Physical Chemistry

TSA CHUAN-SIN and Z. A. IOFA

1960

SovietRxiv

Abstract

Full Text

Physical Chemistry

TSA CHUAN-SIN and Z. A. IOFA

INVESTIGATION OF THE ADSORPTION OF SURFACE-ACTIVE IONS ON A ZINC ELECTRODE BY THE METHOD OF MEASURING DIFFERENTIAL CAPACITANCE

(Presented by Academician A. N. Frumkin, 17 XI 1959)

T. I. Borisova, B. V. Ershler, and A. N. Frumkin ([1]) were the first to use the method of measuring the differential capacitance of the electrical double layer to determine the potential of zero charge $\varphi_{\varepsilon=0}$ on electrodes of solid metals (Pb, Tl, Cd). They showed that the curves of the dependence of the capacitance C on potential, obtained on these metals, are in many respects similar to the well-known C, φ curves for the mercury electrode. The method of measuring C, φ curves was used to determine the value of $\varphi_{\varepsilon=0}$ and to study adsorption on Fe ([2]), PbO_2 ([3]), Zn ([4]), and other metals ([5]).

On solid metals, a complication is the circumstance that the capacitance depends on the frequency of the alternating current used for the measurement (capacitance dispersion). Proceeding from the fact that the dispersion of capacitance with frequency decreases after smoothing the surface of a metal, for example on a fused metal ([1]) and on the face of a single crystal ([6]), it was suggested that the numerous microcracks present on the surface of a polycrystalline metal screen part of the surface as the frequency of the alternating current increases ([2]). Part of the electrode surface actually ceases to participate in the process, which is the reason for the decrease in capacitance at high frequencies. A different interpretation was given by Bockris and Conway ([7]), who explained the appearance of capacitance dispersion by the slowness of relaxation of water molecules on the surface of a solid electrode.

The aim of the present work is to investigate the structure of the electrical double layer on a zinc electrode by the method of measuring differential capacitance.

B. S. Krasikov and V. V. Sysoeva ([4]) measured the capacitance on a zinc electrode in order to determine $\varphi_{\varepsilon=0}$. We, however, under no conditions were able to attain a potential lying near the value indicated by these authors, $\varphi_{\varepsilon=0} = -0.63$ V (the normal potential of the zinc electrode $\varphi^0_{Zn} = -0.76$ V), since when the negative potential is decreased even to -0.85 V, dissolution of zinc and the appearance of anodic current begin. Therefore, those works in which the potential

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

of zero charge of zinc in aqueous solutions is allegedly reached are open to doubt. From data on the measurement of electrocapillary curves in molten salts at high temperatures ([8]), $\varphi_{\varepsilon=0}$ can be found indirectly, by assuming constant the potential difference at the maxima of the electrocapillary curves for the same metal in a melt and in an aqueous solution. From these data, for zinc $\varphi_{\varepsilon=0} \approx -0.65$ V.

We measured the capacitance with the aid of an ordinary bridge for impedance measurement. The electrode under study was prepared by etching a single crystal of spectrally pure zinc in a thin glass, hard-melting tube (with an internal diameter of 0.4-0.5 mm) so that the plane

···of the abscissa was parallel to the axis of the thin wire obtained in this way. The area of the part of the electrode immersed in the solution was determined with the aid of a microscope.

As can be seen from Fig. 1 (curves 1 and 2), which shows the dependence of the differential capacitance on the frequency of the alternating current, the dispersion of the capacitance on monocrystalline zinc in solutions of medium concentration (0.2-1.0 N KCl) is insignificant over a large frequency interval: the capacitance value in the range from 0.4 to 10 kHz changed by only 5-8%. In dilute solutions the dispersion is considerably greater; however, in this case, as we were able to establish, it arises because of the parasitic capacitance of the bridge to ground, since after a compensating capacitor was introduced into the bridge circuit by the method described by B. B. Damaskin (9), the curve of the capacitance-frequency dependence for 0.01 N KCl at $\varphi = -1.22$ V was substantially corrected. Such a correction, however, could be carried out only when the resistance in the cell did not exceed 100 Ω. In 0.001 N KCl ($R = 5000$ Ω), when the circuit was corrected by the indicated method, a satisfactory result was not obtained. The influence of the state of the metal surface on the dispersion of capacitance with frequency is seen by comparing curve 5, taken on polycrystalline zinc, with curve 1 (Fig. 1).

