EFFECTS OF SYNERGISM AND ANTIPATHY, DURING THE ADSORPTION AND REACTION OF SURFACE-ACTIVE SUBSTANCES, ON ELECTROCHEMICAL REACTIONS AND THE CORROSION OF IRON

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An investigation has been carried out on the effect of the interaction of two substances of different nature on the surface of a metal, with respect to adsorption, as measured by the reduction in differential capacity (ΔC), and to the rate of electrochemical reactions, as measured by means of polarization curves, and also the effect on the rate of iron corrosion in 1 N H_2SO_4.

Comparatively little study has been devoted to the interaction of two molecules or ions of different nature adsorbed on iron [1]. It should manifest itself because there exists an interaction between identical molecules, as shown by the logarithmic adsorption isotherms of inhibitors [2].

An interaction between two different particles of surface-active substances (SAS) can lead to an increase (synergism) or decrease (antipathy) in adsorption and in consequence to an increase or reduction of their effects on electrochemical reactions (dischange of hydrogen ions and ionization of iron) and, finally, on the corrosion of the metal.

Let us consider the following possible cases of interaction [3].

1. In the adsorbed layer the distance between molecules of substances 1 and 2 is large, each occupying its own region with almost no interaction between them, so that $W_{12} = 0$. The interaction between identical particles can also be ignored: $\times W_{11} \simeq 0$; $W_{22} \simeq 0$. In this case the total adsorption is equal to the sum of the adsorptions of the individual substances. This is observed in a solution containing low concentrations of inhibitors having small, similar adsorption energies on iron: $A_{1Me} \simeq A_{2Me} \simeq 0$, as for example in dilute solutions (10^{-5}-10^{-4} M) of tribenzylamine (TBA) and tribenzylmethyl ammonium sulfate (TBMAS) in 1 N H_2SO_4 (containing $2 \cdot 10^{-6}$ N KCl to increase adsorptivity). In this case the reduction in the differential capacity of the double layer (ΔC), which determines the degree of adsorption, is equal to the sum of the reductions in capacity caused by each inhibitor separately: $\Delta C_{12} = \Delta C_1 + \Delta C_2$.

2. The molecules in the adsorption layer are close to one another, mixed and uniformly distributed over the surface. The interaction energy between different molecules is small compared with the interaction between identical molecules: $W_{12} < W_{11}$; $W_{12} < W_{22}$. In this case also, $\Delta C_{12} \simeq \Delta C_1 + \Delta C_2$. A mixture of aliphatic alcohols and acids may be taken as an example. However, because of their low adsorptivities on iron the effect on corrosion is very small, evidently as a consequence of the greater adsorption energy of water.

3. The particles on the metal surface are mixed and the interaction energy between different molecules is greater than that between identical molecules: $W_{12} > W_{11}$; $W_{12} > W_{22}$. It is assumed that the interaction between particles of one type is not changed by the presence on the surface of particles of another type,* and that the adsorption energies are similar: $A_{1Me} \simeq A_{2Me}$.

* In real conditions the interaction between different particles reduced the interaction between identical particles.

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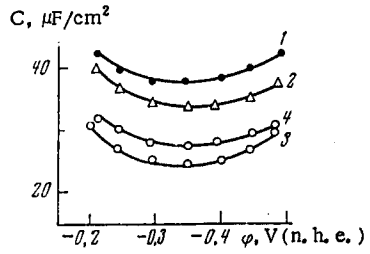

Fig. 1

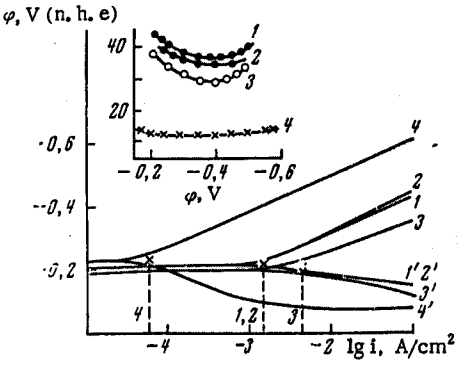

Fig. 2

Fig. 1. Variation of the differential capacity of iron on potential in 1 N H_2SO_4, without additives (1) and with (2) 0.05 M BSA; (3) 0.05 M SSA; (4) 0.05 M SSA + 0.05 M BSA.

