

# Electrical Double Layer on Liquid Sn–Ga Alloy in Aqueous Solutions

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**Abstract**—Double-layer parameters of a liquid Sn–Ga electrode in aqueous electrolyte solutions are studied. It is shown that Sn in the alloy with Ga is a surface-active component and is forced out onto a surface layer of the electrode. The double-layer parameters of an Sn–Ga electrode (8 at. % Sn), which are measured in the experimentally accessible range of charges, differ radically from the parameters of Ga electrodes and are close to those of Sn electrode. Hence, an Sn–Ga electrode containing 8 at. % Sn simulates electrochemical properties of a liquid Sn electrode. The difference between reciprocal “electronic” capacitances of Hg and Sn and a “corrected electrochemical work function” of Sn are determined. It is shown that the chemisorption interaction of an Sn–Ga electrode with water molecules is virtually absent at charges more negative than  $-7 \mu\text{C}/\text{cm}^2$ . A potential drop on uncharged Sn, which is associated with water chemisorption, is  $-20 \text{ mV}$ . Thus, the hydrophilicity of Sn is slightly higher than that of Hg, Bi–Ga, Pb–Ga, and Tl–Ga and significantly lower than that of In–Ga, Cd–Ga, and Ga.

**Key words:** electrical double layer, charge, potential, differential capacitance, Sn–Ga alloy, hydrophilicity of tin

## INTRODUCTION

It was shown [1–3] that adsorption of organic substances depends on the metal nature not only in the presence [4, 5] but also in the absence of a metal–water chemisorption interaction. According to [6, 7], in the absence of metal–water chemisorption interaction, the adsorption energy of organic substances correlates with the variation in the “electronic” capacitance of metal. The data on the electrodes, for which the metal–water interaction is virtually absent or weak in a wide range of negative charges, are of prime interest for this correlation. Tin is one of such electrodes. To estimate the electronic capacitance of a tin electrode in the absence of tin–water chemisorption interaction, precise data on the parameters of the electrical double layer (EDL) near zero charge and at large negative charges are required.

The EDL structure in various aqueous solutions was earlier studied on a polished polycrystalline Sn electrode [8–11], a fused polycrystalline Sn electrode [12], and individual faces of single-crystal Sn [11]. Differential capacitances of a solid tin electrode at large negative charges obtained by different authors differ by more than  $1 \mu\text{F}/\text{cm}^2$ . This is due to the fact that, in the case of solid metal, several complicating factors manifest themselves: the roughness and crystallographic and energetic nonuniformity of a solid-electrode surface,

insufficient reproducibility of its state, the dependence of EDL parameters on the surface preparation method, the accumulation of solution impurities at the interface, etc. These factors taken together can yield a large error, when the electronic capacitance of a metal is estimated. All the above problems disappear when we pass to liquid renewable electrodes. The use of such electrodes enables one to obtain, to a highest accuracy possible, both the values characterizing the electronic metal capacitance and the parameters of adsorption of organic substances on the metal.

Earlier, based on gallam, liquid surfaces of several metal were produced and studied even at ordinary temperatures. The double-layer parameters of liquid Ga alloys with In [13], Tl [14], Cd [15], Pb [16], and Hg [17] approximate those of plain metals. The criteria that enable one to produce liquid surface of various metals were formulated and substantiated in [15, 18]. Specifically, the surface activity of an alloying metal in a liquid alloy is assisted by its higher molar volume as compared with that of the base metal and a lower surface tension at mp. At  $25^\circ\text{C}$ , the molar volume of tin is  $17.4 \text{ cm}^3/\text{mol}$  [19], which is significantly larger than that of gallium ( $11.68 \text{ cm}^3/\text{mol}$  [19]). The surface tensions of tin and gallium at mp is  $0.53$  and  $0.7 \text{ J}/\text{m}^2$  [19]. Thus, according to both criteria, tin alloyed with gallium is the surface-active component and will be forced out to the interface.

