USE OF ELECTROCAPILLARITY MEASUREMENTS TO DETERMINE THE EFFECT OF SURFACE ACTIVE SUBSTANCES UNDER PASSIVATION CONDITIONS

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V. P. Grigor'ev

Rostov-on-Don State University

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It is well known that the inhibiting effect of a number of substances on corrosion is determined by the adsorption of these substances. It was shown in [1] and later in [2-6] that there is a direct relationship between the surface activity of substances on mercury and their inhibiting effect. On the basis of this result, the author in [1] proposed a method of determining the inhibiting properties of substances by measurements of the electrocapillarity [1, 7-11].

One would expect the effect of these substances during passivation of metals to be determined to a great extent also by the capacity of the metal to adsorb these substances. Therefore, it is of interest to use the method of electrocapillarity curves in investigations of the effect of additional elements on the passivation of metals.

The passivating and depassivating effects of different substances were investigated by studying their effects on the passivation current i_p in the case of passivation of 1Kh18N9T steel in sulfuric acid solutions. The values of i_p used were determined from anodic polarization curves; the method of determining these curves was described earlier [12]. Electrocapillarity measurements necessary to determine the adsorptional properties of the additional elements were made on mercury in the same solution by the usual method [13]. The experiments were carried out at 25°C. The electrocapillarity curve was determined at least three times for each solution. The reproducibility of the value of the surface tension in the experiments was ± 1 dyne/cm.*

From the substances previously investigated we selected the following strong depassivators: NaCl, thiourea, and acrylic acid (which considerably decreases the value of i_p). The relationship between the depassivating property of NaCl and its surface activity was examined within a wider range of acidities than for the other additional elements, since the Cl^- ions are widely used depassivators.

Data on the decrease of the surface tension of mercury in a 1 N H_2SO_4 solution containing thiourea were taken from [9].

The potentials were measured with respect to the zero charge of mercury in a pure solution—the maximum on the electrocapillarity curve. In the 1 N H_2SO_4 solution this maximum is equal to 0.21 V with respect to the normal hydrogen electrode.

The method of determining the inhibiting properties of substances from the results of electrocapillarity measurements is based on the use of the φ -scale of potentials [8, 14]. According to this scale, the potential of the metal is calculated with respect to its zero point $E_{q=0}$, i.e., $\varphi = E - E_{q=0}$, where the potentials of the electrode E and $E_{q=0}$ are expressed with respect to the same reference electrode. The charges of the two metals with the same φ -potential are equal. If the adsorption occurs predominantly as the result of electrostatic forces then the conditions of adsorption of the same substance on these metals must be very similar. Thus, the results obtained by the determination of the adsorption of a given element on one metal (mercury, for example) can be used to characterize the adsorption of the same element on another metal.

*The electrocapillarity measurements were made by T. A. Pisarenko.

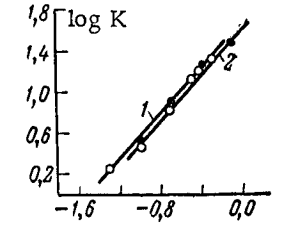

Fig. 1.

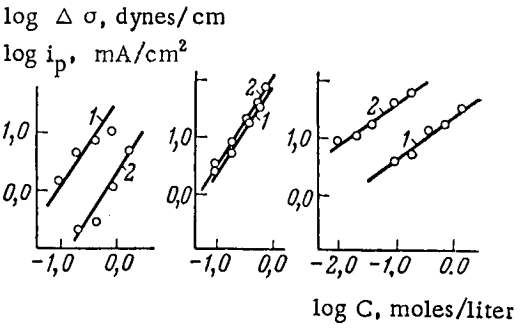

Fig. 2.

Fig. 1. Variation of the corrosion deceleration coefficient K of 1Kh18N9T steel (1) and the decrease of the surface tension of mercury $\Delta\sigma$ (2) in a 7.5 N H_2SO_4 solution with the concentration of NaCl.

