ADSORPTION OF SURFACE-ACTIVE SUBSTANCES ON AN IRON ELECTRODE IN AN ALKALINE SOLUTION

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In order to elucidate the mechanisms whereby various additions affect electrode processes it is desirable to study the adsorption of the additives on the electrodes as well as carry out kinetic measurements. In many cases a convenient method of measuring adsorption is afforded by measurements of the capacity of the electrode in an alternating current. Thus, adsorption of organic compounds is generally accompanied by reduction in the capacity of the electrode in a certain range of potentials in the vicinity of the potential of zero charge, and also by the appearance of characteristic capacity maxima ("desorption peaks") at the limits of this potential range [1]. Considerable practical interest is presented by the selection of surface-active substances that can affect the kinetics of electrode processes at an iron electrode in alkaline solutions; in particular, it is of great importance to find additives that will raise the hydrogen overvoltage at an iron electrode and so reduce the autosolution of this electrode in an alkali accumulator.

EXPERIMENTAL

We studied the relation between the capacity of an iron electrode and its potential in 2 N NaOH for potentials ranging from − 0.5 to + 1.5 v (against a hydrogen electrode in the same solution) in presence of additives, namely, tetrabutylammonium sulfate, 2-naphthalenesulfonic acid, hexanoic acid, octyl alcohol, sodium arsenite, tannin, alizarin, and phenol. Simultaneously with measurements of capacity, hydrogen-overvoltage curves were determined.

The electrode investigated was a fine wire (diameter 0.22 mm) of chemically pure iron placed coaxially in a platinum cylinder, which served as an accessory electrode for the passage of alternating current. All solutions were prepared by dissolving chemically pure reagents in doubly distilled water, and before the experiments they were saturated with nitrogen carefully purified from oxygen. The capacity of the electrode in an alternating current was measured with an impedance-compensation system with separate compensation for capacity and ohmic components. The alternating current used for the measurements had a frequency of 5000 cycles per second. Under these conditions the most probable equivalent scheme of the electrode is a capacity and resistance connected in parallel, and therefore, after subtracting the resistance of the solution, we generally recalculated the measured values of capacity (C_1) and resistance (R_1), corresponding to capacity and resistance in series, to give the value C_2, corresponding to connection in parallel. In most cases the values of C_2 differed little from the corresponding values of C_1, since the value of the tangent of the phase shift was usually greater than unity.

At the beginning of the experiment the iron electrode was subjected to cathodic polarization with a current of high density ($5 \cdot 10^{-2}$ amp/sq. cm).* After this preparation capacity-potential curves were determined first with cathodic and then with anodic polarization.

The relation between the capacity of the electrode (C_2) and the potential in pure 2 N NaOH at 5000 cycles per second is represented in Fig. 1. As the potential of the electrode is displaced in the positive direction, there is a gradual fall in capacity, probably due to increase in the thickness of the passivating oxide layer on

* The stationary potential of such a semipassive electrode was 0.1-0.2 v against a hydrogen electrode in the same solution.

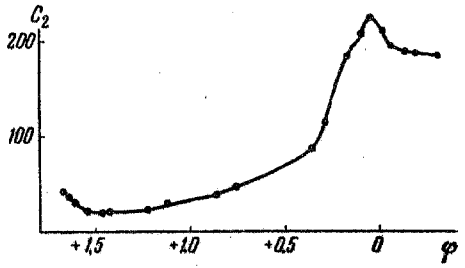

Fig. 1. Relation between capacity and potential of electrode in 2 N NaOH.

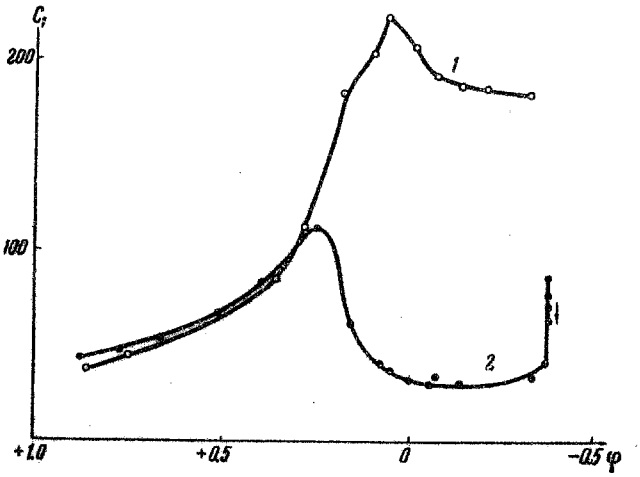

Fig. 2. Effect of tannin on the capacity of the electrode; 1) 2 N NaOH; 2) 2 N NaOH + 2% tannin