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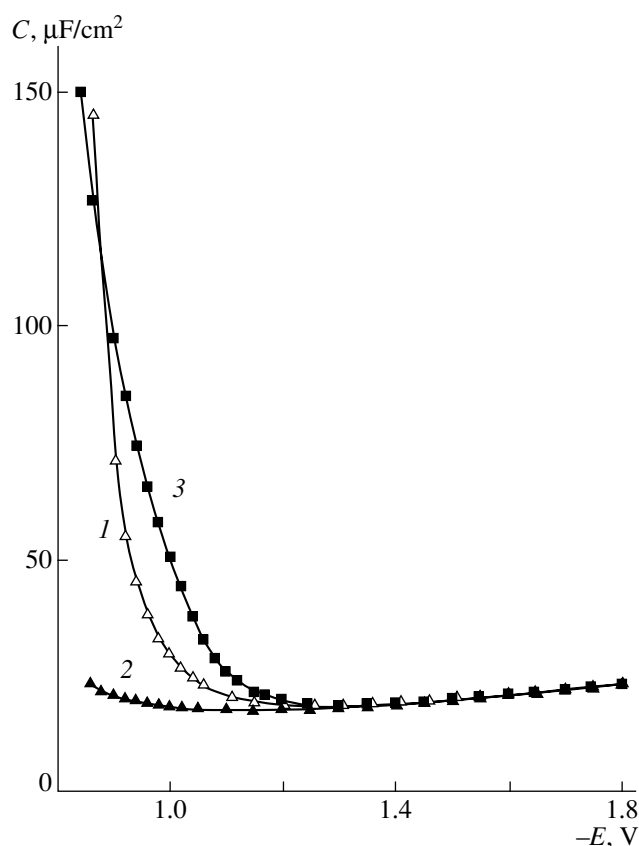


Fig. 1. The  $C$  vs.  $E$  curves for (1) Ga and (2) Sn-Ga in 0.5 M  $\text{Na}_2\text{SO}_4$  and (3) Sn-Ga in 1 M NaI.

In this work, we will create a liquid Sn-Ga electrode simulating properties of an Sn electrode, study the EDL structure on it as compared with an Hg electrode, determine the difference between reciprocal electronic capacitances of Hg and Sn, estimate the hydrophilicity of an Sn-Ga electrode, and determine the charge range where the tin-water chemisorption interaction is absent.

## EXPERIMENTAL

The EDL structure was examined on a dropping Sn-Ga electrode saturated with respect to Sn (8 at. % Sn [20]) at 32°C by measuring the differential capacitance with an ac bridge (designed by V.G. Boitsov of the Frumkin Institute of Electrochemistry, Russian Academy of Sciences). In NaI and KI solutions, simultaneously with the capacitance measurements, the open-circuit potential of a streaming Sn-Ga electrode, whose value determines the potential of zero charge (PZC), was measured in the same cell. A saturated silver-silver chloride electrode was the reference electrode. To prepare an Sn-Ga electrode, gallium G1-000 (99.9998%) and tin (99.9999%) were used. The alloy density at 32°C was determined with a pycnometer. The salts were twice recrystallized from aqueous solutions;

$\text{Na}_2\text{SO}_4$  and  $\text{K}_2\text{SO}_4$  were additionally calcined at 600°C. Solutions were prepared using twice-distilled water.

