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Dependence of the energy of surface-active substances/metal interaction on their ionization potentials. Evaluation of hydrophilicity of metal

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Abstract The function $\Delta(\Delta G_A^0)$, which is the difference of Gibbs energies characterizing surface-active substance (surfactant, SAS) adsorption at metal/solution and air/solution surfaces, has been introduced. The equation connecting the function $\Delta(\Delta G_A^0)$ with SAS ionization potential has been obtained using the elementary theory of donor-acceptor interactions. Published experimental data on SAS adsorption at mercury, bismuth and gold have been used for $\Delta(\Delta G_A^0)$ calculation. The dependence of $\Delta(\Delta G_A^0)$ on ionization potentials can be described by an equation derived in this work. It has been demonstrated that the value of the hydrophilicity of gold is much higher than the values for mercury and bismuth. The lifetime of SAS molecules at a metal surface has been estimated. The question of the possibility of theoretical estimation of standard energies ΔG_A^0 characterizing SAS adsorption at a metal/solution surface has been discussed.

Key words Electronic material · Interface · Adsorption · Surface-active substances

Introduction

When studying organic substance adsorption at a metal/solution interface, one must solve three main problems:

1. The choice of adsorption isotherm
2. Establishment of the dependence of adsorption parameters on metal potential (charge)
3. Establishment of the dependence of adsorption parameters on the chemical nature of the surfactant.

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Often, although great attention is paid to the first two problems [1–4], the third is not adequately studied [5–7].

Nechaev and coworkers [5, 6] found that the curves reflecting the dependence of the standard free energy of adsorption ΔG_A^0 on the first ionization potentials of SAS have maxima and minima. Such a complicated situation may be attributed to the fact [1, 8, 9] that Gibbs energy ΔG_A^0 is dependent on a large number of physico-chemical properties of organic compounds (volume and structure of molecules, presence of hydrophilic groups, molecular orbital energy). Therefore one cannot link the value of ΔG_A^0 to only one property of an organic molecule, e.g. its ionization potential.

The purpose of this work is to determine the dependence of the energy of the metal/surfactant bond on the organic substances' ionization potentials. The solution of this problem enables the quantitative characteristics of hydrophilicity of a metal to be obtained. This investigation is based on two fundamental pieces of research, i.e. [8, 10]. Mercury, bismuth and gold were chosen because the greatest amount of experimental data on SAS adsorption reported in literature was obtained on these metals [1, 3, 7, 11–23].

Methods for the calculation of the energy of electronic interaction between metal and adsorbed organic particles

Let us consider a surfactant solution having both metal/solution and air/solution interfaces. Assume that one mole of SAS transfers from the surface layer of the air/solution interface to a volume and then to the surface layer of the metal/solution interface. At the same time, ν moles of water transfer from the surface layer of the metal/solution interface to a volume and then transfer to the surface layer of the air/solution interface. It is readily seen that this process can be defined by the equation:

$$\Delta(\Delta G_A) = \Delta G_A - \Delta G_{\text{air}} \quad (1)$$

where ΔG_A and ΔG_{air} are free energies of SAS adsorption on the metal/solution and the air/solution interfaces, respectively.

In the case of the SAS adsorption described by the Frumkin or Henry isotherm, the standard free energy of adsorption can be calculated by the equation [1, 3, 4, 9, 24]:

$$\Delta G_A^0 = -RT \ln 55.5 B_{\text{org}}, \quad (2)$$

or

$$\Delta\sigma = \sigma - \sigma_0 = -RT\Gamma_{\text{max}}X_{\text{org}} \exp(-\Delta G_A^0/RT), \quad (3)$$

where ΔG_A^0 (or ΔG_{air}^0) is the standard free energy at $X_{\text{org}} = 1$ and $\theta = 1$ (standard state), X_{org} is the molar fraction of organic substance in the solution, θ is the degree of coverage of metal/solution or air/solution interface with adsorbed SAS molecules, B_{org} is the adsorption constant, σ and σ_0 are the surface tensions in the presence and absence of an organic substance, respectively, Γ_{max} is the maximum number of moles of surface-active substance adsorbed over a unit surface area.

Studying surfactant adsorption at metal/solution and air/solution interfaces, we consider the same standard state in the solution volume. In this case, $\Delta(\Delta G_A^0)$ is the difference of the standard chemical potentials characterizing SAS adsorption at metal/solution and air/solution interfaces at $\theta = 1$, i.e., $\Delta(\Delta G_A^0)$ characterizes the work of transfer of one mole of SAS from the surface layer at the air/solution interface to the surface layer at the metal/solution interface at $\theta = 1$.

Using the standard free energies and well-known thermodynamic equations, Eq. 1 can be written:

$$\begin{aligned} \Delta(\Delta G_A^0) &= \Delta G_A^0 - \Delta G_{\text{air}}^0 \\ &= \Delta H_A^0 - \Delta H_{\text{air}}^0 - T(\Delta S_A^0 - \Delta S_{\text{air}}^0), \end{aligned} \quad (4)$$

where ΔH_A^0 and ΔH_{air}^0 are the standard SAS adsorption enthalpies at the metal/solution and air/solution interfaces, respectively, and ΔS_A^0 and ΔS_{air}^0 are the standard SAS adsorption entropies at the metal/solution and air/solution interfaces, respectively.

In the case of the surface layer taking on the same structure for the air/solution interface as for the metal/solution interface, one obtains

$$\Delta S_{\text{air}}^0 \cong \Delta S_A^0 \quad (5)$$

and Eq. 4 transforms into the equation:

$$\Delta(\Delta G_A^0) = \Delta G_A^0 - \Delta G_{\text{air}}^0 \cong \Delta H_A^0 - \Delta H_{\text{air}}^0 = \Delta(\Delta H_A^0) \quad (6)$$

We consider equations (5) and (6) to be invalid in the case of ejecting a different number of water molecules for the metal surface compared with the air/solution interface.