the iron surface. In the presence of additions of tetrabutylammonium sulfate and naphthalenesulfonic acid there was a slight lowering of capacity (by 10-20%) at potentials more negative than 0.3 v. In presence of additions of hexanoic acid and octyl alcohol no lowering of capacity was observed. These additions have almost no effect on the value of the hydrogen overvoltage; a small lowering of the hydrogen overvoltage (30-40 mv) is observed only in the case of hexanoic acid.

These results show that, within the limits of accuracy of our experiments, we were unable to detect the absorption of these organic substances on an iron surface in an alkaline solution. The reason for the feeble adsorbability of these typical surface-active additives probably lies in the fact that an iron surface in an alkaline solution is almost always oxidized to a greater or lesser extent. Evidence of the presence of an oxidized surface on the iron in our experiments is to be found, in particular, in the high value of the slope of the overvoltage curve (0.2 v). According to the results of Rozentsveig and Kabanov [2], in the case of an unoxidized iron surface the slope is 0.1 v, whereas in the case of oxidized iron it rises to 0.2 v. The literature [3] indicates that oxidized iron has a considerably lower tendency to adsorb organic substances than an iron surface free from oxides. It is probable that the presence of oxides on the metal surface results in such powerful hydrophilization of the surface that specific adsorption becomes impossible. At the same time, adsorption due to chemical interaction between the particles being adsorbed and the electrode surface can occur also at an oxidized surface. Since the typical surface-active additives that we tried had practically no effect on the capacity of an oxidized iron surface, it would appear that, under the given conditions, chemical adsorption also did not occur.

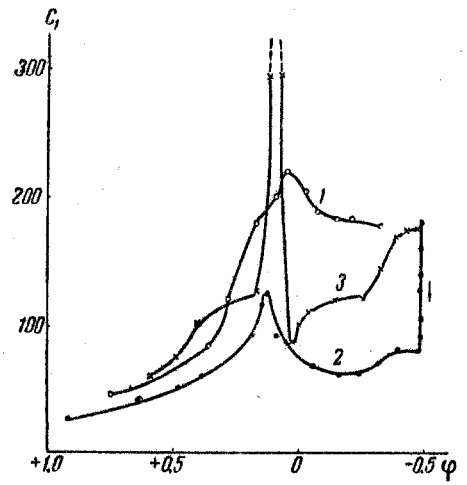

Fig. 3. Effects of alizarin and phenol on the capacity of the electrode: 1) 2 N NaOH; 2) 2 N NaOH + 0.3% alizarin; 3) 2 N NaOH + 0.7 N C_6H_5OH

As pointed out previously [4], it is of interest to study the effect of additions of compounds that readily react chemically with iron, both in the ionic form and in the form of hydroxides, and so should be adsorbed on an oxidized iron surface. As additives of this kind we selected tannin, alizarin, phenol, and arsenious oxide. In presence of 2% tannin, the capacity of an iron electrode (C_1) in the negative potential region (from − 0.3 to 0.0 v) is reduced to approximately one-sixth of the capacity in pure sodium hydroxide solution (Fig. 2). At higher tannin concentrations (6.5%) there is no further lowering of capacity. At potentials more positive than 0.4 v, additions of tannin have no effect on capacity, and at potentials of 0.9-1.0 v, judging from the character of the dependence of potential on current density and on rate of stirring of the solution, anodic oxidation of the tannin occurs. An analogous effect on the