Fig. 2. Cathodic and anodic polarization curves and differential capacity curves for zone-refined iron in 1 N H_2SO_4, without additives (1) and with (2) $5 \cdot 10^{-4}$ M TBMAS; (3) 0.05 M BSA; (4) 0.05 M BSA $+5 \cdot 10^{-4}$ M TBMAS.

For a solution of an individual substance the interaction constant between adsorbed identical particles can be found using the Frumkin adsorption isotherm:

$$Bc = \frac{\theta}{1-\theta} \exp(-2a\theta), \tag{1}$$

where B is the adsorption equilibrium constant and a is the attraction constant. The surface filling constant θ is found from measurements of the differential capacity using the equation $\theta = C_0 - C_X / C_0 - C\infty$, where C_0, C_X, and $C\infty$ are the capacities, respectively, in the absence of the SAS, in the presence of SAS at concentration c, and the specific capacity on formation of a monolayer.

In the case under consideration here, the adsorption of two different types of particles, it is necessary to consider also the attractive interaction, a_3, between particles of types 1 and 2. In this case the adsorption isotherms will have the following forms:

$$B_1 c_1 = \frac{\theta}{1-\theta_1-\theta_2} \exp(-2a_1\theta_1 - 2a_3\theta_2), \tag{2}$$

$$B_2 c_2 = \frac{\theta_2}{1-\theta_1-\theta_2} \exp(-2a_2\theta_2 - 2a_3\theta_1), \tag{3}$$

where B_1 and B_2 are adsorption equilibrium constants, a_1 and a_2 are attraction constants, and θ_1 and θ_2 are the surface coverages for particles of types 1 and 2, respectively. The kinetic and thermodynamic derivations of these equations are given in [3]. For the combined adsorption the capacity is given by the equation

$$C = C_0(1-\theta_1-\theta_2) + C_1\theta_1 + C_2\theta_2, \tag{4}$$

in which C_0 is the capacity of the background solution, i.e., when $\theta_1 = \theta_2 = 0$, and C_1 and C_2 are the capacities when $\theta_1 = 1$ and $\theta_2 = 1$.

To find a_3 it is necessary to solve the system of three equations (2), (3), and (4) having the three unknowns a_3, θ_1, and θ_2 for given concentrations c_1 and c_2. From experimental values of C_0, C_1 and C_2 and calculated values of θ_1 and θ_2 it is possible to solve equation (4) for given values of the concentrations to find the capacity for the combined adsorption of two different SAS's.

If, between different particles adsorbed on a metal, attractive forces operate (positive sign on the attraction constant a_3), the total adsorption increases and the decrease in the differential capacity (ΔC) for the mixture is greater than the total reduction in capacity caused by each component separately: $\Delta C_{12} > \Delta C_1 + \Delta C_2$. If the forces between the adsorbed particles are repulsive (negative sign on the attraction constant), $\Delta C_{12} < \Delta C_1 + \Delta C_2$.