Fig. 1. Curves of the dependence of the double-layer capacitance of monocrystalline zinc on the frequency of the alternating current at $\varphi = -1.22$ V in solutions of 1.0 N KCl (1); 0.2 N KCl (2); 1.0 N KCl (3) on polycrystalline zinc

Fig. 2. Curves of the differential capacitance of the double layer in 0.1 N KCl on electrodes made of: 1—Zn, 2—Ga, 3—Hg (frequency 10 kHz)

Fig. 3. Curves of the differential capacitance on monocrystalline zinc. A—in

Fig. 3

Figure 3: Fig. 3

solutions of 0.5 N KCl (1); 0.5 N KJ (2); 0.5 N KCl + $2.4 \cdot 10^{-4}$ N $N(C_4H_9)_4^+$ (3); 0.5 N KJ + $2.4 \cdot 10^{-4}$ N $N(C_4H_9)_4^+$ (4). B—in solutions of 1.0 N KCl (1); 1.0 N KCl + 0.001 N $N(C_4H_9)_4^+$ (2) (frequency 10 kHz)

In Fig. 2, curve 1 gives the dependence of C on φ, obtained on monocrystalline zinc in 0.1 N KCl. In the same figure, for comparison, the curves for Hg and Ga in the same solution are given according to the data of Grahame (10). In their form all three curves are similar to one another, especially if they are shifted along the abscissa axis so that their minima coincide. They differ in that the rise of the branches from the minimum for Ga and Zn is steeper than for Hg. It could be assumed that the rise of the C, φ curve for zinc with decreasing cathodic poten-

is caused by the appearance of a pseudocapacitance as the potential approaches the normal potential of the metal. However, a simple calculation shows that the value of the pseudocapacitance at the potentials at which the curve rises is still insignificant.* It is evident that the rise of the positive branch of curve 1 in Fig. 2 is caused by adsorption of chloride anions.

Figure 3A gives the C, φ curves for a zinc electrode in solutions containing surface-active ions. The general form of these curves resembles the corresponding curves for mercury, which indicates a similar structure of the double layer on zinc and mercury. However, the difference between curves C, φ 1 and 2 in Fig. 3A is much smaller than between the corresponding curves on mercury ([12]), which is evidently associated with the lower adsorbability of J^- on zinc. It should be noted that the instability constant of halide complexes with mercury is considerably smaller than that of complexes with zinc, and the difference in the magnitude of these constants for Cl^- and J^- is considerably smaller in the case of zinc than in the case of mercury ([13]).

Fig. 4. Curves of hydrogen overvoltage on monocrystalline zinc in solutions of $0.5\,N$ HCl + $0.5\,N$ KCl (1); $0.5\,N$ HCl + $0.5\,N$ KJ (2); $0.5\,N$ HCl + $0.5\,N$ KCl + $4 \cdot 10^{-4}\,N$ $N(C_4H_9)_4^+$ (3); $0.5\,N$ HCl + $0.5\,N$ KJ + $4 \cdot 10^{-4}\,N$ $N(C_4H_9)_4^+$ (4)

Organic cations $N(C_4H_9)_4^+$, as is seen from Fig. 3A, are strongly adsorbed on zinc. Their desorption, as in the case of the mercury electrode, occurs upon attainment of a fairly negative potential ($\varphi = -1.58$ V), but on the curves for the zinc electrode no desorption peak is observed (see Fig. 3B). The absence of a desorption peak for the cations $N(C_4H_9)_4^+$ indicates a much slower establishment of adsorption equilibrium on zinc than on mercury. The desorption potential of

the cations $N(C_4H_9)_4^+$ on zinc, judging from the C, φ curve recorded in $1\,N$ KCl+ $0.001\,N$ $N(C_4H_9)_4^+$ (Fig. 3B), and the desorption peak on the curve recorded on mercury in the same solution ([14]), lie at approximately the same potentials with respect to $\varphi_{\varepsilon=0}$ of the corresponding metal. Thus, on the mercury electrode the desorption peak in $1\,N$ KCl + $0.001\,N$ $N(C_4H_9)_4^+$ lies at -1.28 V, $\varphi_{\varepsilon=0} = -0.28$ V, the difference being -1.0 V. For the zinc electrode the potential of complete desorption lies at -1.58 V, $\varphi_{\varepsilon=0} = -0.65$ V, the difference being -0.93 V.