capacity of an iron electrode is shown also by alizarin and by phenol. As can be seen from Fig. 3, addition of 0.3% of alizarin results in a reduction of the electrode capacity to one-third at potentials ranging from − 0.5 to 0.0 v. Addition of phenol also results in an appreciable reduction in capacity at negative potentials. The sharp drop in the capacity of an iron electrode observed on the introduction of tannin, alizarin, or phenol into the alkaline solution indicates that these substances are adsorbed on the iron surface*. Moreover, at high concentrations of phenol (which, unlike the other additives, is of high solubility in alkali), the capacity-potential curve has a high maximum, which appears to be a desorption peak** [1, 5]; this again indicates adsorption of phenol at negative potentials. As can be seen from Figures 2 and 3, at more positive potentials the effects of tannin, alizarin, and phenol on the capacity of the electrode almost disappear, which indicates that they are desorbed from the electrode surface.

The effect of additions of tannin, alizarin, and phenol on hydrogen overvoltage is shown in Fig. 4. According to Levina's results [4], which refer to the rise in the hydrogen overvoltage at an iron powder electrode at high current density ($5 \cdot 10^{-3} - 5 \cdot 10^{-2}$ amp/sq.cm), in presence of tannin the rise is 40-60 mv and in presence of alizarin it is 60-80 mv.*** It must be pointed out that, when the electrode is immersed in a solution having additions of tannin and alizarin under a powerful cathodic current, constant values of overvoltage and capacity are not established immediately: these is a slow rise in overvoltage with simultaneous gradual lowering of capacity (Figures 2 and 3), and the overvoltage attains a constant value in 20-30 minutes simultaneously with cessation of change in capacity. This shows that raising of the overvoltage by tannin and alizarin is due to the chemical adsorption of these substances. In presence of additions of phenol no rise in overvoltage is observed.

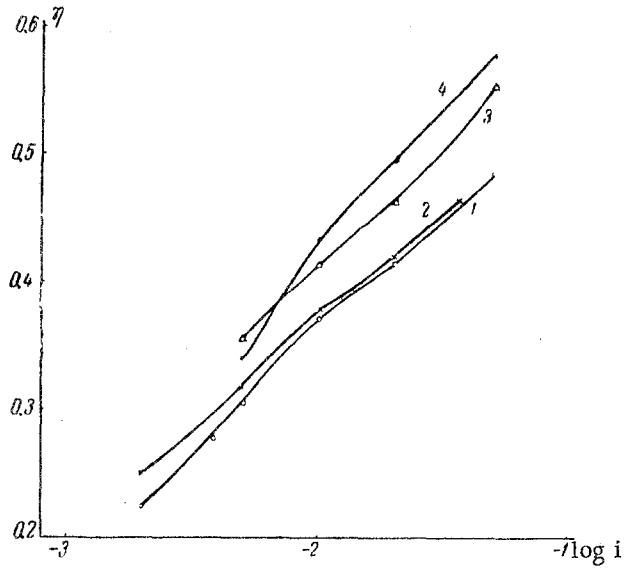

Fig. 4. Effects of tannin, alizarin, and phenol on hydrogen overvoltage: 1) 2 N NaOH; 2) 2 N NaOH + + 0.7 N C_6H_5OH; 3) 2 N NaOH + 2% tannin; 4) 2 N NaOH + 0.3% alizarin.

As well as the effects of the addition of organic substances on the capacity of the iron electrode in alkaline solutions, we studied also the effect of additions of arsenious oxide. Figure 5 shows the relation between the capacity of the electrode (C_2) and its potential for 2 N NaOH with additions of 0.002 and 0.2 M $NaAsO_2$ (arsenic was introduced into the solution as As_2O_3). At the most negative cathodic potentials (from − 0.5 to − 0.6 v), the capacity of the electrode in solutions containing the additions was 100-110 microfarads/sq.cm, and it remained almost unchanged with prolonged cathodic polarization. When the cathode current density was reduced to 2-5 x 10^{-3} amp/sq.cm (the electrode potential then shifted to a value of from − 0.40 to − 0.45 v) in the solution with an addition of 0.2 M $NaAsO_2$, there was a slow fall in capacity down to very low values of the order of 10 microfarads/sq.cm and these values of capacity were maintained over a wide range of potentials. On the capacity-potential curve based on determinations made in the direction from positive potentials to negative (after the electrode had been subjected to powerful anodic polarization), a high

* We give results of measurements of the capacity of electrodes in presence of additions of tannin, alizarin, and phenol for an equivalent scheme of series connection of capacity and resistance, because the phase shift is appreciably greater than 45° in these cases, so that the values of capacities corresponding to the series scheme (C_1) differ little from the values corresponding to the parallel scheme (C_2).