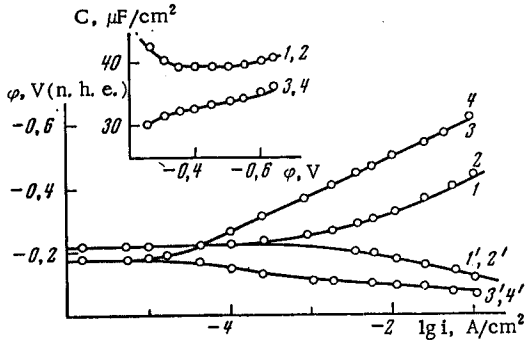

Fig. 3

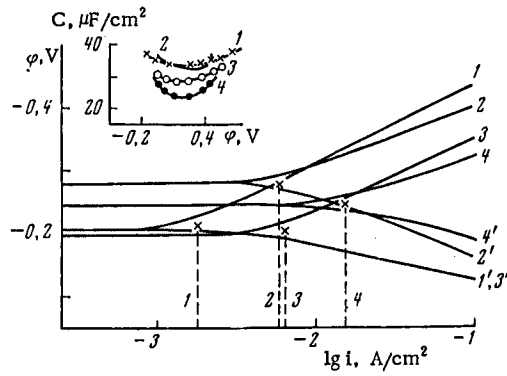

Fig. 4

Fig. 3. Cathodic and anionic polarization curves, and differential capacity curves, for zone-refined iron in 1 N H_2SO_4 without additives (1) and with (2) hexyl alcohol (saturated); (3) 0.1 N KBr; (4) hexyl alcohol (saturated) + 0.1 N KBr (circles).

Fig. 4. Cathodic and anionic polarization curves, and differential capacity curves, for an ion electrode in 1 N H_2SO_4 without additives (1) and with (2) $5 \cdot 10^{-4}$ N Na2S; (3) 0.01 M naphthalene disulfonic acid; (4) $5 \cdot 10^{-4}$ N Na2S + 0.01 M naphthalene disulfonic acid.

TABLE 1. Corrosion Inhibition Coefficients for Armco Iron in 1 N H_2SO_4 Containing Various Organic Compounds: the Effect of Anions

Solution	Concentration, M	Inhibition coefficient, ρ			
		without anion added	+ Na_2S, 0.001N	+ KBr, 0.01 N	+ sulfosalicylic acid
H_2SO_4 (1 N)	0,1	1	0,25	4,0	0,8
+ benzotriazole	—	8	40	420	—
+ diphenylamine	1/2 sat	1,25	0,63	4,0	—
+ benzenesulfonic acid	0,01	0,6	0,27	2,0	—
+ formaldehyde	0,01	7,8	0,26	13	—
+ butyraldehyde	0,01	1,1	7,0	17	—
+ aminoacetic acid	0,1	1,2	0,5	4,5	—
+ Trilon B	0,001	2,1	0,3	3,6	2
+ lysine	0,01	2,0	0,28	3,0	2,5
+ OP-10	2 g/liter	15	8,0	23	—
+ OP-45	2 g/liter	21	9,0	28	—

Calculations of the attraction constant from equation (1) and the capacity measurements shows that in solutions of individual inhibitors of the cationic type repulsive forces operate between the particles on an iron surface: $a = 2.4$ in solutions of TBMAS in 1 N HCl; $a = -1.26$ in allylphenyl thiourea in 1 N H_2SO_4 [4]. Repulsive forces are also observed between adsorbed organic cations on a mercury electrode [5].

As an example of the occurrence of repulsive forces (antagonism) between adsorbed positively-charged particles of different kinds, we present the results of capacity measurements in solutions of TBA (0.001 M) and TBMAS (0.0015 M) in 1 N H_2SO_4, both separately and mixed (the adsorption energies of TBA and TBMAS do not differ greatly). In a TBA solution $\Delta C_1 = 5 \mu F/cm^2$; in a TBMAS solution $\Delta C_2 = 10 \mu F/cm^2$; in their mixture $\Delta C_{12} = 9 \mu F/cm^2$ at $\varphi = -0.35$ V, i.e., $\Delta C_{12} < \Delta C_1 + \Delta C_2$.

The corrosion inhibition constants $\gamma = \rho_0/\rho_i$ (ρ_0 and ρ_i are the corrosion rate in the presence and absence of inhibitor) in a mixture of these inhibitors are also lower than the sum of the individual inhibition constants: $\gamma = 26$ in the TBA solution, 14 in TBMAS solution, 30 in the mixture. Qualitatively similar results were obtained for 0.01 M solutions of benzotriazole (BTA) and tetrabutyl ammonium sulfate in 1 N H_2SO_4. *

* The results reported here were obtained in experiments, all of which were carried out with pure zone-refined Fe at 20 ± 1°C in oxygen-free solutions. Potentials are relative to the normal hydrogen electrode. The differential capacity was measured at 800 Hz ac using a series circuit converted to parallel.

