7. We have discussed ways to influence the electrical interaction between charged species at the interface. But in the case of chemisorbed ions or adatoms on metals, there is a contribution from indirect exchange interaction via the substrate electrons in addition to the electrostatic contribution [6, 7]. By comparison with estimates for indirect interaction on simple metals which are available in the literature [6], one can see that electrostatic interaction will be dominant in certain regions. In addition, a nontrivial dependence of interaction on the value of ε_2 seems to arise only in the electrostatic contribution. In metals for which the tight-binding approximation can be used, indirect interaction is falling off exponentially with distance [7], and can be neglected at large distances. It must be noted, however, that the screening model used [1] may not work well for these metals.

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ADSORPTION OF CYANIDE IONS ON SILVER. THE EFFECT OF ADSORPTION ON DOUBLE-LAYER CAPACITY AND ON THE POTENTIAL OF ZERO CHARGE

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In the literature dealing with the behavior of silver in cyanide electrolytes [1, 2], it is stressed that interaction of the silver surface with the cyanide ions has a strong effect on the kinetics of electrodeposition and on the quality of the cathodic deposits. Certain special features of the electrochemical processes in cyanide silver-plating baths are attributed to this phenomenon; the behavior observed is explained in terms of the adsorption of CN^- ions [2-4]. But cyanide adsorption has not been studied quantitatively on silver. We made an attempt, therefore, to study this effect by measuring electrode impedance. In the present work we examine the effect of CN^- ion adsorption on the differential capacity and zero-charge potential of silver electrodes.

The studies were performed in aqueous 1 M Na_2SO_4 solution to which NaCN was added in amounts between $1.1 \cdot 10^{-5}$ and $3.2 \cdot 10^{-3}$ mole/liter. The temperature was maintained at 20 ± 0.5°C. The solution pH was brought to a value of 12.3 ± 0.1 by NaOH addition; at this pH, practically all cyanide is present in the solution in the form of CN^- ions. Prior to the experiments, hydrogen obtained electrolytically was passed through the solution in order to remove oxygen.

The studies were performed with electrodes which, prior to each measurement, underwent surface renewal by means of the setup described in [5]. The resistive (R_a) and reactive (R_x)

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components of impedance were measured as series equivalents with the instrument described in [6]. The impedance measurements were made at fixed frequencies between 19 and 100,000 Hz while scanning the potential from −1.4 to −0.2 V (here and in the following, the potentials are stated relative to the normal hydrogen electrode) after each surface renewal. The results could be reproduced with a mean-square error of ±6%, which chiefly arose from surface area variations between cuts. The electrode's surface area was determined as in [7], and measured $6.5 \cdot 10^{-3}$ cm².

The parallel equivalent of capacitance, C_p, was calculated from the experimental impedance values via the relation

$$C_p = \frac{1}{\omega} \frac{R_x}{R_x^2 + (R_a - R_{el})^2}, \quad (1)$$

where ω is the angular frequency, and R_{el} is the electrolyte resistance found by extrapolating R_a to infinite frequency.

Figure 1 shows the current densities, i, as functions of electrode potential, φ, for sodium sulfate solutions without (curve 1) and with added cyanide (curve 2). Without cyanide, i is not over 10 μA/cm² over the potential range from +0.15 to −0.8 V, and is determined chiefly by the reduction of residual oxygen contained in the solution (in unpurged solutions, i reaches 200 μA/cm²). At $\varphi < -0.7$ V, hydrogen begins to be evolved on the electrode, which can be seen from the marked increase in current. It had been shown in [8] that in Na_2SO_4 solutions at frequencies between 1 and 10 kHz, C_p is frequency-independent at φ more positive than −1.5 V. We studied the wider range of frequencies from 25 to 20,000 Hz. But, even in this range we did not find any marked frequency dispersion of C_p at potentials more positive than −1.3 V. At φ more negative than −1.3 V, the current is higher than 1 mA/cm². Under these conditions, R_x is almost an order of magnitude smaller than R_a at the lowest frequencies (below 75 Hz), which makes an exact determination of C_p very difficult. For frequencies above 75 Hz and potentials more positive than −1.4 V, R_x and R_a are of comparable size, and C_p can be calculated quite accurately for this frequency range. The results of the calculations show that within the possible experimental errors, C_p does not depend on frequency. This means that pure resistances are a good approximation in the equivalent circuit of impedance for both oxygen reduction and hydrogen evolution.