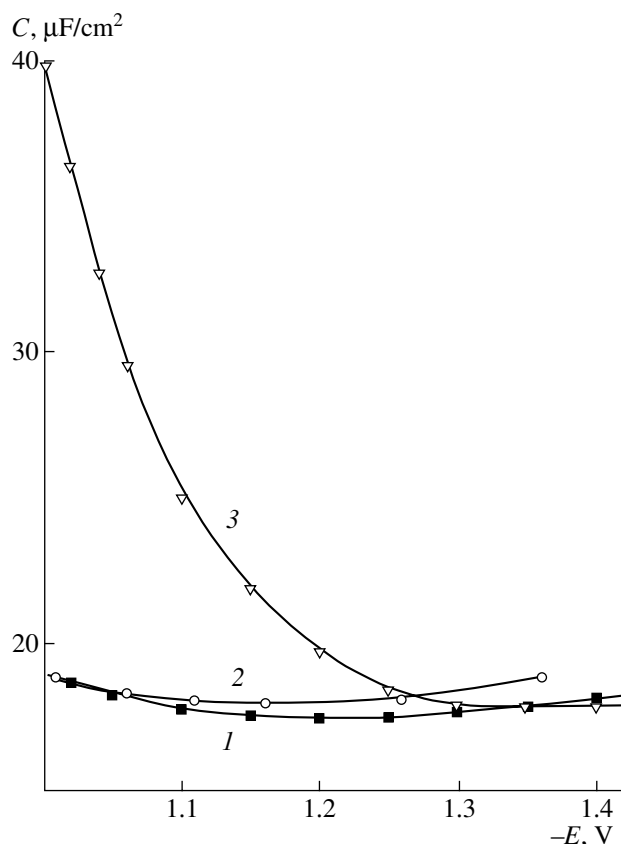
## RESULTS AND DISCUSSION

The  $C$  vs.  $E$  curves ( $C$  is the differential capacitance and  $E$  is the potential) were obtained on the Sn-Ga electrode in 0.05 and 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solutions. It was found that adding tin to gallium substantially affected ideal polarizability of the electrode. On Ga in the neutral  $\text{K}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  solutions, the capacitance is independent of the ac frequency at  $-1.6$  to  $-1.2$  V, while on Sn-Ga, at  $-1.8$  to  $-1.0$  V. At less negative potentials, dispersion of capacitance, which is caused by the electrode dissolution and oxidation, emerges on Sn-Ga. When the solution was acidified, the range of ideal polarizability shifted to more positive potentials, as with polycrystalline Sn (pcSn) [10]. A frequency-independent capacitance was pH-independent. A total  $C$  vs.  $E$  curve for Sn-Ga, which comprised fragments obtained in neutral and acidified solutions, was frequency-independent at  $-1.8$  to  $-0.85$  V. The Sn-Ga capacitance was measured mainly at 420 Hz.

Figure 1 compares our  $C$  vs.  $E$  curve for Sn-Ga in 0.5 M  $\text{Na}_2\text{SO}_4$  with that for Ga [21, 22]. As seen, adding 8 at. % Sn to Ga substantially affects the double-layer parameters, especially at potentials more positive than  $-1.2$  V. With the potential altered from  $-1.3$  to  $-0.86$  V, the capacitance on Ga and Sn-Ga increases by 130 and 3  $\mu\text{F}/\text{cm}^2$ , respectively. At  $-0.86$  V (PZC of Ga), the Sn-Ga capacitance is 7 times as small as that of Ga [21, 22]. Hence, in Sn-Ga, Sn is a surface-active component and is forced out to a surface layer of the electrode.

Figure 2 compares our  $C$  vs.  $E$  curve for Sn-Ga in 0.05 M  $\text{Na}_2\text{SO}_4$  with those for Ga and pcSn [10]. Double-layer parameters of individual faces of single-crystal Sn weakly depend on the reticular density of faces and are close to those of pcSn [11]. The curve for Sn-Ga differs substantially from that for Ga and is close to that for pcSn (Fig. 2). Somewhat lower capacitances on Sn-Ga as compared to pcSn lie within the measurement error typical for solid electrodes and may be associated with the inaccuracy of determination of the solid-electrode area due to its roughness and heterogeneity. Thus, an Sn-Ga electrode containing 8 at. % Sn simulates electrochemical properties of pcSn. This conclusion agrees with experimental data for In-Ga, Tl-Ga, Cd-Ga, Pb-Ga, and Hg-Ga [13–18]: double-layer parameters of these alloys are completely determined by the nature of atoms forming their surface layer.

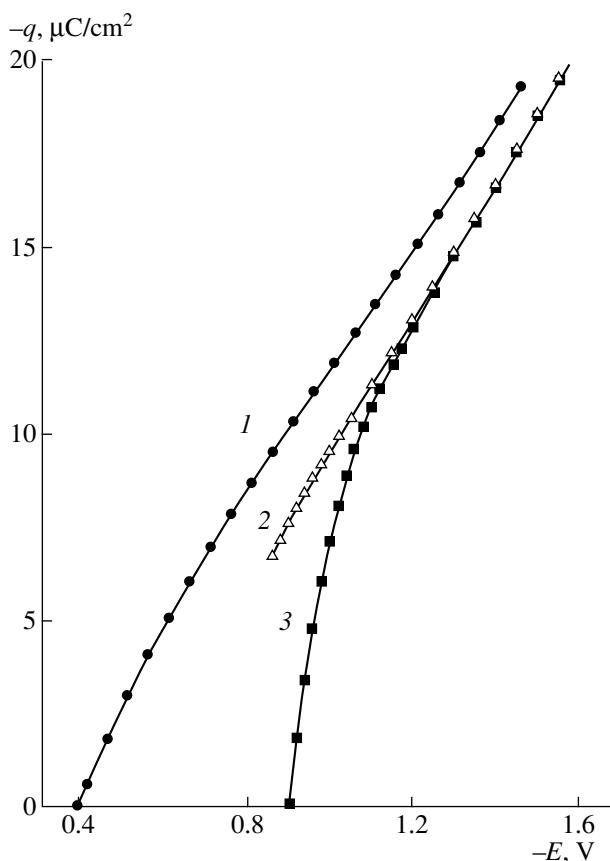
To estimate the difference between reciprocal electronic capacitances of Hg and Sn, it is necessary to compare the corresponding dependences of capacitance and potential on the electrode charge  $q$ , which are not distorted by specific adsorption of ions. We failed to measure PZC and the EDL capacitance near  $E_{q=0}$  on Sn-Ga in aqueous surface-inactive electrolytes due to