The number of water molecules forced off the surface can be calculated using the approximate equation [7, 11]

$$v = \Gamma_{\text{max,H}_2\text{O}}/\Gamma_{\text{max}} = A_{\text{SAS}}/A_{\text{H}_2\text{O}} \quad (7)$$

where $\Gamma_{\text{max,H}_2\text{O}}$ is the maximum number of water molecules adsorbed over 1 cm² of surface, and A_{SAS} and $A_{\text{H}_2\text{O}}$ are the surface areas occupied by one molecule of adsorbed surfactant and water, respectively. It is generally believed that $\Gamma_{\text{max,H}_2\text{O}} = 12 \times 10^{-10}$ mol/cm² [11, 12]. The number of water molecules (v_{air}) forced off the surface layer of the air/solution interface in the case of SAS molecule adsorption can be calculated by the following equation [1, 8]:

$$\begin{aligned} \Delta G_{\text{air}}^0 &= RT \ln (C_{\text{org(sat)}}/55.5) - RT \ln (P_{\text{org}}/p^0) \\ &\quad + v_{\text{air}}[RT \ln (p_{\text{H}_2\text{O}}/p^0)] \end{aligned} \quad (8)$$

where p_{org} and $p_{\text{H}_2\text{O}}$ are partial saturated vapor pressures of an organic substance and water at temperature T , respectively, $C_{\text{org(sat)}}$ is the saturation concentration of SAS, and p^0 is the pressure at standard conditions.

It is generally assumed [25] that in solutions the change of enthalpy in the first approximation is equal to the change of intrinsic energy. The difference between the values of enthalpies (energies) at air/solution and metal/solution interfaces results from interaction of adsorbed SAS and water molecules with the metal surface.

The validity of Eq. 5 permits one, according to Bockris [8], to write the following expression:

$$\Delta(\Delta G_A^0) \cong \Delta(\Delta H_A^0) \cong \Delta(\Delta U_A^0) \cong U_{\text{Me-SAS}}^\Sigma - v u_{\text{H}_2\text{O}}^\Sigma \quad (9)$$

where $U_{\text{Me-SAS}}^\Sigma$ and $u_{\text{H}_2\text{O}}^\Sigma$ are the energies of interaction of one molecule of SAS and one molecule of water with metal, respectively.

The energy of interaction of one molecule of SAS or one molecule of water with metal is the sum of the energies of the electronic and dispersion interactions. We consider the energy of dispersion interaction between an adsorbed SAS molecule and metal to the first approximation to be equal to the energy of dispersion interaction of v water molecules with metal, i.e.

$$U_{\text{Me-SAS}}^\Sigma = U_{\text{Me-SAS}} + v u_{\text{H}_2\text{O}}^{\text{dis}} \quad (10)$$

where $U_{\text{Me-SAS}}$ is the energy of one SAS molecule/metal electronic interaction, and $u_{\text{H}_2\text{O}}^{\text{dis}}$ is the energy of water/metal dispersion interaction. For a water molecule, one can write the similar equation:

$$u_{\text{H}_2\text{O}}^\Sigma = u_{\text{Me-H}_2\text{O}} + u_{\text{H}_2\text{O}}^{\text{dis}} \quad (11)$$

It follows from Eqs. 9–11 that Eq. 9 contains the difference between the energies characterizing the electronic interaction of SAS and water with metal.

According to Hacherman and coworkers [10], the dependence of electronic interaction $U_{\text{Me-SAS}}$ on SAS ionization potentials I can be described by the following equations, corresponding to the donor-acceptor interaction theory [26]:

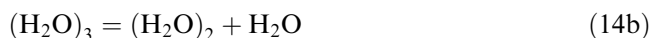
$$-U_{\text{Me-SAS}} \cong X_0 = 48.24[-W_{\text{SAS}} + (W_{\text{SAS}}^2 + 4\beta^2)^{1/2}] \quad (12)$$

$$W_{\text{SAS}} = I - W_e - e^2/4R \quad (13)$$

where X_0 is the heat of SAS adsorption at the metal surface from a gas phase, β is the integral of electronic interaction, W_e is the electronic work function, $e^2/4R$ is the energy of mirror image forces, and R is the distance between the charge and its mirror image in metal. $U_{\text{Me-SAS}}$ is expressed in kJ/mol; I and W_e are expressed in eV.

Single molecules and associates of water adsorbed at the metal surface should be considered as a surface-active substance. Thus we can assume that adsorbed molecules have the definite values of interaction energy $U_{\text{Me-H}_2\text{O}}$ and ionization potentials $I_{\text{H}_2\text{O}}$. $U_{\text{Me-H}_2\text{O}}$ can be found from Eqs. 12 and 13.

In accord with [27, 28], we have considered that associates of three water molecules mainly exist at the metal surface. We assume [29] that the following fast reactions take place on the metal surface:



Therefore the associates of two, three, four or more water molecules are displaced from the surface. This depends on the SAS molecule size.

Using Eqs. 12 and 13, one can write the following expressions for the energy of interaction between the metal and an associate of v water molecules:

$$-v/3 \cdot U_{\text{Me-H}_2\text{O}} = 48.24(v/3) \cdot [-W_{\text{H}_2\text{O}} + (W_{\text{H}_2\text{O}}^2 + 4\beta^2)^{1/2}] \quad (15)$$

$$W_{\text{H}_2\text{O}} = I_{\text{H}_2\text{O}} - W_e - e^2/4R \quad (16)$$

where $U_{\text{Me-H}_2\text{O}}$ is the energy of interaction between the metal and an associate of three water molecules, and $v = 2, 3, 4, \dots$

As we consider the energy of the metal/water interaction to be an additive quantity, Eq. 15 is approximate. In fact, the energy of interaction between metal and an associate of four water molecules is not equal to the sum of energies for four single molecules of water.

It follows from Eqs. 9, 12, 13, 15 and 16 that

$$\Delta(\Delta G_A^0) \cong \Delta(\Delta U_A^0) = 48.24[(W_{\text{SAS}} - W_{\text{H}_2\text{O}} \cdot v/3) - (W_{\text{SAS}}^2 + 4\beta^2)^{1/2} + (v/3) \cdot (W_{\text{H}_2\text{O}}^2 + 4\beta^2)^{1/2}] \quad (17)$$

where $\beta^2, e^2/4R$ and $W_{\text{H}_2\text{O}}$ are variable parameters, which can be found from the experimental dependence of $\Delta(\Delta G_A^0)$ on I . Having found these parameters, one can easily calculate the values of $U_{\text{Me-SAS}}$ and $U_{\text{Me-H}_2\text{O}}$ using Eqs. 12, 13, 15 and 16. The numerical value of $U_{\text{Me-H}_2\text{O}}$ characterizes the hydrophilicity of the metal.