Fig. 2. Dependence of the decrease of the surface tension of mercury $\Delta\sigma$ (1) and of the passivation current i_p of 1Kh18V9T steel (2) on the concentration of NaCl in sulfuric acid solution. a) 2.5; b) 5.0; c) 10.0 N H_2SO_4.

The following relationships must exist between the coefficient of deceleration of corrosion K_{corr}* (or the current of spontaneous dissolution of the metal), the decrease of the surface tension of mercury $\Delta\sigma$, and the bulk concentration of the additional element C at $\varphi_{Me} = \varphi_{Hg}$ for any given solution investigated [7, 9-11]:

$$\log K_{corr} = \text{const}_{corr} + \beta_{corr} \log C \quad (1)$$

$$\log \Delta\sigma = \text{const} + \beta \log C \quad (2)$$

where $\beta_{corr} = \beta$. This makes it possible to determine the inhibiting properties of elements within a wide range of concentrations by Eq. (1) practically without any corrosion tests (only one corrosion test is needed to determine const_{corr}; the value of β_{corr} is found from the results of electrocapillarity measurements).

Antropov's method [1] of determining the adsorption of acrylic acid on 1Kh18N9T steel is acceptable, but it requires some additional clarification as far as Cl^- and thiourea are concerned. It is well known that halogen ions and sulfur ions form chemisorption compounds when adsorbed on the surface of iron and probably also on steel [15-18], unlike the case of adsorption on mercury. However, this fact does not exclude the possibility of using the method of electrocapillarity curves, although it does require some modification, as was indicated in the description of the method [1, 7]. The possibility of using this method to study the adsorption of chemisorbed particles is indicated, for example, by the dependence of the surface concentration of chemisorbed particles on the potential [16, 19-20]. This dependence indicates that chemisorption is to some extent determined by electrocapillary forces. The electrocapillarity curves method was used successfully to determine the inhibiting effect of organic substances on the corrosion of iron in acid media containing Cl^- ions [7] and also in the investigation of the protection of iron against corrosion by the use of thiourea [9]. It is well known that sulfur ions are chemisorbed in the presence of thiourea in acid solutions. Also, the preliminary experiments on the determination of the relationship between the surface activity of Cl^- ions on mercury and their inhibiting effect on the corrosion of 1Kh18N9T steel give the same relationship as in the case of additional elements which are physically adsorbed on mercury and iron (Fig. 1).

These results justify the attempt to use Antropov's method also to determine the relarionship between the depassivating effect of chemisorbed elements and their surface activity on mercury.

Figures 2-4 show the dependences of the passivation current i_p and of the decrease of the surface tension of mercury $\Delta\sigma$ on the concentration of additional elements in the same solutions. The values of $\Delta\sigma$ were determined by electrocapillarity curves in the case of $\varphi_{Hg} = {}_{Me}\phi_{pass}$. The values of E_{pass} needed to calculate

*The coefficient of the deceleration of corrosion K_{corr} is equal to i^0/i, where i^0 and i are the currents of spontaneous dissolution of the metal in pure acid solutions and acid solutions with an inhibitor respectively.

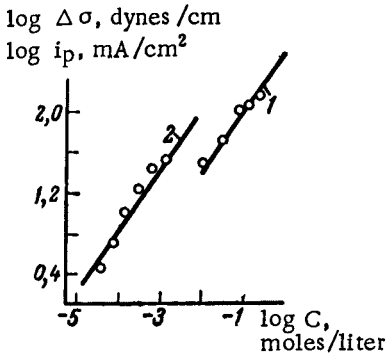

Fig. 3

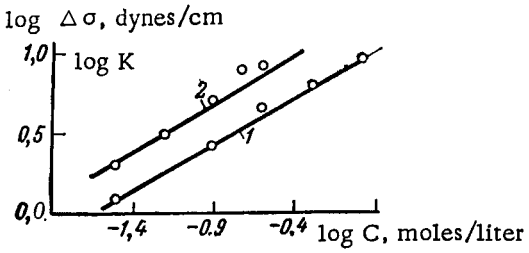

Fig. 4

Fig. 3. Dependence of the decrease of surface tension of mercury $\Delta\sigma$ (1) and of the passivation current i_p of 1Kh18N9T steel (2) on the concentration of thiourea in 1.0 N H_2SO_4.