The potential dependence of the current changes drastically at $\varphi > -0.35$ V when cyanide is added to the solution (curve 2). In this region the cathodic current becomes an anodic current, which is due to the dissolution of silver in cyanide. In NaCN-containing solutions, the steady potential chiefly depends on NaCN concentration (it becomes more negative as this increases). At $\varphi < -0.5$ V there is no important difference between the i vs. φ curves in solutions with and without NaCN. In this potential range, the currents recorded in the presence of cyanide ions can be somewhat higher or somewhat lower than those in the pure base electrolyte, depending on the degree of oxygen removal from the solution.

The impedance measurements at the silver electrodes in the presence of CN^- ions show that in this case, in contrast to the behavior of silver in Na_2SO_4 solution, C_p strongly depends on frequency. It was seen when examining the frequency dependence of C_p, that in the plots of C_p against $\sqrt{\omega}$ at $-0.6 \leq \varphi \leq -1.4$ V, a linear section can be distinguished in the low-frequency range ($\omega < 10^3$ sec^{-1}). According to Lorenz [9], such a relation between C_p and $\sqrt{\omega}$ will be found at low frequencies when the adsorption process is composed of an adsorption and a desorption step (accomplished in a single act) and of a step bringing the material to the electrode, the latter being rate-determining. In this case, one can determine the equilibrium capacity, C(0), by extrapolating the linear section to $\omega = 0$. Deviations from this model lead to nonlinearity of the C_p vs. $\sqrt{\omega}$ dependence. This behavior is found at potentials more positive than −0.6 V. The reasons for it can be diverse, and will be discussed in later papers. In the present paper, the experimental data are analyzed quantitatively in the potential range between −0.6 and −1.4 V.

The fact that the capacity values obtained by extrapolating the C_p vs. $\sqrt{\omega}$ plot to $\omega = 0$ correspond to the equilibrium value, C(0), can be tested as follows. According to [10], when the model of single-step adsorption is valid, the equilibrium capacity, C(0), is given by the sum: $C(0) = C_d + C_{11}$, where C_d is the capacity at infinite frequency, and C_{11} is the adsorption capacity. The elements of the equivalent network for the adsorption process, among them C_d and C_{11}, can be calculated from the frequency dependence of electrode impedance. Using a computer we calculated the elements of this network for several potentials by mini-

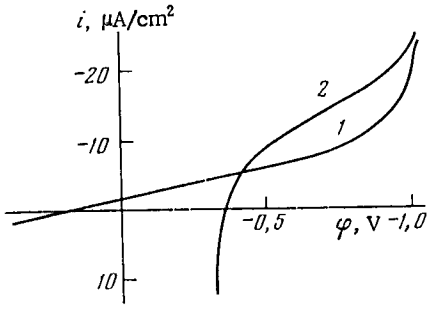

Fig. 1

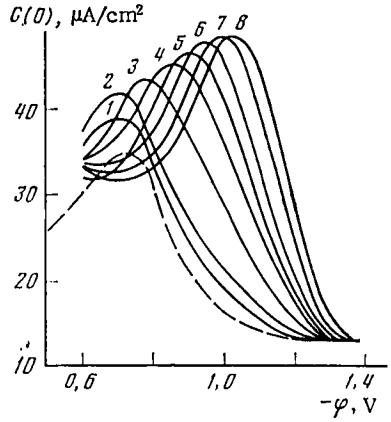

Fig. 2

Fig. 1. Current density i, as a function of potential, φ, of the silver electrode in 1 M Na_2SO_4 solution without NaCN (1) and with the addition of $3.2 \cdot 10^{-3}$ M NaCN (2).

