NATURE OF THE "CRITICAL POTENTIALS" IN THE INHIBITION OF METAL CORROSION IN NEUTRAL MEDIA

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The mechanism of the protection of metals from corrosion in neutral media with the aid of anions still remains far from clear. Even in the case of such a well-studied anionic inhibitor as benzoate, there is no single viewpoint concerning the nature of its inhibiting ability [1-7].

Of great interest for an understanding of the mechanism of the action of anionic inhibitors are data indicating that their inhibiting effect may be manifested only within a definite region of potentials [8, 9]. This phenomenon has been investigated in the greatest detail by D. Brasher [10], who has shown that benzoate is an inhibitor of the corrosion of iron in 0.01 N NaCl only in the case when the potential of the corroding sample is more positive than -0.28 V on the hydrogen scale. Analogous experiments conducted with sodium biphosphate have shown that its protective action is detected at potentials more positive than -0.43 V.

The most negative potential value at which an inhibiting effect of anions is still observed has been called the critical potential. Brasher at first identified the critical potentials with the zero point ε_N of iron. Subsequently this hypothesis was discarded, and a new hypothesis was advanced, according to which the critical potentials do not necessarily coincide with the zero points, but should be somehow related to them.

The nature of the critical potentials thus remains insufficiently clear and will require further study.

This work represents an attempt to obtain some supplementary information on the mechanism of the action of anionic inhibitors, in particular, benzoate, and a clarification of the essence of the "critical potentials" on this basis.

PROCEDURE

Armco iron in solutions of NaCl with additions of sodium benzoate were subjected to corrosion tests. The samples, cut out of ribbons 0.5 mm thick in the form of a circle with total area 6.5 cm^2, were degreased successively in ether, alcohol, and electrochemically, washed thoroughly, dried, and weighed. Then the samples were suspended for 120 h in beakers with the test solution at a depth of 3 cm from the surface of the electrolyte. The rate of corrosion was determined by a gravimetric method. In addition, corrosion tests (duration 12 h) at constant potential were conducted with the aid of an electromechanical potentiostat [11].

The electrocapillary curves were taken on the Gui electrometer. All the experiments were conducted at the temperature 25 ± 0.1°. The solutions were prepared in double-distilled water from recrystallized salts, C.P. grade. In addition to sodium benzoate, inorganic inhibitors NaH_2PO_4, Na_2HPO_4, $NaNO_2$ were also used as additives in the work. In all cases the reference electrode was a saturated calomel electrode; the potentials were converted to the hydrogen scale.

EXPERIMENTAL DATA AND THEIR DISCUSSION

The amount of sodium benzoate required for complete protection of the surface of iron from corrosion, as is indicated by corrosion investigations, increases with increasing sodium chloride content in solution, in a first approximation obeying the equation

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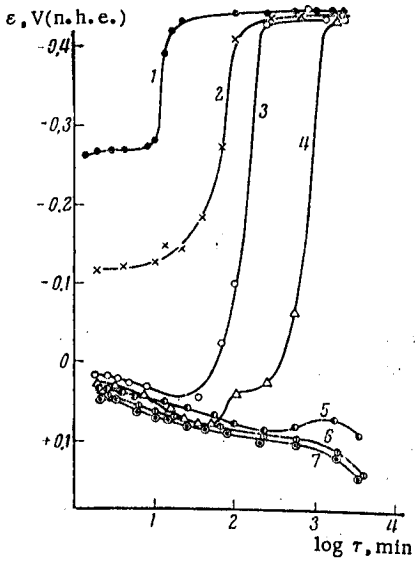

Fig.1. Influence of sodium benzoate on the electrode potential of iron in 0.1 N NaCl solution: sodium benzoate concentration (M): 1) 0; 2) 0.02; 3) 0.04; 4) 0.08; 5) 0.1; 6) 0.18; 7) 0.2.

$$_{prot}C_{Na\ benz} = 0.01 + 2C_{NaCl} \quad (1)$$

The addition of benzoate to a sodium chloride solution shifts the initial corrosion potential in a positive direction (Fig.1). At benzoate concentrations insufficient for protection of the sample from corrosion, the potential at first is either unchanged or is somewhat shifted in the positive direction, but then it sharply "deteriorates" to the stationary potential of corrosion. In the case of protective or close to protective concentrations, the potential is gradually shifted in the positive direction, which indicates an inhibition of the anodic process. Such stable inhibition of the process occurs only when the initial potential of the sample is shifted to values of ± 0.00-0.05 V.