Figure 4 gives the curves of the dependence of hydrogen overvoltage on the logarithm of the current density on monocrystalline zinc in solutions containing surface-active ions. These curves, like the capacitance curves, are similar to the corresponding curves obtained on a mercury electrode. Adsorption of iodide anions lowers the overvoltage, but, judging from the $\eta, \lg i$ curves, as from the C, φ curves, the effect on zinc is smaller than on a mercury electrode ([15]). A decrease in the overvoltage during hydrogen evolution due to adsorption of Cl^- and Br^- ions was also observed by Ya. V. Durdin and E. G. Tsvetarnyi on an amalgamated zinc cathode ([16]). From Fig. 4 it is seen that the cations $N(C_4H_9)_4^+$, as on mercury, strongly–

---

* The magnitude of the pseudocapacitance was calculated by formula (11)

$$C_n = \frac{n^2 F^2 D^{1/2} c}{RT\sqrt{\omega}},$$

taking $n = 2$, $F = 10^5 \frac{\text{coulomb}}{\text{mol}}$, $R = 8.3 \frac{\text{joule}}{\text{mol}}$, $D = 10^{-5}$ cm^2/sec, $\omega = 10000 \cdot 2\pi$. At $E = -0.76$ V, with $c = 10^{-3}$ mol/cm^3, $C = 2 \cdot 10^5$ $\mu\mu$F/cm^2; at $E = -0.88$ V, with $c = 10^{-7}$ mol/cm^3, $C = 20$ $\mu\mu$F/cm^2; at $E = -0.91$ V, with $c = 10^{-8}$ mol/cm^3, $C = 2$ $\mu\mu$F/cm^2. Since all capacitance measurements referred to potentials more negative than -0.91 V, the pseudocapacitance in our experiments was therefore less than 2 $\mu\mu$F/cm^2.

but they increase the hydrogen overvoltage on zinc. Unfortunately, we did not succeed in reaching the desorption potential of these cations while measuring the overvoltage. In the joint presence of $N(C_4H_9)_4^+$ and J^- anions, the η, $\lg i$ curves occupy an intermediate position between curves 2 and 3 in Fig. 4. With decreasing negative potential, adsorption of the J^- anions increases and the overvoltage decreases. The effect associated with the mutual enhancement of adsorption, observed in the case of the mercury cathode [15], was not found on zinc in the potential region studied.

We express our gratitude to Academician A. N. Frumkin for his attention and advice during the performance of this work.

Moscow State University
named after M. V. Lomonosov

Received
16 XI 1959

REFERENCES

1. T. I. Borisova, B. V. Ershler, A. N. Frumkin, ZhFKh, **22**, 925 (1948); **24**, 337 (1950).

2. E. O. Ayazyan, DAN, **100**, 473 (1955); V. V. Losev, DAN, **88**, 499 (1953).

3. B. N. Kabanov, I. G. Kiseleva, D. I. Leikis, DAN, **99**, 808 (1954).

4. B. S. Krasikov, V. V. Sysoeva, DAN, **114**, 826 (1957).

5. V. L. Kheifets, B. S. Krasikov, DAN, **109**, 586 (1956); ZhFKh, **31**, 1992 (1957).

6. D. I. Leikis, B. N. Kabanov, Tr. Inst. fiz. khim. AN SSSR, no. 6 (1957).

7. J. O' Bockris, B. E. Conway, J. Chem. Phys., **28**, 707 (1958).

8. S. Karpachev, A. Stromberg, ZhFKh, **18**, 47 (1944).

9. B. B. Damaskin, ZhFKh, **32**, 2199 (1958).

10. D. C. Graham, Tr. 4th Conference on Electrochemistry, Publishing House of the USSR Academy of Sciences, Ann. Chem., **30**, 1736 (1958).

11. A. N. Frumkin, V. S. Bagotskii et al., *Kinetics of Electrode Processes*, Moscow, 1952.

12. A. N. Frumkin, B. B. Damaskin, N. V. Nikolaeva-Fedorovich, DAN, **115**, 751 (1957).

13. K. B. Yatsimirskii, V. P. Vasil' ev, *Instability Constants of Complex Compounds*, Publishing House of the USSR Academy of Sciences, 1959.

14. B. B. Damaskin, Dissertation, Moscow State University, 1959.

15. Tza Chuan-sin, Z. A. Iofa, DAN, **125**, 1065 (1959).

16. Ya. V. Durdin, E. G. Tsventarnyi, Vestn. Leningr. Univ., No. 10, 119.

Note: Figure translations are in progress. See original paper for figures.