Soviet-era science, translated into English

PHYSICAL CHEMISTRY

B. B. DAMASKIN, E. SHVARTS, and Academician A. N. FRUMKIN

1961

SovietRxiv

View the original and related papers at https://sovietrxiv.org/items/ru-196101.88310

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

PHYSICAL CHEMISTRY

B. B. DAMASKIN, E. SHVARTS, and Academician A. N. FRUMKIN

ON DIFFERENTIAL CAPACITANCE CURVES IN SOLUTIONS OF $K_4Fe(CN)_6$

Curves of the dependence of the differential capacitance C on the electrode potential φ in the presence of various singly and doubly charged anions were studied in works ($^{1-4}$), and it was shown that the hump on the C–φ curves at potentials anodic to the point of zero charge (p.z.c.) depends strongly on the nature of the anion. It was of interest to study the influence on the shape of the C–φ curve of the adsorption of the multicharged anion $Fe(CN)_6^{4-}$.

Fig. 1. Differential-capacitance curves in solutions of $K_4Fe(CN)_6$.
1 –1 N; 2 –0.1 N; 3 –0.01 N; 4 –0.001 N; 400 cps, 25°

For this purpose, using an impedance bridge, the circuit of which is described in work (^{5}), we measured C–φ curves on a dropping mercury electrode in 1; 0.1; 0.01; 0.001 N solutions of $K_4Fe(CN)_6$ at 25°. The data obtained are shown in Fig. 1. As can be seen from the figure, at negative surface charges the shape of the C–φ curves resembles analogous curves obtained in NaF solutions (^{6}): in dilute solutions, near the p.z.c., the C–φ curve has a distinctly expressed minimum associated with the diffuse structure of the double layer, and with a further increase in the negative polarization the capacitance passes through a shallow maximum at $\varphi \simeq -0.75$ V (n.c.e.). However, when the potential is changed toward positive surface charges, a sharp, almost vertical rise in capacitance is observed on the C–φ curve near the p.z.c., followed by a characteristic maximum (hump), which is noticeably higher and narrower than the analogous maxima in solutions containing other anions. Such a form of the C–φ curve was not observed in the presence of other previously studied anions ($^{1-4}$) and requires more detailed consideration.

By the Grahame method (^{6}), from the differential-capacitance data in 1 N $K_4Fe(CN)_6$, we calculated the C–φ curves in 0.1; 0.01 and 0.001 N solutions.

$K_4Fe(CN)_6$, proceeding from the assumption that the anion $Fe(CN)_6^{4-}$ is not specifically adsorbed on mercury and that the p.z.c. in all solutions is equal to

SovietRxiv

Fig. 2. Differential-capacitance curves in 0.01 N K4Fe(CN)6 solution. 1 —experiment, 2 —calculation

Figure 2: Fig. 2. Differential-capacitance curves in 0.01 N K4Fe(CN)6 solution. 1 —experiment, 2 —calculation

−0.473 V (n.c.e.), i.e., is equal to the p.z.c. in NaF solutions (6)*. The calculated and experimental curves for a 0.01 *N* solution of $K_4Fe(CN)_6$ are shown in Fig. 2. It is evident from the figure that the displacement of the minimum on the $C-\varphi$ curve from the p.z.c. is the same for the experimental and calculated curves and, consequently, is caused by the asymmetrical valence type of the salt $K_4Fe(CN)_6$, and not by specific adsorption of the anion $Fe(CN)_6^{4-}$ at the p.z.c. Moreover, at φ more negative than −0.65 V (n.c.e.) the experimental and calculated curves practically coincide. On the other hand, at positive surface charges the calculation, based on the assumption of the absence of specific adsorption, differs considerably from the experimental capacitance values. Thus, we come to the conclusion that at positive surface charges the anion $Fe(CN)_6^{4-}$ possesses appreciable specific adsorbability on the mercury surface, whereas on passing to negative surface charges desorption of this anion occurs, accompanied by a sharp drop in capacitance. The coincidence of the descending branch on the calculated and experimental $C-\varphi$ curves indicates that the sharp desorption of the anion $Fe(CN)_6^{4-}$ from the mercury surface is determined mainly by the electrostatic interaction of the multicharged anion with the mercury surface.