To determine the critical potentials (ε_{prot}) at which the protection of iron samples by various additions of benzoate is achieved, we conducted corrosion experiments in 0.01 M and 0.1 M NaCl at constant potentials within the interval from -0.3 to +0.2 V*.

From Table 1 it is evident that the value of ε_{prot} depends both upon the sodium chloride concentration and upon tha amount of added benzoate. However, there is a benzoate concentration (for 0.01 M NaCl it comprises 0.02 mole/liter, while for 0.1 M NaCl it is approximately 0.15 mole/liter), below which protection cannot be achieved at any of the investigated potential values. Thus, in addition to the critical potentials there is also a critical volume concentration of the inhibitor; moreover, these quantities are closely interrelated. The existence of such a relationship is an indication that the guarantee of protection of a metal from corrosion necessitates some minimum surface concentration of benzoate, since the adsorption of particles from solution is determined by their volume concentration and by the potential or, more accurately, by the charge of the metal with respect to the solution. The value of the latter, as is well known, can be replaced with some approximation by the electrode potential in the reduced or φ-scale (12-15), representing the difference between the electrode potential under the given conditions and its zero point

$$\varphi = \varepsilon - \varepsilon_N \quad (2)$$

To evaluate the adsorbability of benzoate ions, we conducted electrocapillary measurements on mercury in solutions with various chloride and sodium benzoate contents. Figures 2 and 3 present the electrocapillary curves taken in 0.01 M and 0.1 M NaCl. The adsorption of benzoate ions begins at potentials more negative than the maximum of the electrocapillary curve in a pure NaCl solution; moreover, the potential of the beginning of adsorption† depends upon the sodium ion and benzoate concentrations in solution (Fig.4).

The critical potentials at which protection of iron by benzoate is achieved are substantially more positive than the values corresponding to the beginning of the adsorption of benzoate on mercury (under the condition that the zero points of iron and mercury are equal to ± 0.0 V and -0.19 V, respectively). Consequently, the appearance of benzoate ions on the metal surface still is not sufficient for its protection. The critical potentials also differ from the potentials of the maxima of the electrocapillary

* Anodic dissolution of iron begins at the potential + 0.2 V.

† The position of the right-hand branch of the electrocapillary curve depends upon the total sodium ion content and practically does not change with the chloride ion concentration. Therefore, in determining the beginning of adsorption of benzoate ions, the electrocapillary curve obtained in a NaCl solution with the same sodium ion content as the solution of sodium chloride and benzoate was taken as the initial curve. The potential of the beginning of adsorption was taken at this potential, equal to the potential of the divergence of these two curves (see Figs.2 and 3).

TABLE 1

Composition of solution	ε_{prot}, V, from corrosion tests	ε_{prot}, V, from electrocapillary curves
0.01 *M* NaCl + 0.01 *M* Na benz.	—	—
0.01 *M* NaCl + 0.02 *M* Na benz.	+0.05	+0.05
0.01 *M* NaCl + 0.03 *M* Na benz.	±0.0	±0.0
0.01 *M* NaCl + 0.09 *M* Na benz.	−0.15	−0.2
0.01 *M* NaCl + 0.2 *M* Na benz.	−0.2	−0.44
0.01 *M* NaCl + 0.04 *M* Na benz.	—	—
0.01 *M* NaCl + 0.12 *M* Na benz.	—	+0.2
0.01 *M* NaCl + 0.15 *M* Na benz.	+0.1	+0.1
0.01 *M* NaCl + 0.2 *M* Na benz.	+0.05	+0.05
0.01 *M* NaCl + 0.6 *M* Na benz.	−0.1	−0.24

curves in a given solution, i.e., from the potential of the uncharged surface $\varepsilon_{q=0}$.*