To derive Eq. 17, we assumed that the structures of the surface layers consisting of water molecules were the same for air/solution and metal/solution interfaces, i.e., Eq. 5 is valid. If Eq. 5 is not valid, for surfactants be-

longing to the same organic substances class, $T(\Delta S_A^0 - \Delta S_{\text{air}}^0) = \text{const}$ in the first approximation. In this case Eq. 17 should also describe the experimental data. In the plot of $\Delta(\Delta G_A^0)$ vs I for different SAS classes, there would be several curves that are shifted relative to each other along the $\Delta(\Delta G_A^0)$ axis.

To solve Eq. 17, let us apply the function that characterizes the deviations of the value of $\Delta(\Delta G_A^0)_i$ calculated using Eq. 17 from the experimental value:

$$f_i = \Delta(\Delta G_A^0)_i - 48.24[(W_{\text{SAS}} - W_{\text{H}_2\text{O}}v/3) - (W_{\text{SAS}} + 4\beta^2)^{1/2} + (W_{\text{H}_2\text{O}} + 4\beta^2)^{1/2}v/3] \quad (18)$$

To find out the values of the variable parameters we minimize the sum of f_i . As a result we obtain the system of transcendental equations for $W_{\text{H}_2\text{O}}, \beta, e^2/4R$. We carry out the solution of the system using the Newton method of approximation of derivatives by the finite-difference approach [30].

Analysis of experimental data on surfactant adsorption on an uncharged metal surface

Mercury

The values of $\Delta(\Delta G_A^0)$ that we have calculated using Eq. 4 are listed in Table 1. The values of ΔG_A^0 are taken from the references. The values of ΔG_{air}^0 are taken from [9, 13] or calculated by equations reported in those papers. When computing $\Delta(\Delta G_A^0)$, we apply a correction for free energy of salting-out (ΔG_{sal}^0) [9, 31].

The SAS ionization potentials [12, 32–35] are given in Table 1. According to [11] we can assume that for adsorption of aliphatic alcohols and acids at mercury it is possible to maintain that the group $-\text{CH}_3$ is positioned on the metal surface and the polar groups $-\text{OH}$ and $-\text{COOH}$, because of their interaction with water, are at the end of the organic molecule facing the water phase. Therefore Table 1 lists the values of ionization potentials I corresponding to an electron being displaced [32, 33] from a $-\text{CH}_3$ group. For the remaining SASes we take the values of the first ionization potentials.

The dependence of $\Delta(\Delta G_A^0)$ on I is shown in Fig. 1. The experimental data is described by two curves, each of which corresponds to the equation

$$\Delta(\Delta G_A^0) = M_0 - M_1/I, \quad (19)$$

where M_0 and M_1 are the empirical constants. For the first curve $M_0 = 34.2$ kJ/mol, $M_1 = 3.62 \times 10^4$ (kJ/mol)² and for the second, $M_0 = 22.4$ kJ/mol, $M_1 = 2.2 \times 10^4$ (kJ/mol)². Table 1 also contains values of v for the mercury electrode that were calculated from Eq. 7 and values of v_{air} calculated from Eq. 8.

Table 1 and Fig. 1 demonstrate that the first curve corresponds to the SASs which have similar values of v and v_{air} . This permits us to draw the conclusion that in

Table 1 Adsorption parameters and ionization potentials of SASs adsorbed at an uncharged mercury surface

SAS, reference	ν	ν_{air}	I (eV)	$\Delta(\Delta G_A^0)$ (kJ/mol)
1 Butyl alcohol [9]	3	2.2	12.2	2.5
2 Valeric acid [9]	3	3.2	12.2	3.0
3 Acetonitrile [36]	2	1.5	12.2	0.0
4 Pyridine [13]	3	–	9.65	–3.8
5 α -Picoline [37]	3	3.4	9.3	–3.0
6 Imidazole [38]	3	–	8.8	–6.0
7 Phenol [13]	3	2.9	8.7	–7.2
8 Quinoline [39]	4	3.2	8.62	–9.5
9 Isoquinoline [40]	4	3.1	8.54	–8.5
10 Cinnamaldehyde [41]	3	–	8.4	–10.0
11 Hydroquinone [7]	4	3.8	7.95	–15.5
12 Phloroglucinol [42]	5	4.8	7.9	–12.5
13 α -Naphthol [7]	4	2.6	7.8	–16.5
14 α -Naphthaldehyde [7]	5	–	7.7	–15.3
15 <i>p</i> -Toluidine [13]	2.7	2.2	7.24	–8.4
16 <i>o</i> -Toluidine [13]	3.2	2.4	7.44	–9.2
17 Aniline [13]	3.6	2.5	7.8	–6.2
18 Toluene [13]	3.6	0.5	8.8	–4.0
19 Benzene [13]	3.0	0.0	9.3	–2.1

the case of adsorption of SAS presented in Table 1 (numbered 1–14) the structure of the surface layer for an air/solution interface is the same as that for a metal/solution interface. Therefore we consider that, for these surfactants, Eq. 5 is valid in the first approximation, and the dependence of $\Delta(\Delta G_A^0) \cong \Delta(\Delta U_A^0)$ on I can be described by Eq. 17. The parameters comprising Eq. 17 we can find in various ways. We consider W_e to be 4.5 eV. In the first case, the values of $\Delta(\Delta G_A^0)$, I and ν given in Table 1 have been used, and we assume that $e^2/4R = 1.8$ eV [10]. The dependence of $\Delta(\Delta G_A^0)$ on I is defined for the following values of the variable parameters: $\beta^2 = 0.492$ (eV)² and $W_{H_2O} = 5.13$ eV. The standard deviation S_n is equal to ± 2 . The values of I_{H_2O} and U_{H_2O} calculated by From Eqs. 15 and 16 at $\nu = 3$ are 11.4 eV and -9.2 kJ/mol, respectively.