**Fig. 2.** The  $C$  vs.  $E$  curves for (1) Sn–Ga, (2) pcSn, and (3) Ga in 0.05 M  $\text{Na}_2\text{SO}_4$ .

the emergence of gallium atoms on the electrode surface and their oxidation and dissolution. However, at high KI and NaI concentrations, due to specific adsorption of the  $\text{I}^-$  ion, PZC becomes much more negative and can be measured. For Sn–Ga in 1 M NaI and KI, PZC was determined using a streaming electrode. By integrating the  $C$  vs.  $E$  curve for 1 M NaI (Fig. 1) we calculated dependences of  $C$  and  $E$  on  $q$  for Sn–Ga in 1 M NaI and, using reverse integration of a  $C$  vs.  $E$  curve in 0.5 M  $\text{Na}_2\text{SO}_4$ , obtained relevant  $q$  vs.  $E$  and  $C$  vs.  $q$  curves for a surface-inactive electrolyte.

The  $q$  vs.  $E$  (Fig. 3) and  $C$  vs.  $q$  (Fig. 4) curves for Sn–Ga in 0.5 M  $\text{Na}_2\text{SO}_4$  are compared with a similar curve for Hg. Figure 3 gives also the data for Sn–Ga in 1 M NaI. The increase in  $C$  for Sn–Ga upon going from  $\text{Na}_2\text{SO}_4$  to NaI (Fig. 1) is associated with specific adsorption of the  $\text{I}^-$  ion. At the same time, for Ga [21, 22], Sn [10], and consequently Sn–Ga,  $\text{Na}_2\text{SO}_4$  is a surface-inactive electrolyte in the charge range studied. The  $C$  dependence on the metal nature in a surface-inactive electrolyte evidences different interactions of metals with water molecules. That the Ga capacitance at charges more positive than  $-13 \mu\text{C}/\text{cm}^2$  is higher than that of Hg and Sn–Ga points to an increase in the fraction of water dipoles whose negative ends face the Ga surface, at the expense of a Ga–water chemisorption



**Fig. 3.** The  $q$  vs.  $E$  curves for (1) Hg and (2) Sn–Ga in 0.5 M  $\text{Na}_2\text{SO}_4$  and (3) Sn–Ga in 1 M NaI.

interaction. However, at  $q < -13 \mu\text{C}/\text{cm}^2$ , the metal–water chemisorption interaction vanishes even on hydrophilic Ga [22–24], whereas the capacitance continues to depend on the metal nature and increases in the series  $\text{Hg} < \text{Sn–Ga} < \text{Ga}$ . This evidences different physical interactions of metals with solvent.

The hydrophilicity of a metal with respect to that of Hg can be judged from the charge dependence of  $(\Delta_M^{\text{Hg}} C_i^{-1}) = (C_i^{-1})^{\text{Hg}} - (C_i^{-1})^{\text{M}}$  ( $C_i$  is the capacitance of the inner layer of EDL in a surface-inactive electrolyte) [23–25]. For Sn–Ga this quantity  $(\Delta_M^{\text{Hg}} C_i^{-1})$  is virtually charge-independent at  $-7 \geq q \geq -20 \mu\text{C}/\text{cm}^2$ . The average value of  $\Delta_{\text{Sn–Ga}}^{\text{Hg}} C_i^{-1}$  in this charge range is  $0.0045 \text{ cm}^2/\mu\text{F}$  and the charge dependence of  $C^{\text{cor}} = 1/[(C_i^{-1})^{\text{Hg}} - \Delta_{\text{Sn–Ga}}^{\text{Hg}} C_i^{-1}]$  on Sn–Ga virtually coincides with relevant experimental  $C$  vs.  $q$  curve (Fig. 4). This evidences an identical orientation of water dipoles in the inner layers on Sn–Ga and Hg and the absence of metal–water chemisorption interaction. The absence of such an interaction for some metals enables one to estimate the ratio between electronic capacitances of metals from values of  $\Delta_M^{\text{Hg}} C_i^{-1}$ . In the context of modern concepts on