Repulsive forces also operate in the case of coadsorption of negatively charged particles. The results given to illustrate this (Fig. 1) show that the joint adsorption of the indicated sulfo-acids give a capacity reduction at $\varphi = -0.3$ V ($\Delta C_{12} = 10.5$ $\mu F/cm^2$) which is lower than ΔC only for the sulfosalicylic acid (SSA) ($\Delta C = 13$ $\mu F/cm^2$).

For the capacity reduction measurements it is not possible to estimate the rates of the electrochemical reactions, including the corrosion of iron. Changes in the rates of these reactions are largely determined by changes in the structure of the double electrical layer set up by adsorbed ions or dipolar molecules, by a change in the strength of the atomic hydrogen–metal bond, and also by the development of an adsorption ψ_1-potential of different sign and magnitude. During the adsorption of cations a ψ_1-potential of positive sign develops and the indicated reactions are slowed down. When anions are adsorbed a negative ψ_1-potential is developed and these reactions are accelerated.* Therefore, on adsorption of two anionic SAS's with a decrease in surface coverage the activating effect of the mixture on the corrosion of iron may be reduced compared with the sum of the effects of each SAS taken separately. We have in mind here specific or electrostatic adsorption. When chemisorption is stronger (for example, halide anions on iron) the reduction in the binding energy of the hydrogen atom, leading to a slowing down of the electrochemical reactions and of iron corrosion, prevails over the ψ_1 effect. In this case antipathy during coadsorption would lead to a decrease in the inhibiting effect on the mixture.

The curves in Fig. 2 may serve as an example of a positive interaction (synergism) during the coadsorption of particles with different signs. These curves show that TBMAS at $5 \cdot 10^{-4}$ M does not reduce the rate of hydrogen evolution or iron ionization (curves 1,1':2,2'). The addition of 0.05 M benzene sulfonic acid (BSA) appreciably reduces the capacity, affecting the adsorption and accelerating the indicated reactions (curves 3,3'). The simultaneous presence of TBMAS and BSA greatly reduced both the capacity and the rates of the electrochemical reactions and the corrosion (curves 4,4').

Synergism is observed during the coadsorption of amines, quaternary bases, pyridine derivatives, quinoline, alkaloids, and other organic onium compounds with several inorganic and organic anions, both with those which themselves inhibit the corrosion of iron (Cl^-, Br^-, I^- [4, 6]) and with those which stimulate it (anions of sulfides, sulfonic acids, rhodanides, etc.). These effects have been described in [2, 7-10] and are widely used in practice. However, they cannot be explained only by the attractive interactions of adsorbed particles, since an equilibrium distribution of cations and anions over the surface would be expected to give (simultaneously with an increased total adsorption) a reduced effect because of the reduction in the ψ_1-potential.

An increase in the inhibitory action of a cationic SAS in the presence of adsorption-active anions can be explained by the formation of anionic bridges [7, 8]. Specifically adsorbed anions, interacting electrostatically with inhibitor cations, promote the adsorption of the latter, forming dipoles with their positive ends towards the solution. At the same time the adsorbed anions are screened, preventing their activating action, and the positive ψ_1-potential is increased.

4. If the difference in the adsorption energies of the SAS's on the metal is large ($A_{1Me} \gg A_{2Me}$), the first component is preferentially adsorbed. This is observed in mixtures of organic acids or alcohols with halide ions or sulfonic acids (Fig. 3). We cite another example: for the solution comprising 1 N H_2SO_4 + 0.001 M BTA, $\Delta C_1 = 12$ $\mu F/cm^2$; for 1 N H_2SO_4 + 0.01 N KBr, $\Delta C_2 = 3.0$ $\mu F/cm^2$ at $\varphi = 0.3$ V; in their mixture, $\Delta C_{12} = 17.5$ $\mu F/cm^2$. If the BTA concentration is increased to 0.01 M the surface becomes saturated ($\Delta C = 24$ $\mu F/cm^2$) and the addition of 0.01 N KBr does not change the capacity. However, if KI, a salt with a more adsorption-active anion, is added instead of KBr, increases occur in adsorption and in the inhibitory effect of BTA.