Fig. 4. Dependence of the decrease of the surface tension of mercury $\Delta\sigma$ (1) and of the coefficient of the decrease of the passivation current K of 1Kh18N9T steel (2) on the concentration of acrylic acid in 14.3 N H_2SO_4.

$\varphi_{pass} = E_{pass} - E_{q=0}$ were obtained from polarization measurements. The zero point of 1Kh18N9T steel was taken as equal to 0.45 V with respect to the normal hydrogen electrode.* The value of φ_{pass} was between 0.3 and 0.5 V, depending on the conditions.

Figures 2-3 show that when the depassivators NaCl and thiourea are added then the relationships log i_p = f(log C) and log $\Delta\sigma$ = f(log C) are linear and are straight parallel lines. The angles of the slopes of these dependent on the concentration of the acid: In 10 N H_2SO_4 the angle is considerably smaller than in the 2.5 and 5 N H_2SO_4 solutions (Fig. 2).

Formally, a similar relationship between i_p and $\Delta\sigma$ exists also in the presence of acrylic acid, which decreases the intensity of the current of anodic passivation of the metal (Fig. 4).

Thus, the coefficient of the change of the passivation current K_{pass}† can be expressed by the following equation, which is similar (to 1):

$$\log K_{pass} = \text{const}_{pass} + \beta_{pass} \cdot \log C \qquad (3)$$

From Eqs. (2) and (3) we have

$$\log K_{pass} = \text{const} \cdot \Delta\sigma \qquad (4)$$

where const is a constant value depending on the nature of the metal and the nature of the solution; $\Delta\sigma$ is the decrease of the surface tension of mercury in the same solution when $\varphi_{Hg} = {}_{Me}\varphi_{pass}$.

The similarity of the effect of the additional elements on the currents of spontaneous dissolution of metals in the active state (not inhibited) and of the passivation current allows us to derive the following simple relationship.

*In the literature there are no data on the zero point of 1Kh18N9T steel. The value used was based on the following considerations: 1Kh18N9T steel in the austenitic state is a solid solution. The zero points of solid solutions usually coincide with the zero point of the most electronegative component even when its concentration in the alloy is very low [21]. In 1Kh18N9T steel this component is chromium: $E_{q=0} = -0.45$ V with respect to the normal hydrogen electrode [14]. The effect of titanium was not taken into account, since its concentration does not exceed 0.7% [22].

†The coefficient K_{pass} is the ratio i_p/i_p^0 in the case of the addition of depassivating elements or the ratio $i^0{}_p/i_p$ in the case of the addition of inhibiting elements. The values of i_p^0 and i_p are the passivation currents in the presence and absence of additional elements.

In the general case, when φ_{pass} is considerably lower than φ_{corr}, it follows from Eqs. (1) and (3) that

$$\log \frac{K_{pass}}{K_{corr}} = \text{const} + (\beta_{pass} - \beta_{corr}) \log C \qquad (5)$$

i.e., the logarithm of the ratio of the coefficients of the change of the passivation and the spontaneous dissolution of the metal is a linear function of the logarithm of the concentration of the additional element.

When the values of φ_{pass} and φ_{corr} are close to each other the angular coefficients in Eqs. (1) and (3) must be equal ($\beta_{corr} = \beta_{pass}$) because within a wide range of φ -potentials the angle of the slope of the adsorption isotherm does not change to any significant degree. Taking this into account, we obtain from (5):

$$\frac{K_{pass}}{K_{corr}} = \text{const} \qquad (6)$$

i.e., the ratio of the coefficients of the changes of the passivation and spontaneous dissolution of metals is independent of the concentration of the additional element.

The results of this investigation show that one can use the Antropov ϕ-scale of potentials and electrocapillarity measurements to investigate the passivation of metals in the presence of additional elements. This method facilitates the selection of additional elements to decrease the passivation current and is definitely of interest for the rapidly developing method of anodic protection of metals against corrosion.

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