However, as can easily be ascertained, the critical potentials correspond to those values of the charge of the metal surface at which a definite decrease in the surface tension of mercury is reached in a solution with a given benzoate concentration, in comparison with the initial sodium chloride solution, containing no inhibitor. Thus, in 0.01 M NaCl, the addition of 0.03 mole/ liter sodium benzoate at an initial potential $\varphi = \pm 0.0$ V entirely ensures the protection of iron from corrosion during the entire time of the testing; the value of the decrement $\Delta\sigma$ of mercury is approximately 6.5 dyn·cm^{-1} at this potential (Fig.2). Assuming that the value $\Delta\sigma = 6.5$ dyn·cm^{-1} corresponds to the initial surface concentration of benzoate necessary for complete protection of iron in 0.01 M NaCl at room temperature, the values of the potentials at which such a decrease in the surface tension is achieved were found for each benzoate concentration according to the electrocapillary curves. In the region of positive potentials, these quantities are in good agreement with the data of direct corrosion measurements, performed on iron (see Table). In the case of a shift in the direction of negative potentials, such convergence is disturbed – the accomplishment of protection requires benzoate concentrations giving somewhat larger values of $\Delta\sigma$ (Fig.2). Evidently the adsorption of sodium ions, which complicates the general picture, has an effect here.

* The zero point of metals represents the particular value of the potential of the uncharged metal surface [15], measured in a solution containing no surface-active substances. It is therefore natural that the critical potentials cannot be identified with the zero point, as was originally assumed [10].

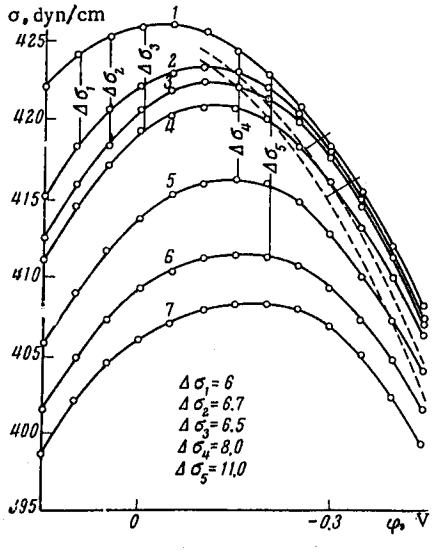

Fig.2

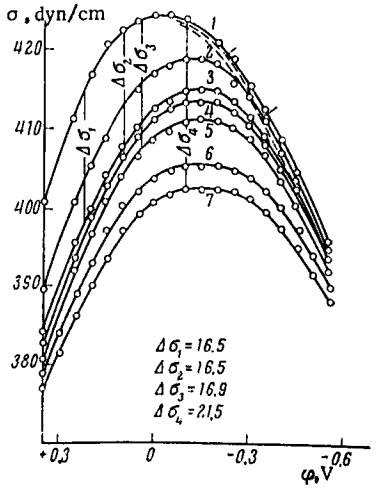

Fig.3

Fig.2. Electrocapillary curves in 0.01 M NaCl with additions of sodium benzoate (M): 1) 0; 2) 0.01; 3) 0.02; 4) 0.03; 5) 0.09; 6) 0.2; 7) 0.3; the dotted lines correspond to electrocapillary curves taken in 0.1 M (a) and 0.31 M (b) NaCl.

Fig.3. Electrocapillary curves in 0.1 M NaCl with additions of sodium benzoate (M): 1) 0; 2) 0.04; 3) 0.12; 4) 0.15; 5) 0.2; 6) 0.4; 7) 0.6; the dotted lines correspond to electrocapillary curves taken in 0.14 M (a) and 0.22 M (b) NaCl.