5. When the difference in the adsorption energies of the SAS's is not large ($A_{1Me} \simeq A_{2Me}$), competition can occur between them for adsorption sites. This was proven by experiments in which changes were made in the order of addition of inhibitors coming into contact with the electrode. For example, if a 0.06% solution of catapin (methylbenzyl pyridine chloride) is first brought into contact with the electrode, $\Delta C = 12$ $\mu F/cm^2$ for $\varphi = -0.35$ V. On subsequent addition of 10^{-4} M TBMAS, ΔC is increased to 20 $\mu F/cm^2$. If the 10^{-4}

* If the adsorbed anionic SAS does not have a very high molecular weight then shielding of the electrode surface does not occur. We do not consider here the case of chemical reaction of the SAS, the formation of phase films during adsorption, or high surface loadings leading to blocking of the surface.

M TBMAS is introduced first ($\Delta C = 2.5\ \mu F/cm^2$), then the 0.06% catapin, ΔC increases to 10 $\mu F/cm^2$. In the latter case the large TBMAS molecules occupy the more active absorption sites and the subsequent introduction of catapin produces a smaller effect. A similar phenomenon is observed on changing the order of contact with iron of KI and TBMAS, but with time this system approaches an adsorption equilibrium and the effect of the order of introduction of the inhibitors gradually disappears.

As has been reported previously [11], HS^- anions coadsorbed with several SAS's show a substantially different behavior than other anions. They reduce the inhibitory effect of amines having weak basic properties, such as diphenylamine, most of whose molecules are not protonated in 1 N H_2SO_4, and amino acids, whereas when these amines and amino acids are coadsorbed with halide anions or sulfonic acids their inhibitory action is strengthened (see Table 1). The combined action of HS^- and halide anions depends on the ratio of their concentrations. For example, in 1 N H_2SO_4 + 0.01 N KBr the addition of 10^{-4} N Na_2S inhibits iron corrosion, whereas 10^{-3} N Na_2S promotes it. The coadsorption of HS^- with various sulfonic acid anions produced an increase, rather than a decrease, in adsorption; there is a corresponding increase in the promoting effect of mixtures on corrosion. For example, in Fig. 4 are shown plots of C versus φ and φ versus log i for an iron electrode in 1 N H_2SO_4 containing $5 \cdot 10^{-4}$ N Na_2S and 0.01 M napthalenesulfonic acid. It can be seen that $\Delta C_{12} = 11\ \mu F/cm^2$, while $\Delta C_1 + \Delta C_2 = 2 + 6 = 8\ \mu F/cm^2$. The spontaneous solution rate of iron in the indicated mixture of SAS's ($\rho = 1.6 \cdot 10^{-2}$ A/cm^2) is greater than in the presence of each of these compounds separately ($\rho = 6 \cdot 10^{-3}$ and $6.3 \cdot 10^{-3}$ A/cm^2).

The adsorption of HS^- jointly with organic acids and alcohols decreases their inhibitory, or increases their promoting, action. Aliphatic aldehydes, which inhibit iron corrosion, in the presence of HS^- behave differently depending on the acid concentration and the length of the aldehyde molecule chain. Propionaldehyde in 1 N H_2SO_4, like the alcohols and acids, increases the promoting effect of hydrogen sulfide, but in 8 N H_2SO_4 it slows down the corrosion process. Butyraldehyde in 1 N H_2SO_4 inhibits weakly, but in the presence of H_2S it has a greater effect [9].

CONCLUSIONS

Several cases have been considered of the interaction between molecules and substances of different types when adsorbed on the surface of iron. When the attractive forces between the particles predominate, the interaction leads to increased adsorption and a stronger retarding action by the inhibitors on iron corrosion (synergism). The appearance of repulsive forces causes the opposite effect (antipathy). The effects observed during the coadsorption of inhibitors with anions and with other inhibitors are illustrated by the results of measurements of the differential capacity of the double layer, by cathodic and anodic polarization curves, and by data on the rate of iron corrosion.

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