Fig. 2. The equilibrium capacity, C(0), as a function of potential, φ, in 1 M Na_2SO_4 solutions without (the dashed line) and with NaCN additions: 1) $1.1 \cdot 10^{-5}$, 2) $4.3 \cdot 10^{-5}$, 3) $1.2 \cdot 10^{-4}$, 4) $3.1 \cdot 10^{-4}$, 5) $6.6 \cdot 10^{-4}$, 6) $1 \cdot 10^{-3}$, 7) $1.5 \cdot 10^{-3}$, and 8) $3.2 \cdot 10^{-3}$ M.

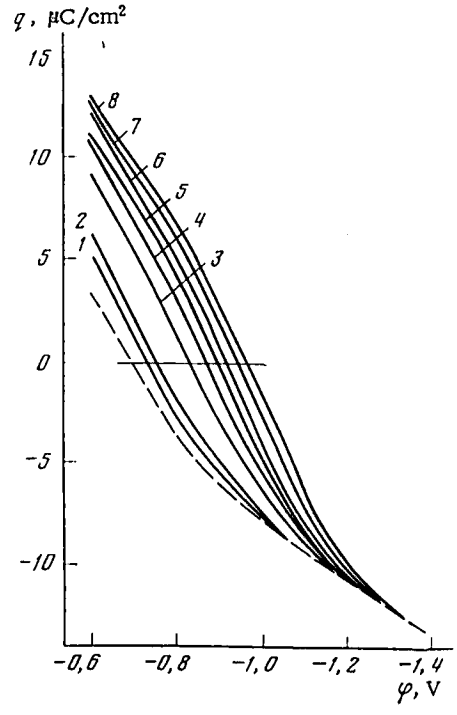

Fig. 3

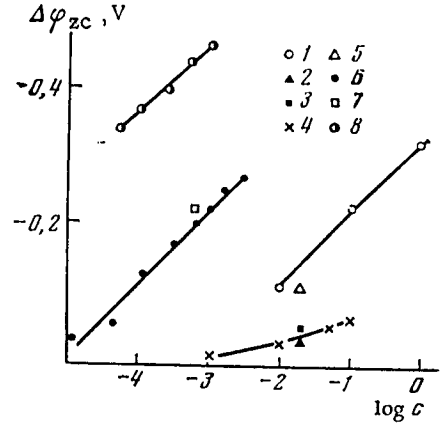

Fig. 4

Fig. 3. Electrode charge q, as a function of potential, φ, in 1 M Na_2SO_4 solutions containing NaCN. Numbering of the curves is the same as in Fig. 2.

Fig. 4. The shift, $\Delta\varphi_{zc}$, of the potential of zero charge as a function of the logarithm of concentration of surface-active materials, log c (in mole/liter). 1) Adsorption of CN^- ions on mercury; 2) to 8) adsorption of ions on silver: 2) CO_3^{2-}, 3) SO_3^{2-}, 4) Cl^-, 5) Br^-, 6) CN^-, 7) I^-, and 8) HS^-.

mizing, with Polyak's program [11], the root-mean-square deviations of the calculated impedance values from the experimental values. It was found that the C(0) values calculated by computer and the values determined by extrapolating the C_p vs. $\sqrt{\omega}$ plots to zero frequency differed by no more than 5%. This is evidence in favor of the single-step adsorption model with slow diffusion when describing the adsorption of cyanide ions on silver at potentials $\varphi \leq -0.6$ V.

Plots of C(0) against φ for 1 M Na_2SO_4 solutions with and without NaCN are presented in Fig. 2. One can see from this figure that the addition of NaCN to Na_2SO_4 solution leads to a change in the character of the C(0) vs. φ curve which becomes evident at $\varphi > -125$ V for a cyanide concentration of $c = 1.1 \cdot 10^{-5}$ M. For $c = 3.2 \cdot 10^{-3}$ M, this difference arises at still more negative potentials (about −1.4 V).