Fig. 2. Differential-capacitance curves in a 0.01 *N* solution of $K_4Fe(CN)_6$. 1 —experiment, 2 —calculation

A characteristic feature of the data obtained by us in a 1 *N* solution of $K_4Fe(CN)_6$ is the relatively high value of the capacitance at the maximum on the $C-\varphi$ curve ($C_m = 59.0\,\mu F/cm^2$, whereas in 1 *N* KCl $C_m = 43.2\,\mu F/cm^2$), and also the presence, at the potentials of the maximum, of a polarization resistance equal to $0.31\,\Omega \cdot cm^2$. According to the Watts-Tobin theory (9), the hump on the $C-\varphi$ curves is connected with a maximum in the effective dielectric constant of the layer of adsorbed water dipoles. This theory does not consider the influence of specific adsorption of anions on changes in the orientation of water dipoles, and the absence of a hump on the $C-\varphi$ curves in KOH and K_2CO_3 solutions (2) is explained, by analogy with KJ solutions, by a sharp rise in capacitance, which—

* It should be noted that the p.z.c. in a 1 *N* solution of $K_4Fe(CN)_6$ cannot be determined by the method of reverse integration (7), since the negative branch of the $C-\varphi$ curve in 1 *N* $K_4Fe(CN)_6$ lies somewhat lower than in 1 *N* KCl. This result is apparently connected with a decrease in the activity of K^+ cations due to the reaction $K^+ + Fe(CN)_6^{4-} = KFe(CN)_6^{3-}$ at high concentration of $K_4Fe(CN)_6$, and not with destruction of the complex $H_2O + K_4Fe(CN)_6 = K_3Fe(CN)_5 \cdot (H_2O) + KCN$ (8), since with the appearance of CN^- ions one would expect a rise on the $C-\varphi$ curve at substantially more negative potentials

Fig. 3. Curves of integral capacitance in 0.1 N K4Fe(CN)6 solution at temperatures: 1 –0°; 2 –25°; 3 –50°; 400 Hz

Figure 3: Fig. 3. Curves of integral capacitance in 0.1 N K4Fe(CN)6 solution at temperatures: 1 –0°; 2 –25°; 3 –50°; 400 Hz

(4).

masks the hump and is due to strong specific adsorption of the anions OH^- and CO_3^{2-}, comparable with the adsorption of the anion J^-. It is difficult to agree with this explanation, since adsorption of OH^- and CO_3^{2-} ions, unlike J^-, does not lead to a shift of the p.z.c. in the negative direction (^{2}). Moreover, according to (^{9}), one would have to expect the absence of a hump in solutions of $K_4Fe(CN)_6$, since adsorption of the anion $Fe(CN)_6^{4-}$ leads to a sharp increase in capacitance; however, this does not correspond to the experimental data (Fig. 1).

Fig. 3. Curves of integral capacitance in 0.1 *N* $K_4Fe(CN)_6$ solution at temperatures: **1** –0°; **2** –25°; **3** –50°; 400 Hz

Finally, theory (^{9}) does not make it possible, without additional assumptions, to explain the appearance of polarization resistance at the potentials of the hump on the C–φ curves.

In the general case, the presence of a hump on the C–φ curves is determined by a negative value of $\partial C/\partial\varphi$. If ε is the charge of the electrode; φ_a is the potential measured from the p.z.c. in the given solution; ξ is the potential of the zero point corresponding to that orientation of the water dipoles which exists at the given potential φ_a ($\xi = f(\varphi_a)$), and K_0 is the true integral capacitance, determined by the relation $\varepsilon = K_0(\varphi_a - \xi)$, then the differential capacitance C and the formal integral capacitance K can be expressed by the following equations:

$$C = \frac{\partial\varepsilon}{\partial\varphi} = \frac{\partial K_0}{\partial\varphi}(\varphi_a - \xi) + K_0\left(1 - \frac{\partial\xi}{\partial\varphi}\right), \tag{1}$$

$$K = \frac{\varepsilon}{\varphi_a} = K_0\left(1 - \frac{\xi}{\varphi_a}\right), \tag{2}$$

whence

$$\frac{\partial C}{\partial\varphi} = 2\frac{\partial K_0}{\partial\varphi}\left(1 - \frac{\partial\xi}{\partial\varphi}\right) + \frac{\partial^2 K_0}{\partial\varphi^2}(\varphi_a - \xi) - K_0\frac{\partial^2\xi}{\partial\varphi^2}, \tag{3}$$

$$\frac{\partial K}{\partial\varphi} = \frac{\partial K_0}{\partial\varphi}\left(1 - \frac{\xi}{\varphi_a}\right) + \frac{K_0}{\varphi_a^2}\xi - \frac{K_0}{\varphi_a}\frac{\partial\xi}{\partial\varphi}. \tag{4}$$