** This maximum is observed for cathodic polarization and is therefore not associated with the anodic oxidation of phenol.

*** These effects of raising the overvoltage are observed when alkaline solutions containing the additives are prepared several days before the beginning of the experiment (tannin) or when polarization experiments have already been carried out in the given solution (alizarin); in the case of freshly prepared solutions effects of enhanced overvoltage are insignificant (less than 40 mv). It would appear that products formed in the slow processes of polymerization or oxidation of the additives in alkaline solutions can have a great effect on overvoltage.

maximum is observed (Fig. 5, Curve 3') in approximately the same range of potentials as on the capacity curve obtained in absence of arsenic.

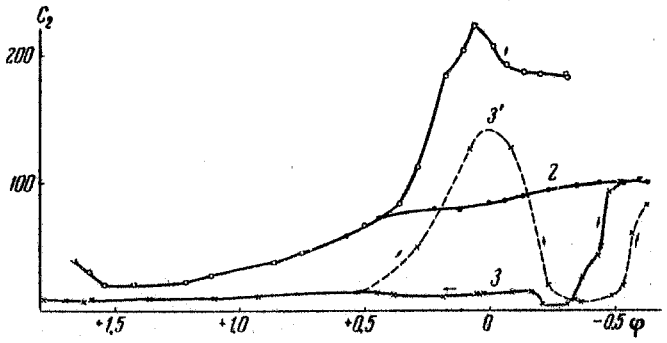

Fig. 5. Effect of $NaAsO_2$ on the capacity of the electrode; 1) 2 N NaOH; 2) 2 N NaOH + 0.002 M $NaAsO_2$; 3) and 3') 2 N NaOH + 0.2 M $NaAsO_2$.

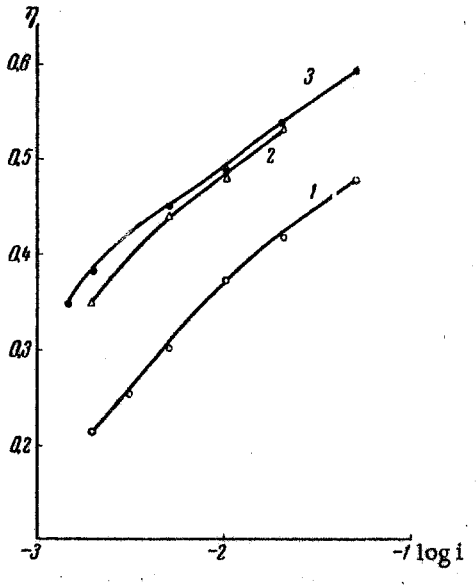

Fig. 6. Effect of $NaAsO_2$ on hydrogen overvoltage: 1) 2 N NaOH: 2) 2 N NaOH + 0.002 M $NaAsO_2$; 3) 2N NaOH + 0.2 M $NaAsO_2$.

This maximum probably indicates partial desorption of arsenic from the strongly oxidized surface of the iron electrode. In fact, the sharp fall in capacity after the maximum on Curve 3' is observed only for cathodic polarization when potentials ranging from − 0.1 to − 0.2 v are attained, i.e. adsorption of arsenic occurs only after partial reduction of the surface oxides. In solutions to which only a small amount of arsenic (0.002 M) has been added, no sharp fall in capacity is observed, although the capacity in the potential range of − 0.3 to + 0.2 v is still reduced to almost one-half of its value in pure sodium hydroxide solution. Figure 6 gives hydrogen-overvoltage curves for solutions with the same additions of arsenic. It will be seen that addition of very small amounts of $NaAsO_2$ (0.002 M) raises the hydrogen overvoltage by about 100 mv and further increase in the concentration of arsenic has almost no effect on the overvoltage. We must mention that, at potentials corresponding to powerful cathodic polarization, evolution of hydrogen at the electrode is accompanied by partial reduction of AsO_2^- ions to As.