In the second case, we considered the parameters β^2 , $e^2/4R$ and W_{H_2O} to be variable. The dependence of $\Delta(\Delta G_A^0)$, on I has been described at $\beta^2 = 0.261$ (eV)², $W_{H_2O} = 3.85$ eV, and $e^2/4R = 2.55$ eV. The standard deviation is equal to ± 1.4 . The value of I_{H_2O} is equal to 10.9 eV, and $U_{Hg-H_2O} = -6.4$ kJ/mol.

In the third case, we assumed that for the SAS given in Table 1 (1–14) the value of ν was 3. The dependence of $\Delta(\Delta G_A^0)$, on I was described at $\beta^2 = 0.45 \pm 0.15$ (eV)², $e^2/4R = 1.8 \pm 0.4$ eV, and $I_{H_2O} = 10.9 \pm 0.3$ eV. The value of U_{Hg-H_2O} calculated using Eqs. 15 and 16 at $\nu = 3$ is -8.4 kJ/mol.

Using the parameters found by the third method, we calculated the dependence of $\Delta(\Delta G_A^0)$, on I by Eq. 17. This dependence is presented in Fig. 1.

Figure 1 demonstrates that the calculated curve describes experimental data perfectly. This shows that discrepancies between values of metal/surface associate energies for different number of associated water molecules are practically insignificant. This results from

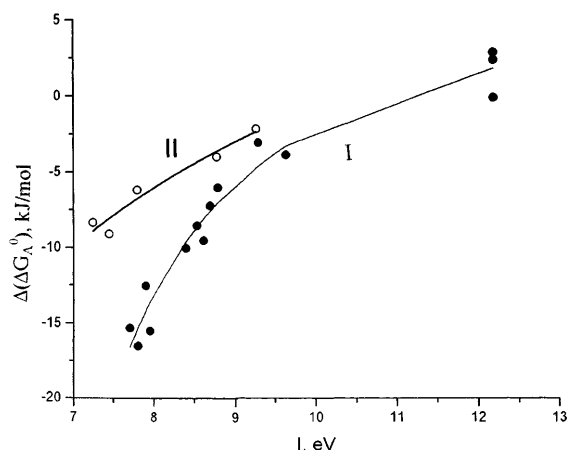


Fig. 1 The dependence of $\Delta(\Delta G_A^0)$ on SAS ionization potentials at an uncharged mercury surface. SASs numbered 1–14 in Table 1 (●); and those numbered 15–19 (○). Curve I is calculated from Eq. 17 at the following values: $\beta^2 = 0.422$ (eV)², $e^2/4R = 1.8$ eV, $W_{H_2O} = 4.6$ eV, $\nu = 3$. Curve II is calculated from Eq. 19

Eqs. 14a and b and from a weak electronic interaction of water with an uncharged mercury surface. According to the calculations, we found $U_{Hg-H_2O} = -(7.5 \pm 1.5)$, and the average interaction energy for one water molecule is -2.5 kJ/mol. As is well known [32], the ionization potential for water in the gaseous state is 12.62 eV, and for the dimer I_{H_2O} is 12.1 eV, i.e., the association of molecules results in I_{H_2O} decreasing. The values of ionization potentials for water adsorbed on copper or silicon from gas phase are reported in [32]. These values are in remarkable agreement with I_{H_2O} found by our investigations.

For the substances presented in Table 1 (numbered 15–19), $\nu > \nu_{\text{air}}$. The most significant discrepancy is observed for benzene and toluene. This shows that the structure of the surface layer consisting of the molecules of these organic substances on the air/solution interface differs from the structure of the surface layer on the metal/solution interface. As a consequence, Eq. 5 is not valid. The difference between experimental values of $\Delta(\Delta G_A^0)$, and values of $\Delta(\Delta U_A^0)$ calculated from Eq. 17 is 4–5 kJ/mol. It follows from Eqs. 4, 9, 10, and 11 that $T(\Delta S_A^0 - \Delta S_{\text{air}}^0) = -(4-5)$ kJ/mol.

The discrepancy between ν and ν_{air} for aniline and toluidine is equal to only one water molecule. From our point of view, this is not enough to explain the significant discrepancy between experimental values of $\Delta(\Delta G_A^0)$ and values of $\Delta(\Delta U_A^0)$ calculated from Eq. 17.

This difference may be attributed to the interaction of the $-NH_2$ group with the solvent. This can change the energy of the highest molecular orbital and the ionization potential. On the other hand, removal of the $-NH_2$ group from the metal surface results in decreasing the parameter $e^2/4R$. The change in entropy $(\Delta S_A^0) - (\Delta S_{\text{air}}^0)$ must not be ruled out either. It should be mentioned that one cannot adequately describe the experimental data corresponding to the second curve in Fig. 1 by Eq. 17. This indicates that the dependence of

$\Delta(\Delta G_A^0)$ on I has a more complex nature. It is possible that the dependence of $\Delta(\Delta G_A^0)$ on I for benzene, toluene and compounds containing the $-\text{NH}_2$ group can be described by two different curves.

Bismuth

Experimental values of $\Delta(\Delta G_A^0)$ for the bismuth electrode are reported in the paper [13]. Figure 2 shows that the dependence of $\Delta(\Delta G_A^0)$ on I can be described by two curves (as for mercury). The second curve corresponds to benzene, toluene, aniline and toluidine. Consequently, the picture for mercury and bismuth is not due to the nature of the metal but to the nature of the adsorbed molecules. Curve II in Fig. 2 is described by Eq. 19, where $M_0 = 21.4$ kJ/mol, $M_1 = 2.0 \times 10^4$ (kJ/mol)². Curve II in Fig. 2 can be described by Eq. 17. Param-