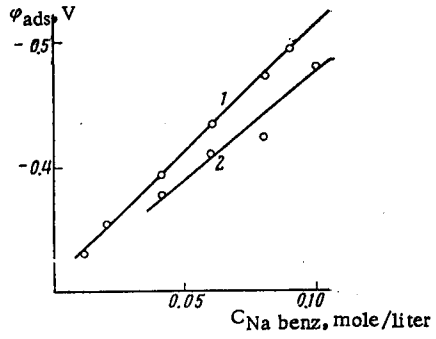

Fig.4. Dependence of the potential of the beginning of adsorption of sodium benzoate upon its concentration. Sodium ion concentration (mole/liter): 1) 0.1; 2) 0.12.

Analogous results were also obtained in 0.1 M NaCl (Fig.3), but with the difference that here the value of the decrement $\Delta\sigma$ corresponding to protection in the region of positive potentials is 16.5 dyn·cm^{-1}. From the value of $\Delta\sigma$ critical for a given sodium chloride content, we can find the minimum volume concentration of benzoate at which the prevention of corrosion of iron is still theoretically possible. Evidently this is the concentration at which at least one of the possible values of the potential corresponds to a value of $\Delta\sigma$ equal to the critical value for a given solution. Thus, for 0.01 M NaCl it should lie between 0.02 and 0.01 mole/liter benzoate, while for 0.1 M NaCl, it should lie between 0.12 and 0.15. It should be emphasized that the protective action of sodium benzoate is manifested only in the case when the sample of iron is immersed in a solution already containing an addition of the inhibitor. If, on the other hand, the iron sample was in an aggressive medium, and the stationary potential of corrosion, equal to approximately -0.44 V in 0.1 N NaCl, was reached, then the addition of a protective concentration of sodium benzoate would not lead to a cessation of the corrosion process. This confirms the need for a shift of the initial potential in the positive direction to create conditions ensuring adsorption of benzoate ions.

From the data cited it follows that the critical potentials represent the potentials at which the "critical" degree of surface coverage by benzoate anions, sufficient for the realization of protection, is ensured in a given solution. At φ-potentials close to the potentials observed under the conditions of protection of an iron surface in corrosion testing (+0.00 V to +0.05 V), the degree of surface coverage of mercury θ, calculated from electrocapillary curves, is about 50%. The degree of coverage calculated for mercury naturally may not coincide with the value of the surface coverage of iron at the same charge; but their changes with the conditions of the experiment should be analogous. It should be noted that the indicated value of the degree of coverage without a subsequent increase in the protective film is insufficient for the realization of protection of the iron surface from corrosion in neutral medium.

As it follows from the electrocapillary curves taken in solutions of HCl, nondissociated molecules of benzoic acid, which appear in solution as a result of the hydrolysis of sodium benzoate, are molecular-type surfactants with a greater adsorption capacity than that of the benzoate ion. However, in neutral media, where the corrosion tests were conducted, the concentration of benzoic acid is so low that its inhibiting effect can be neglected.

Electrocapillary curves taken in solutions of NaCl with additions of NaH_2PO_4, Na_2HPO_4, and $NaNO_2$, indicated that the anions of these salts do not possess capillary activity on mercury. Their inhibiting effect in the corrosion of iron in neutral media, in contrast to the opinion of certain authors [17, 18], cannot be evaluated on the basis of the data of electrocapillary measurements on mercury. In the mechanism of protection with the aid of these inhibitors, the surface activity evidently plays a secondary role.

CONCLUSIONS

1. The value of the critical potential of the inhibition of corrosion of iron in neutral salt media by sodium benzoate depends upon the composition of the solution, in particular, upon the concentration of sodium chloride and sodium benzoate. The critical potential corresponds to a charge of the metal at which a definite degree of shielding of the surface is achieved under the given conditions, ensuring a further stable inhibition of the anodic reaction. The use of electrocapillary data obtained on mercury permits an estimation of the change in the value of the critical potential with the composition of the solution with a sufficient degree of approximation.

2. The inhibiting effect of inorganic anions ($H_2PO_4^-$, HPO_4^{2-}, NO_2^-), in contrast to benzoate ions, is not directly related to their surface activity, and cannot be estimated on the basis of the data of electrocapillary measurements on mercury.

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