The question naturally arises of whether the above-described raising of hydrogen overvoltage and reduction in the capacity of the electrode is not associated with the appearance of a surface layer of reduced arsenic covering much of the iron surface and whether the measured values of capacity and overvoltage are not really to be attributed to the arsenic, rather than to the iron electrode. It is difficult to solve this question finally on the basis of our results. However, the fact that, even with prolonged cathodic polarization at a high current density at potentials ranging from − 0.5 to − 0.6 v, the capacity of the electrode is not reduced, whereas at somewhat higher potentials the capacity falls to approximately one-tenth of its original value, indicates that this reduction in capacity is due mainly not to the formation of a layer of reduced arsenic, but to some other effect, e.g. the formation of an adsorptional surface compound of arsenic with iron oxides. Thus, according to the literature [6], hydrated ferric oxide is capable of absorbing arsenious oxide from solution and the process has the character of reversible adsorption.

DISCUSSION OF RESULTS

This investigation has shown that additions of various typical ionic and nonionic surface-active compounds (tetrabutylammonium sulfate, naphthalenesulfonic acid, hexanoic acid, octyl alcohol) have little effect on the hydrogen overvoltage at an iron electrode in alkaline solutions and do not reduce the capacity of the electrode appreciably; these substances are apparently not adsorbed on an iron surface under the given conditions. On the other hand, additions of substances such as tannin, alizarin, phenol, and arsenious oxide raise the hydrogen overvoltage somewhat (except in the case of phenol) and greatly reduce the capacity of the iron electrode at negative potentials (from + 0.1 to − 0.4 v); at more positive potentials these additions (apart from arsenic) have almost no effect on the capacity of the electrode. Hence, these additions are adsorbed strongly at negative potentials and are desorbed at more positive potentials. The common characteristic determining the chemical properties of the organic additives (tannin, alizarin, and phenol) is the presence of hydroxy groups of the phenolic type. In alkaline solutions these compounds dissociate to a greater or lesser extent with formation of the corresponding anions. Numerous data in the literature [7] show that these compounds readily react in the form of the ion with hydrated metal oxides, and in particular iron oxides, with formation of insoluble adsorption compounds. For example, in the interaction of alizarin with hydrated ferric oxide it may be supposed that the process proceeds as follows:

$$Fe(OH)_3 + NaAz \rightarrow Fe\begin{matrix}OH\\ \\ Az\end{matrix} + NaOH.$$

The resulting molecule of the alizarin compound of iron appears to remain attached to the surface oxide, i.e. a new phase compound is not formed, but an adsorption compound is produced. It is known [8], moreover, that the surface of a smooth iron electrode in an alkaline solution is always more or less oxidized; under these conditions even prolonged cathodic polarization at high current density will not succeed in reducing the iron surface completely. It is therefore very probable that the mechanism of the adsorption of tannin, alizarin, and phenol at an iron electrode also consists in the chemical interaction of the hydroxy groups of these compounds or the corresponding anions with surface oxides of the iron.

We express our indebtedness to S. D. Levina for valuable advice, which was of great help to us in carrying out this work.

SUMMARY

1. The effects of various surface-active additives on the electrochemical behavior of an iron electrode in 2 N NaOH were investigated with the aid of measurements of capacity in an alternating current and of determinations of polarization curves.

2. Octyl alcohol molecules and tetrabutylammonium, naphthalenesulfonate, and hexanoate ions do not reduce the capacity of an iron electrode and have little effect on the hydrogen overvoltage; these species, therefore, are not adsorbed appreciably on the iron surface.

3. Compounds that are able to react chemically with ions or oxides of iron (tannin, alizarin, arsenious oxide, and to a lesser extent phenol) greatly reduce the capacity of an iron electrode at potentials more negative than the stationary potential, and they also raise the hydrogen overvoltage to some extent; this indicates that these compounds are adsorbed at the slightly oxidized iron surface. At potentials that are more positive than the stationary potential, these additives (with the exception of arsenic) have no effect on the capacity and are probably desorbed from the iron surface.

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