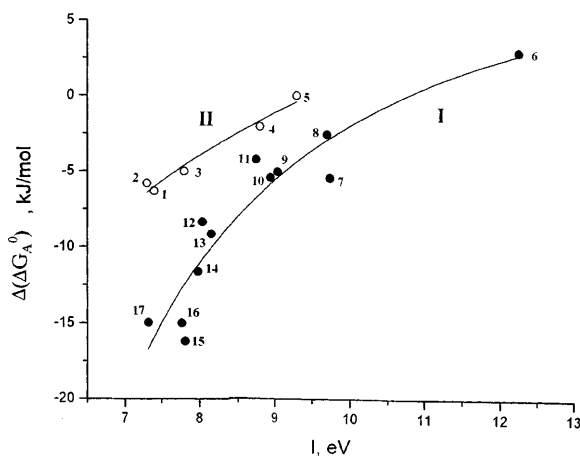


Fig. 2 The dependence of $\Delta(\Delta G_A^0)$ on SAS ionization potentials at an uncharged bismuth surface: 1 *o*-toluidine, 2 *p*-toluidine, 3 aniline, 4 toluene, 5 benzene, 6 butyl alcohol, 7 benzoic acid, 8 pyridine, 9 *m*-cresol, 10 *p*-cresol, 11 phenol, 12 *o*-phenylenediamine, 13 *m*-phenylenediamine, 14 hydroquinone, 15 α -naphthol, 16 β -naphthol, 17 α -naphthylamine

eters β^2 , $e^2/4R$, $W_{\text{H}_2\text{O}}$ we can calculate by two ways. In the first case we used the experimental values of $\Delta(\Delta G_A^0)$, I , and ν , and changed the values of β^2 , $e^2/4R$, and $W_{\text{H}_2\text{O}}$. We obtained $\beta^2 = 0.306$ (eV)², $W_{\text{H}_2\text{O}} = 4.99$ eV, $e^2/4R = 1.94$ eV and $S_n = \pm 2.5$. Using Eqs. 15 and 16 at $\nu = 3$, we obtained $U_{\text{Bi-H}_2\text{O}} = -5.9$ kJ/mol and $I_{\text{H}_2\text{O}} = 11.4$ eV. In the second case, we assumed that $\nu = 3$ and $e^2/4R = 1.8$ eV [10] for all surface-active substances. In this case the dependence of $\Delta(\Delta G_A^0)$ on I we can describe as $\beta^2 = 0.35$ (eV)² and $W_{\text{H}_2\text{O}} = 4.41$ eV. The standard deviation is ± 2.2 . Using Eqs. 15 and 16 we obtained $U_{\text{Bi-H}_2\text{O}} = -7.7$ kJ/mol and $I_{\text{H}_2\text{O}} = 10.7$ eV. We found the average value of $U_{\text{Bi-H}_2\text{O}}$ to be $-(7 \pm 1)$ kJ/mol. This value closely agrees with the value of $U_{\text{Hg-H}_2\text{O}}$. This demonstrates that hydrophilicity for mercury has approximately the same value as that for polycrystalline bismuth.

The calculated values of $I_{\text{H}_2\text{O}}$ for both metals are practically the same.

Gold

Table 2 lists the experimental values of $\Delta(\Delta G_A^0)$. All data (except pyrazine) were obtained on an uncharged surface of polycrystalline gold. Pyrazine adsorption has been investigated at an Au (111) single-crystal surface. The values of ΔG_A^0 obtained while studying the adsorption of pyridine at Au (111) and Au (100) single-crystal surfaces are practically the same as the values obtained at polycrystalline gold [21–22]. It was found [43] that the hydrophilicity of an Au (110) single-crystal surface and that of polycrystalline gold are the same. As a consequence, we can assume that the value of ΔG_A^0 for pyrazine obtained at Au (111) coincides with the value of ΔG_A^0 obtained at polycrystalline gold.

The values of ΔG_A^0 for benzene, naphthalene and benzoic acid were calculated from Eq. 2. The values of B_{org} were found from the adsorption isotherm [19, 23, 44] as the slope of the tangent to the $\Gamma - C_{\text{org}}$ at $C_{\text{org}} \rightarrow 0$.

Table 2 Adsorption parameters and ionization potentials of SASs adsorbed at a gold electrode

	SAS	ΔG_A^0 (kJ/mol), reference	$\Delta G_{\text{air}}^0, a$ (kJ/mol)	$\Delta(\Delta G_A^0)$, (kJ/mol)	I (eV)	ν
1	$\text{C}_3\text{H}_7\text{OH}$	-5.0 [15–18]	-13.8	8.8	12.2	3
2	$\text{C}_4\text{H}_9\text{OH}$	-8.5	-17.3	8.8	12.2	3
3	$\text{C}_7\text{H}_{15}\text{OH}$	-21.2	-26.5	5.3	11.2	3
4	Benzoic acid	-27.5	-19.5	-8.0	9.7	3
5	Pyridine	-37.0 [22]	-14.5	-22.5	9.65	2
6	Pyrazine [Au (111)]	-27.0 [45]	-12.0	-15.0	9.4	3
7	Benzene	-27.5 ^b	-16.5	-11.0 ^b	9.3	3
		-29.0 ^c [19]		-12.5 ^c		
8	Imidazole	-35.5 [18]	-9.5	-26.5	8.8	3
9	Naphthalene	41.0 ^b	-21.0	-20.0 ^b	8.15	4
		43.0 ^c [19]		-22.0 ^c		

^a The values of ΔG_{air}^0 are taken from [9, 13] or calculated from equations reported in these papers

^b Vertical orientation

^c Horizontal orientation

We have found the values of ΔG_A^0 for benzoic acid at gold and copper electrodes to be -27.5 kJ/mol and -29 kJ/mol, respectively. That agrees well with the conclusions of [44]. The authors concluded that Gibbs energies of adsorption of benzoic acid at gold and copper had practically the similar values. At the same time, the above-mentioned paper [44] gives the values of ΔG_A^0 for benzoic acid adsorbed at copper and gold; these values are -26.4 kJ/mol and -16.4 kJ/mol, respectively. For the calculations we used the value of ΔG_A^0 obtained in our investigations (Table 2).

In the data on the adsorption of benzene at mercury given above, one can see the difference between the values of $\Delta(\Delta G_A^0)$ and $\Delta(U_A^0)$. Therefore we apply the correction for a change of entropy. For our calculations we used the value $\Delta(U_A^0) = -17$ kJ/mol.

We have found the ionization potentials of the surface-active organic compounds [32–35] listed in Table 2. For heptanol, we used the effective ionization potential obtained from the dependence of $\Delta(\Delta G_A^0)$ on I (Fig. 1, curve I). The adsorption of aliphatic alcohols at mercury has been investigated by Moncelli et al. [46]. Using the value of ΔG_{air}^0 calculated earlier [9], we have found, for heptanol adsorbed at mercury at potential of zero charge (pzc), $\Delta(\Delta G_A^0) \cong 0.4$ kJ/mol.

