ ; 3  $3.1 \cdot 10^{-4}$ ; 4  $4.5 \cdot 10^{-4}$

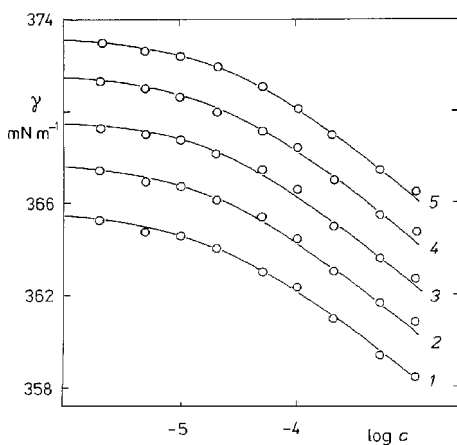


FIG. 2  
 $\gamma$ - $\log c$  plot of Sb(III) ions in 2.9 M  $\text{HClO}_4$  + 0.4 M  $\text{HCl}$  mixture at various potentials  $E$ : 1 -0.17; 2 -0.18; 3 -0.19; 4 -0.20; 5 -0.21

zation (the factor of the linear regression analysis varied between 0.996 to 0.999 for different potentials) indicates that the interfacial behavior of the studied system at lowest concentrations can be interpreted in terms of the Langmuir model. It means, that there is only small mutual interaction between the species in adsorbed state. According to the obtained value of  $\beta$  the adsorptivity of the studied system can be characterized as medium to strong, ref.<sup>21</sup>.

TABLE II

Adsorption data in terms of a relative surface coverage  $\Gamma$  plotted vs concentration  $c$  of Sb(III) ions in 2.9 M HClO<sub>4</sub> + 0.4 M HCl mixture

$c, \text{ mol } \Gamma^{-1}$	$\Gamma \cdot 10^7 \text{ mol m}^{-2}$				
	$E = -0.17 \text{ V}$	$E = -0.18 \text{ V}$	$E = -0.19 \text{ V}$	$E = -0.20 \text{ V}$	$E = -0.21 \text{ V}$
$2 \cdot 10^{-6}$	1.74	1.55	1.33	0.90	0.77
$5 \cdot 10^{-6}$	2.06	1.64	1.43	2.16	1.22
$1 \cdot 10^{-5}$	2.27	2.61	2.28	3.11	2.29
$2 \cdot 10^{-5}$	3.10	3.24	3.29	3.47	3.23
$5 \cdot 10^{-5}$	4.78	4.83	5.05	4.68	4.96
$1 \cdot 10^{-4}$	6.35	7.28	5.87	5.87	6.32
$2 \cdot 10^{-4}$	7.44	7.80	7.10	7.08	6.96
$3 \cdot 10^{-4}$	7.95	7.70	6.99	7.44	6.95

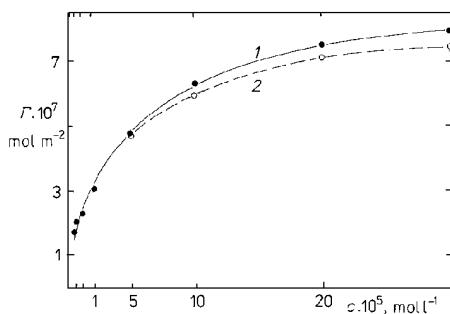


FIG. 3

$\Gamma$  vs  $c$  curves of Sb(III) ions in 2.9 M HClO<sub>4</sub> + 0.4 M HCl at two potentials  $E$ : 1 -0.17; 2 -0.20

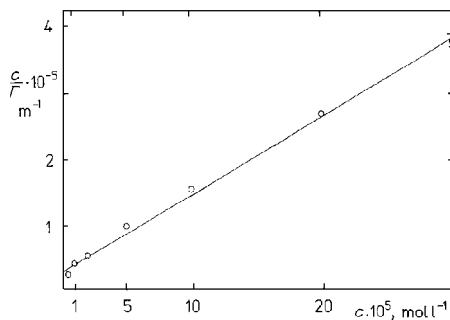


FIG. 4

Linearized Langmuir isotherm ( $c/\Gamma$  plotted vs  $c$ ) of Sb(III) ions in 2.9 M HClO<sub>4</sub> + 0.4 M HCl mixture at -0.17 V

From the maximum surface concentration  $\Gamma_m = 0.84 \cdot 10^{-6} \text{ mol m}^{-2}$  and the Avogadro number the surface area occupied by the adsorbed antimony species has been determined as about  $20 \text{ nm}^2$ . From this relatively high value it can be concluded that the adsorption of antimony takes place in form of complexes with chloride.

Comparison with the literature shows, that  $\Gamma_m$  values of the same order were obtained using another method. Verplaetse and others<sup>8</sup> have studied the adsorption of Sb(III) ions at mercury electrodes in 4 M HCl and HClO<sub>4</sub> by means of double potential step chronocoulometry. The error in the adsorbed amounts varied from 9 to 36% depending on their absolute value. For the adsorption of Sb(III) in 1 M HCl + 3 M HClO<sub>4</sub> using Langmuir isotherm they obtained  $\Gamma_m$  values between  $1.4 \cdot 10^{-6}$  to  $1.7 \cdot 10^{-6} \text{ mol m}^{-2}$ , depending on the initial potential. From the correlation between the extent of adsorption with the amount of adsorbed Cl<sup>-</sup> ions and the distribution of the complex species in solution it is suggested that SbCl<sub>3</sub> or SbCl<sub>4</sub> are probably the adsorbing species.

For halide complexes of Cd(II) ions similar  $\Gamma_m$  values were obtained by other authors. Fatas-Lahos et al.<sup>12</sup> investigated iodide solutions at the adsorption of cadmium from bromide and iodide solutions at the dropping mercury electrodes by means of admittance analysis. They interpreted the admittance parameters in terms of Langmuir isotherm with a potential dependent adsorption coefficient  $\beta$  and for the different systems they calculated  $\Gamma_m^0$  between  $0.66$  to  $1.11 \cdot 10^{-6} \text{ mol m}^{-2}$ . From the  $\partial q/\partial \Gamma$  values they concluded that the adsorbed species are most probably neutral molecules CdI<sub>2</sub> and CdBr<sub>2</sub>, with some co-adsorption of the anion at potential negative to the potential where the "o" is maximum, and with some desorption of the anion at the positive side.

Our present results have demonstrated that the determination of the maximum surface concentration by means of the drop-time method is applicable not only to organic substances but also to inorganic adsorbing species.

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Translated by the author (L. N.).