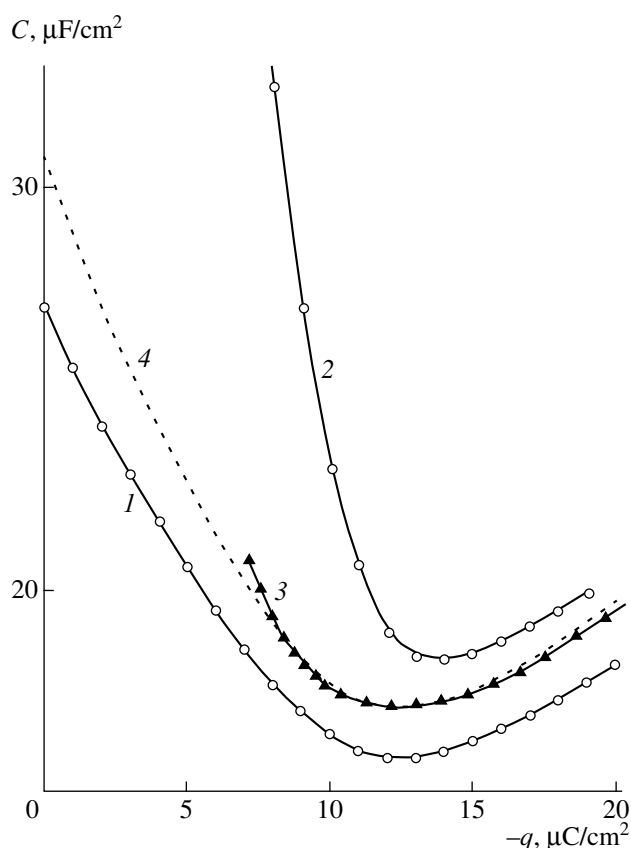


Fig. 4. The  $C$  vs.  $q$  curves for (1) Hg, (2) Ga, and (3) Sn–Ga in 0.5 M  $\text{Na}_2\text{SO}_4$ ; curve 4 is a  $C^{\text{cor}}$  vs.  $q$  plot for Sn–Ga.

the EDL structure [26–28],  $C_i$  contains two components. The first component is the metal contribution  $C_m$ , which is associated with the spread of metal electron density beyond the ionic skeleton and a gap between the ionic skeleton and the solvent molecules. The second component is the solution contribution  $C_s$ , which is associated with the solvent dipoles in the inner layer and the dependence of their orientation on  $q$ . Quantities  $C_i$ ,  $C_m$ , and  $C_s$  are related by the equation [26–28]

$$C_i^{-1} = C_m^{-1} + C_s^{-1}. \quad (1)$$

At  $q \leq -7 \mu\text{C}/\text{cm}^2$ , on Hg, Sn–Ga, and consequently Sn, water molecules are similarly oriented in the inner layer ( $\Delta_M^{\text{Hg}} C_s^{-1} = 0$ ), and according to [23–25],  $(\Delta_M^{\text{Hg}} C_i^{-1}) =$

$(\Delta_M^{\text{Hg}} C_m^{-1})_{\text{phys}}$ , where  $(\Delta_M^{\text{Hg}} C_m^{-1})_{\text{phys}}$  is the difference between the metal capacitances of metal M and Hg in the absence of a metal–water chemisorption interaction. Thus, based on the data for Sn–Ga,  $(\Delta_{\text{Sn-Ga}}^{\text{Hg}} C_m^{-1})_{\text{phys}} = 0.0045 \text{ cm}^2/\mu\text{F}$ .

The dependence of  $(C_m^{-1})_{\text{phys}}$  on the metal nature can be attributed to different spreads of electron density beyond the ionic skeletons. The magnitude of  $(C_m^{-1})_{\text{phys}}$  characterizes the distance of the nearest approach of solvent dipoles to the ionic skeleton of metal [26–28]. From the above data it follows that  $(C_m^{-1})_{\text{phys}}$  decreases upon going from Hg to Sn–Ga and to Ga and, consequently, water molecules approach the ionic skeleton of Sn–Ga closer than that of Hg; however, this distance is slightly longer than in the case of Ga.