Figure 1 demonstrates that for heptanol the value of I is 11.2 eV. Table 2 gives the values of ν calculated from Eq. 7. It was demonstrated [21, 22] that, for pyridine adsorption at gold, the value of Γ_{max} at pzc was $6-7 \times 10^{-10}$ mol/cm², so the value of ν for pyridine is 2.

We have used two systems of calculation. We consider W_e to be 4.8 eV [47]. In the first case the values of $\Delta(\Delta G_A^0)$, I and ν for all SASs listed in Table 2 were used. We changed the values of β , $e^2/4R$, and $W_{\text{H}_2\text{O}}$. We obtained the optimal values of the variable parameters: $\beta^2 = 1.93$, $W_{\text{H}_2\text{O}} = 4.18$ eV, $e^2/4R = 1.75$ eV. $S_n = \pm 1.65$. The curve of $\Delta(\Delta G_A^0)$ vs I calculated at the values reported above and for various values of ν are represented in Fig. 3. Using Eqs. 15 and 16 at $\nu = 3$ we obtained $U_{\text{Au-H}_2\text{O}} = -40.5$ kJ/mol and $I_{\text{H}_2\text{O}} = 10.7$ eV.

It was reported [48] that for gold (unlike mercury) $-\text{OH}$ groups of *tert*-amyl alcohol are situated on the metal surface. If it is valid for other aliphatic alcohols (Table 2), we should use the values of the first ionization potentials of these SASs lying in the range 10.4–10.8 eV [32–35]. Therefore, in the second system of calculation, the data on aliphatic alcohols (Table 2) was excepted. We obtained $W_{\text{H}_2\text{O}} = 4.12$ eV, $\beta^2 = 1.96$ (eV)², $e^2/4R = 1.77$ eV, and $S_n = \pm 2$. Using Eqs. 15 and 16 we found the values of $U_{\text{Au-H}_2\text{O}}$ and $I_{\text{H}_2\text{O}}$ to be -41.6 kJ/mol and 10.7 eV, respectively. The results obtained by the first and the second calculation systems are in remarkable agreement with each other. This demonstrates the similar orientation of alcohol molecules at mercury and gold. It should be mentioned that reorientation of molecules of *tert*-amyl alcohol can take place only due to the strong interaction of $-\text{OH}$ groups with the metal surface. In this case a deviation from the

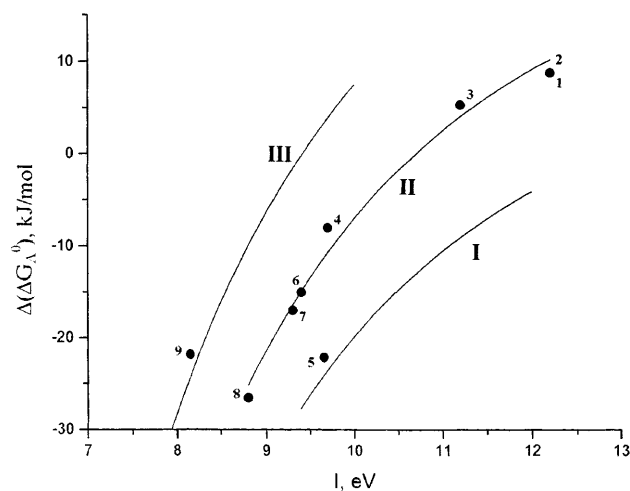


Fig. 3 The dependence of $\Delta(\Delta G_A^0)$ on I at an uncharged gold surface. Curves I–III are calculated from Eq. 17 at $\beta^2 = 1.96(\text{eV})^2$, $W_{\text{H}_2\text{O}} = 4.12$ eV, $e^2/4R = 1.77$ eV, $\nu = 2, 3$ and 4. Points correspond to experimental values of $\Delta(\Delta G_A^0)$ given in Table 2

parabolic dependence of ΔG_A^0 on potential should take place, but this was not observed [48].

Using the experimental data numbered 4, 6–8 in Table 2 ($\nu = 3$), we have calculated the values of $W_{\text{H}_2\text{O}} = e^2/4R, \beta^2$ (Eq. 17). We have obtained $I_{\text{H}_2\text{O}} = 10.5$ eV, $e^2/4R = 3.0$ eV, $\beta^2 = 0.94$ (eV)² and $U_{\text{Au-H}_2\text{O}} = 30$ kJ/mol. The values of $e^2/4R, \beta^2$ and $U_{\text{Au-H}_2\text{O}}$ significantly differ from the values obtained before. It should be mentioned that these parameters characterize the adsorption of SASs (Table 2) having ionization potentials lying in the range from 9.7 to 8.8 eV. Therefore the values of $e^2/4R, \beta^2$ and $U_{\text{Au-H}_2\text{O}}$ depend on the range of values of I used for the calculations. At the same time, the values of $I_{\text{H}_2\text{O}}$ are practically the same in every variant of the calculations used in the work. Parameters $e^2/4R = 3.0$ eV and $\beta^2 = 0.94$ (eV)² were used to calculate the values of $\Delta(\Delta G_A^0)$ for alcohols, pyridine ($\nu = 2$) and naphthalene ($\nu = 4$) from Eq. 17. Calculated values of $\Delta(\Delta G_A^0)$ for alcohols and pyridine are in very good agreement with experimental ones. For the naphthalene molecule, the value of $\Delta(\Delta G_A^0)$ calculated from Eq. 17 at $\nu = 4$ is almost half the experimental value. It shows that the parameters $e^2/4R = 3.0$ eV and $\beta^2 = 0.94$ (eV)² can be used to calculate $\Delta(\Delta G_A^0)$ and $U_{\text{Au-H}_2\text{O}}$ for the SASs having the ionization potentials lying in the range between 8.8 and 12.2 eV.

The comparison between the parameters found on gold and mercury allows us to make some conclusions. Ionization potentials of associates of three water molecules on mercury, bismuth and gold are practically the same. At the same time, the absolute value of $U_{\text{Au-H}_2\text{O}}$ is 3–5 times as high as the value of $U_{\text{Me-H}_2\text{O}}$ obtained on mercury and bismuth.

