POTENTIAL OF ZERO CHARGE OF IRON

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It was shown in [1] that, in the case of polished iron with a surface free from oxide, in dilute solutions of nonsurfactive electrolytes, the C, φ curves showed minima, reflecting a change in the diffusivity of the double layer with potential. According to the position of this minimum we determined the zero-charge potential (z.c.p.), equal to −0.7 V (normal hydrogen electrode). Because the preliminary cathodic reduction of the iron surface, to remove oxide, was carried out in 0.03 N H_2SO_4, it might be feared that the stated value of the z.c.p. referred to hydrogenated iron.

In order to determine the z.c.p. of iron free from oxides and adsorbed hydrogen, we carried out measurements on a renewable surface, obtained by cutting a thin layer of metal with a ruby cutter, immediately before the measurements in the working solution [2]. The measuring apparatus, described in [3], made it possible, at fixed frequency, rapidly (in less than a minute) to record the curve relating $1/\omega C$ and φ .

Measurements, in dilute solutions of sodium sulfate, showed that the C, φ curves registered a minimum, which deepened with dilution. The potential of the minimum in 0.01 N Na_2SO_4 solution was equal to −0.73 V, which coincided with the values obtained in [1]. The measurements were carried out at frequencies of 20 and 200 Hz. Considering that the method of rapid measurements, on a freshly renewed surface, as opposed to the method of [1], makes it possible to carry out measurements in nonacidified solutions, we performed some measurements in dilute potassium fluoride solutions. In this case the minimum of the C, φ curve was found at a potential of −0.7 V.

Comparison of the data obtained with dilute solutions of Na_2SO_4 and KF showed that in the case of iron, as with other metals [4] in an asymmetric electrolyte, there was a shift in the potential minimum characterizing the diffusivity of the double layer. The results enabled us to conclude that the sulfate ion, like the fluoride ion, on iron did not give rise to any significant surface activity.

The measurements carried out in solutions of potassium chloride indicated the specificity of the adsorption of chloride ion on iron. The shift of the potential minimum in 0.004 N KCl, relative to the value of 0.004 N KF, amounted to about 90 mV.

With measurements on a freshly renewed surface, as in the case of [1], we observed a considerable effect of preliminary residence of the electrode in the vicinity of the stationary potential. Thus, a capacity minimum was not observed in repeat (without renewal of the surface) measurements at an electrode which had been held at $\varphi = -0.5$ V for 3 min. Reduction of this electrode, by cathodic polarization in the same solution, did not lead to the appearance of a minimum.

Our measurements supported the view that determination of the zero-charge potential of iron could be achieved only on an iron surface free from oxides. In our view, the data obtained can serve as additional confirmation of the conclusion that the z.c.p. of iron is close to −0.7 V (relative to a hydrogen electrode) and relates to a nonhydrogenated electrode.

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