According to [10], the chemisorption drop of the water potential on Sn with respect to the potential on Hg  $(\Delta_{\text{Sn}}^{\text{Hg}} E_{\text{chem}})_{q=0}$  is 0.10 V; hence, tin is relatively hydrophilic metal. In [10],  $(\Delta_{\text{Sn}}^{\text{Hg}} E_{\text{chem}})_{q=0}$  was estimated with the relation

$$(\Delta_M^{\text{Hg}} E_{\text{chem}})_{q=0} = \Delta_M^{\text{Hg}} E_{q=0} - \Delta_M^{\text{Hg}} E_{q \ll 0}, \quad (2)$$

where  $\Delta_M^{\text{Hg}} E_{q \ll 0}$  is the potential difference between Hg and M at large negative charges. However, given  $(\Delta_{\text{Sn-Ga}}^{\text{Hg}} C_m^{-1})_{\text{phys}} \neq 0$ , such an estimation of  $(\Delta_M^{\text{Hg}} E_{\text{chem}})_{q=0}$  is fallacious [22–24].

Our data for Sn–Ga enables us to estimate the Sn hydrophilicity at  $q = 0$ . To do this, from the  $q$  vs.  $E$  curves (Fig. 3) in the range of negative charges where water chemisorption is absent on both electrodes, it is necessary to determine the potential difference  $(\Delta_M^{\text{Hg}} E_{q1})$  for Hg and Sn–Ga at a fixed charge  $q_1$ . At  $q_1 = -15 \mu\text{C}/\text{cm}^2$ , it equals 0.10 V and coincides with that for solid Sn [5, 10] (table). Given  $(\Delta_{\text{Sn-Ga}}^{\text{Hg}} C_m^{-1})_{\text{phys}}$  and  $\Delta_M^{\text{Hg}} E_{q1}$ , it is possible to determine a “corrected difference between the electrochemical work functions” [24, 29] for Sn and Hg:

$$(\Delta_{\text{Sn-Ga}}^{\text{Hg}} W_e/e_0)_{\text{el}} = \Delta_{\text{Sn-Ga}}^{\text{Hg}} E_{q1} + q_1(\Delta_{\text{Sn-Ga}}^{\text{Hg}} C_m^{-1})_{\text{phys}}, \quad (3)$$

Characteristics of EDL on pcSn and Sn–Ga in an aqueous surface-inactive electrolyte

Electrode	$(\Delta_M^{\text{Hg}} C_m^{-1})_{\text{phys}}$ , $\text{cm}^2/\mu\text{F}$	$\Delta_M^{\text{Hg}} E_{q1}$ , V at $q_1 = -15 \mu\text{C}/\text{cm}^2$	$(\Delta_M^{\text{Hg}} E_{\text{chem}})$ , V	$(\Delta_M^{\text{Hg}} W_e/e_0)_{\text{el}}$ , V	$(\Delta_M^{\text{Hg}} W_e/e_0)_{\text{vac}}$ , V
PcSn	–	0.09–0.10 [10]	0.10 (equation (2)) [10]	0.09–0.10 [10]	0.15 [5]
SnGa	0.0045	0.10	0.02 (equation (4))	0.17	

where  $e_0$  is the electron charge. Specifically,  $\Delta_{\text{Sn-Ga}}^{\text{Hg}} W_e/e_0$  is 0.17 V, which is close to the work functions for Sn and Hg (0.15 V [5]). According to [24, 29], the metal hydrophilicity at  $q = 0$  can be judged from the chemisorption potential drop

$$(\Delta_{\text{M}}^{\text{Hg}} E_{\text{chem}})_{q=0} = \Delta_{\text{M}}^{\text{Hg}} E_{q=0} - (\Delta_{\text{M}}^{\text{Hg}} W_e/e_0)_{\text{el}}. \quad (4)$$

Values of PZC for In–Ga, Tl–Ga, Cd–Ga, and Pb–Ga to a high accuracy coincide with PZC for pure In, Tl, Cd, and Pb [13–16]. Therefore, PZC for Sn (–0.38 V vs. a hydrogen electrode [10–13]) can be used as  $\Delta_{\text{Sn-Ga}}^{\text{Hg}} E_{\text{chem}}$ , and  $\Delta_{\text{Sn-Ga}}^{\text{Hg}} E_{q=0} = 0.19$  V, because PZC for Hg is –0.19 V [5]. Using (4) we obtain  $(\Delta_{\text{Sn-Ga}}^{\text{Hg}} E_{\text{chem}})_{q=0} = -20$  mV. Thus, the hydrophilicity of Sn–Ga and, consequently, Sn is slightly higher than that of Hg, Bi–Ga, Pb–Ga, and Tl–Ga and considerably lower than that of In–Ga, Cd–Ga, and Ga. The table lists the EDL parameters for pcSn [10] and Sn–Ga (this work).

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