SovietRxiv

It is natural to assume that $\partial K_0/\partial\varphi \geqslant 0$, and also $|\xi/\varphi_a| < 1$ and $|\partial\xi/\partial\varphi| \ll 1$. Under these conditions, as is evident from equation (3), the appearance of a region in which $\partial C/\partial\varphi < 0$ can be explained either by a negative value of $\partial^2 K_0/\partial\varphi^2$, or by a positive value of $\partial^2\xi/\partial\varphi^2$.

As is seen from Fig. 3, in a $0.1\,N$ solution of $K_4Fe(CN)_6$ at 0° a maximum is also observed on the $K{-}\varepsilon$ curve, i.e., in this case there exists a region where $\partial K/\partial\varphi < 0$. According to equation (4), this result indicates that either $\xi < 0$ at $\varphi_a > 0$, or $\partial\xi/\partial\varphi > 0$. The first possibility was considered by Watts-Tobin[9], according to whom, for a negative value of $\partial C/\partial\varphi$ to arise, the principal role is played by the term with $\partial^2 K_0/\partial\varphi^2 < 0$, and, apparently, by a positive value of $\partial^2\xi/\partial\varphi^2$ at $\xi < 0$, corresponding to the completion of the reorientation of water molecules. Another possible interpretation of the humps on the $C{-}\varphi$ and $K{-}\varepsilon$ curves is based on the assumption of orientation of the water dipoles with the negative end toward the mercury surface at the p.z.c. and of a change in this orientation when anions possessing sufficient polarizing ability enter the dense double layer. In this case, at $\varphi_a > 0$ the quantities ξ, $\partial\xi/\partial\varphi$, and $\partial^2\xi/\partial\varphi^2$ are positive, and the latter quantity plays the principal role in the appearance of a region with a negative value of $\partial C/\partial\varphi$ (see equation (3)). The height and shape of the hump on the $C{-}\varphi$ curves under these conditions will depend on the adsorbability of the anion and its polarizing ability (hydration).

The anion $Fe(CN)_6^{4-}$ is strongly hydrated, and its adsorbability, as we have shown, increases sharply on passing to positive surface charges. Therefore one should expect a sharp change in the orientation of the adsorbed water dipoles when $Fe(CN)_6^{4-}$ anions enter the double layer. Thus, the experimental data obtained by us in $1N$ $K_4Fe(CN)_6$ are in better agreement with the second variant of the interpretation of the hump on the $C{-}\varphi$ curves. Indeed, the sharp change in the orientation of adsorbed water dipoles determines the high and relatively narrow maximum on the $C{-}\varphi$ curve, while the polarization resistance observed at these same potentials corresponds to the process of restructuring of the double layer upon entry into it of $Fe(CN)_6^{4-}$ anions. The second variant of the interpretation of humps on $C{-}\varphi$ curves in the presence of various anions has been considered by us in greater detail in work[10].

Moscow State University
named after M. V. Lomonosov

Received
27 VI 1961

REFERENCES

[1] M. A. Vorsina, A. N. Frumkin, ZhFKh, **19**, 171 (1945).
[2] D. C. Grahame, M. A. Poth, J. I. Cummings, J. Am. Chem. Soc., **74**, 4422 (1952).
[3] A. Watanabe, F. Tsuji, S. Ueda, Bull. Inst. Chem. Res. Kyoto Univ., **34**, 1, 65 (1956).

[4] G. C. Barker, R. L. Faircloth, *Advances in Polarography*, 1, Oxford, 1960, p. 313.
[5] B. B. Damaskin, ZhFKh, **32**, 2199 (1958).
[6] D. C. Grahame, J. Am. Chem. Soc., **76**, 4819 (1954).
[7] D. C. Grahame, E. M. Coffin, J. I. Cummings, M. A. Poth, J. Am. Chem. Soc., **74**, 1207 (1952).
[8] W. L. Reynolds, R. H. Lumry, J. Chem. Phys., **23**, 2460 (1955).
[9] R. J. Watts-Tobin, *Phils. Mag.*, **6**, No. 61, 133 (1961).
[10] E. Shvarts, B. B. Damaskin, A. N. Frumkin, ZhFKh (in press).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.