Results and discussion

The analysis has shown that Eq. 17 was able to describe the experimental data on SAS adsorption at mercury, bismuth and gold. Using the results presented above, we discuss three problems:

1. Evaluation of hydrophilicity of metal
2. Evaluation of the energies ΔG_A^0 on solid metals
3. Evaluation of the lifetime of SAS and water molecules on a metal surface.

Let us consider the first problem. The question of the hydrophilicity of mercury and gold has been discussed in the literature [20, 47, 49, 50]. There are two opposite points of view. The authors [47, 49] have concluded that the hydrophilicity of gold is significantly higher than that of mercury. In other work [20, 50], it is stated that the hydrophilicities of gold and mercury are approximately equal. Let us consider in more detail the methods for evaluation of hydrophilicity of gold used by Lipkowski et al. [20]. Values of ΔG_A^0 for diethyl ether obtained on mercury and various kinds of gold monocrystals were compared [20]. The value of ΔG_{air}^0 for the SAS chosen as a standard is constant. Therefore, to evaluate the hydrophilicity of a metal one has to compare the values of $\Delta(\Delta G_A^0)$ obtained on different metals. Figures 1–3 demonstrate that the value of $\Delta(\Delta G_A^0)$ depends on I , and at $I = \text{const}$ and $v = \text{const}$ it depends on the slope of the $\Delta(\Delta G_A^0)$ vs I curve. For mercury, bismuth and gold the value of $I_{\text{H}_2\text{O}}$ at $v = 3$ is 10.7–11 eV. If the ionization potential of standard SAS at $v = 3$ is close to $I_{\text{H}_2\text{O}}$, then absolute values of $\Delta(\Delta G_A^0)$ for all metals should be low, consistent with errors of evaluation of ΔG_A^0 and ΔG_{air}^0 (not depending on the curve slope).

Therefore, the use of these SASes for the evaluation of metal hydrophilicity is not reasonable. The ionization potential of diethyl ether is 9.5 eV [34]. However, the hydrophobic groups $-\text{C}_2\text{H}_5$ of diethyl ether are on the metal surface, and the $-\text{O}-$ group is far from it and interacts with water. Therefore the effective ionization potential of this SAS differs from the value mentioned above.

Let us evaluate the value of this effective potential. The adsorption of diethyl ether at mercury has been investigated [51]. It was found that in 0.1 M NH_4Cl solution $\Delta G_A^0 = -15.3$ kJ/mol. For this supporting electrolyte, the salting-out free energy ΔG_{sal}^0 is -1.0 kJ/mol [9, 31]. The value of ΔG_{air}^0 is $-(16 \pm 1)$ kJ/mol [9, 31]. It follows from Eq. 4 that $\Delta(\Delta G_A^0) = 1.7$ kJ/mol. Calculations carried out using Eqs. 7 and 8 showed that $v = 3$ and $v_{\text{air}} = 0.8$. Consequently the value of $\Delta(\Delta G_A^0)$ for diethyl ether should lie on the second curve (Fig. 1). The value of the effective ionization potential of diethyl ether calculated from Eq. 19 is 11.0 eV. If in the case of this SAS adsorption at gold the value of v is approximately 3 [51], the values of $\Delta(\Delta G_A^0)$ and ΔG_A^0 calculated from Eqs. 17 and 4 are 2.0 kJ/mol and -14 kJ/mol, respectively. The latter value is consistent with the values obtained in [51].

Our calculations prove that one cannot use the value of ΔG_A^0 obtained for diethyl ether to evaluate the hydrophilicity of a metal because the ionization potential of this compound is close to $I_{\text{H}_2\text{O}}$. Earlier we showed that the energy of the water/gold interaction is 5–6 times that of the water/bismuth and water/mercury interaction. That conclusion is based on calculations using Eq. 17 which agrees with the elementary theory of donor-acceptor interaction.

It would be interesting to introduce a parameter characterizing the hydrophilicity of a metal, the value of which is not dependent on the model describing the metal/adsorbed SAS molecule interaction used in this work. It may be the dimensionless function $h \equiv \{\partial[\Delta(\Delta G_A^0)]/\partial I\}_{I,v}$ at $v = \text{const}$ and $\Delta(\Delta G_A^0) = 0$. It follows from Figs. 1–3 that at $v = 3$ for mercury and bismuth $h = 0.02 - 0.03$, and for gold $h = 0.085$. This demonstrates that the hydrophilicity of gold is 3–4 times the value for mercury and bismuth.

Data on pyridine adsorption [21, 22] show that the value of the water-gold interaction energy should be high. It was found that reorientation of the adsorbed molecules takes place in the region of zero-charge potential. At pzc, pyridine molecules adsorbed at gold have vertical orientation (unlike mercury). It shows that the values of the electronic interaction of adsorbed water molecules with gold should be high. For the pyridine molecule, the values of the ionization potentials of a lone pair of electrons of a nitrogen atom $I(\sigma, n)$ and π -electrons of the ring are close: $I(\sigma, n) = 9.7$ eV and $I(\pi) = 9.8$ eV [34]. Therefore, the change of molecule orientation does not affect the SAS/metal electronic interaction energy.

According to Eqs. 4 and 9, the values of $\Delta(\Delta U_A^0)$ and ΔG_A^0 considerably depend on the value of v . The value of ΔG_{air}^0 for pyridine is known. Calculations using Eqs. 17 and 4 demonstrate that, in the case of planar orientation of pyridine molecule ($v = 3$) at a gold electrode at pzc, the value of ΔG_A^0 is -25 kJ/mol, and, in the case of vertical orientation ($v = 2$), $\Delta G_A^0 = -38.5$ kJ/mol. Consequently, the vertical orientation is preferable. At the mercury electrode the difference between ΔG_A^0 values for planar and vertical orientation is about 2 kJ/mol. Because of dispersion interaction, planar orientation should be preferable for mercury. Independent studies have shown [44] that the transfer of one water molecule from an uncharged gold surface to a volume requires 20 kJ/mol. We showed that the energy of electronic interaction of one water molecule with a gold surface is -13.5 kJ/mol. The energy of dispersion of the water molecule/metal interaction lies in range -10 to -15 kJ/mol [25, 52]. Therefore, the full energy of one water molecule/gold interaction calculated from Eq. 11 is ca. -25 kJ/mol. This value agrees well with the value given in [44]. It was found [23] that the adsorption equilibrium is reached slowly. This indicates that the absolute values of $U_{\text{Au-SAS}}$ and $U_{\text{Au-H}_2\text{O}}$ should be high.

Let us consider the problem of the feasibility of assessment of the ΔG_A^0 value at a gold electrode. Ac-

ording to Eq. 6, to calculate ΔG_A^0 one must know ΔG_{air}^0 and $\Delta(\Delta G_A^0)$. The value of ΔG_{air}^0 one can obtain by experiment or calculate from equations reported in [9, 31]. The value of $\Delta(\Delta G_A^0) \cong \Delta(\Delta U_A^0)$ can be obtained from Eq. 17. The problem of ΔG_A^0 assessment for diethyl ether and pyridine has been reported above. The adsorption of isoquinoline was investigated in [53]. The ionization potential of the isoquinoline molecule $I(\pi_5)$ is 8.45 eV. This corresponds to π -electron withdrawal from the cycle. The potential $I(n) = 9.3$ eV corresponds to withdrawal of an electron of the nitrogen lone pair [34]. For the quinoline molecule, ΔG_{air}^0 is -21 kJ/mol [54]. Using Eq. 17 at $\nu = 4$ and $I = 8.45$ eV, we obtain $\Delta(\Delta G_A^0) = 14.5$ kJ/mol; consequently $\Delta G_A^0 = -35.5$ kJ/mol. This value agrees well with the experimental value of ΔG_A^0 [53] found at potentials of about -0.5 to -0.35 V (SCE). The planar orientation of isoquinoline molecules was observed at these potentials.

The value of ν is 2 and $I = 9.3$ eV for vertical orientation when the nitrogen atom is on the metal surface. Using these parameters, we calculated from Eqs. 17 and 6 $\Delta G_A^0 = -49$ kJ/mol. The value of the Gibbs energy at pzc $\Delta G_{\theta=1}^0$ at full coverage of metal surface by adsorbed molecules was found to be -44 kJ/mol [53]. If at vertical orientation of isoquinoline molecules there is repulsion interaction, $|\Delta G_{\theta=1}^0| < |\Delta G_A^0|$. In this case, good agreement between experimental and calculated values of ΔG_A^0 is found.

It is known [55] that the lifetime τ of an adsorbed particle at an adsorbent surface can be estimated by the equation:

$$\tau = \tau_0 \exp(X_0/RT) \quad (20)$$

where $\tau_0 = 10^{-12}$ to 10^{-14} s and X_0 is the heat of adsorption. Using the model presented above $X_0 \cong -U_{\text{Me-SAS}}^{\Sigma}$. The values of $U_{\text{Me-SAS}}^{\Sigma}$ and $U_{\text{H}_2\text{O}}^{\Sigma}$ can be calculated from Eqs. 10 and 11. The energy of interaction between one water molecule with gold, $U_{\text{H}_2\text{O}}^{\Sigma}$, is ca. -25 kJ/mol. For benzoic acid, we obtained $U_{\text{Au-SAS}}^{\Sigma} = -84$ kJ/mol and $\tau = 5 \times 10^2$ s. Because of attraction between benzoic acid molecules [23], the lifetime of a molecule on a gold surface at $\theta = 1$ should be higher than the calculated value. This demonstrates that the desorption process takes place slowly. It agrees well with experimental data presented in [23]. For benzoic acid adsorption at mercury, the value of $U_{\text{Hg-SAS}}^{\Sigma}$ obtained from Eq. 12 at $I = 9.7$ eV [32, 35] and corresponding values of variable parameters is -11.6 kJ/mol. The energy of dispersion of the mercury/water molecule interaction is ca. -10 kJ/mol [25, 52]. So, the value of $U_{\text{Hg-SAS}}$ calculated from Eq. 10 at $\nu = 3$ is -41.6 kJ/mol and $\tau = 1.5 \cdot 10^{-5}$ s. For valeric acid, $I = 12.2$ eV (Table 1) and $\tau = 10^{-6}$ s. This agrees well with results presented in [56]. For benzoic acid adsorbed at platinum, $\Delta(\Delta G_A^0) = -49.5$ kJ/mol [44] and $\Delta(\Delta G_A^0) = -30$ kJ/mol as $\Delta G_{\text{air}}^0 = -19.5$ kJ/mol (Table 2). It would be interesting to estimate the value of β for platinum from Eq. 17. We supposed the sum of parameters $W_e + e^2/4R$ to be 5.6, 6.3 and 7.0 eV. We

assumed that $\nu = 3$. Hence we obtained the values of β^2 equal to 23, 16 and 10.9, respectively. At these values of β^2 and $W_e + e^2/4R$ and $\nu = 3$, we calculated the values of $U_{\text{Pt-SAS}}$ and $U_{\text{Pt-H}_2\text{O}}$ using Eqs. 12, 13, 15 and 16. Average values are $U_{\text{Pt-H}_2\text{O}} = -(220 \pm 50)$ kJ/mol and $U_{\text{Pt-SAS}} = -(250 \pm 50)$ kJ/mol. The value of τ for benzoic acid obtained from Eq. 20 at $\tau_0 = 10^{-14}$ s [55] and $T = 298$ is 10^{29} s. It should be mentioned that the values of $U_{\text{Pt-SAS}}$ and $U_{\text{Pt-H}_2\text{O}}$ obtained by our calculations correspond to reversible adsorption. Sobcowski et al. [44] suppose that the adsorption of benzoic acid at platinum is partly irreversible.

Conclusions

1. Excessive values of Gibbs energy $\Delta(\Delta G_A^0)$ characterizing change of free energy of adsorption on going from air/solution to metal/solution surface have been calculated.
2. It has been shown that the dependence of $\Delta(\Delta G_A^0)$ on the SAS ionization potential can be described by an equation corresponding to the elementary theory of donor-acceptor interaction.
3. The values of the energies characterizing SAS/metal interaction have been found.
4. It has been demonstrated that the hydrophilicity of gold is significantly higher than those for mercury and bismuth.

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