The merger of the C(0) vs. φ plots at $\varphi \approx -1.4$ V in solutions which do and do not contain NaCN indicates that cyanide is desorbed from the surface at these potentials. This means that the charge on the electrode in the presence of cyanide (Fig. 3) can be calculated by back integration [12] while taking into account that the potential of zero charge in pure Na_3SO_4 solution is given by $\varphi_{zc} = -0.7$ V [7]. One can see from Fig. 3 that NaCN addition to the Na_2SO_4 solution causes a strong shift of φ_{zc} in the negative direction.

The variation of the potential of zero charge relative to φ_{zc} in the base electrolyte, $\Delta\varphi_{zc}$, is shown in Fig. 4 (the full circles). According to Esin and Markov, the φ_{zc}-shift plotted against the logarithm of concentration of the surface-active material is a straight line. In our case, the slope of the straight-line plot of $\Delta\varphi_{zc}$ against log c is −105 mV. In terms of discrete double-layer theory [12], the slope is determined by

$$d\varphi_{zc}/d \log c \approx 2{,}3RT/\lambda zF, \qquad (2)$$

where λ is the ratio between micro- and macropotential; the other symbols are those commonly used. The value of λ determined from relation (2) is 0.55. This λ-value indicates that the compact part of the double layer more closely resembles a "network," with adsorbed CN^- ions in the junction points, than a plane with uniformly "smeared-out" charge.

Figure 4 also shows the effect of the concentration of surface-active material on $\Delta\varphi_{zc}$ in the adsorption of cyanide on mercury [13] and in the adsorption of certain anions on silver [14-16]. It follows from the plots that cyanide is better adsorbed on silver than on mercury; the same magnitude of $\Delta\varphi_{zc}$ is attained with NaCN concentrations differing by two orders of magnitude. One can see when comparing the adsorbabilities of cyanide and the other anions on silver that CN^- adsorbs better than CO_3^{2-}, SO_3^{2-}, Cl^-, and Br^- (F^-, SO_4^{2-}, and OH^- are not surface-active at all [7, 17]). The I^- ions display somewhat higher surface activity than CN^-. The HS^- ions are much more adsorbed than CN^-. Thus, the anions, according to their adsorbabilities on silver, can be arranged in the following series: $F^- = SO_4^{2-} = OH^- < CO_3^{2-} \leq Cl^- \leq SO_3^{2-} < Br^- < CN^- \leq I^- < HS^-$.

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OVERVOLTAGE IN ELECTROCRYSTALLIZATION. THE TRANSLATION OF PARALLEL STEPS

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The concept of electrocrystallization going through a step of adion formation (i.e., the formation of intermediates existing in an adsorbed state on the surface and reaching the growth sites by surface diffusion) is one of the two conceivable alternatives for this process, the other being the direct addition of discharging particles to the growth sites. In the present communication this model will be examined for the simplest case of parallel growth steps spaced equal distances apart. To a first approximation, this model also will describe a system of growth steps in arbitrary positions, since usually the distances between these steps will deviate little from the average, and curvature is small as compared to the average distance between steps.

In most cases, the surface on which crystallization occurs can be visualized as consisting of some system of growth steps at which (and at which exclusively) particles of the new phase are added. With a relatively uniform step distribution, this system can be characterized by the step density ρ or, in an equivalent manner, by the average distance $2x_0$ between the steps, where $x_0 = 1/(2\rho)$. Another adequate model for such a surface, in a certain approximation, will be a system of parallel growth steps spaced distances $2x_0$ apart (provided the distance between the steps and the size of the surface section examined are smaller than their radius of curvature). The steps can have different height and a different number of kinks; however, the steps are of interest to us only insofar as they are sinks for the crystallizing material, and we shall assume that the single parameter θ will suffice to describe them. We shall call θ the step efficiency, and assume it to be proportional to step height and kink concentration. Thus, the surface will be characterized by the two quantities x_0 and θ.

Two types of exchange equilibrium evidently can be realized: (i) solution ions — adions, and (ii) adions — lattice ions in the growth sites. We shall introduce rate constants for each of these processes: $\vec{K}_1$ for the transition from solution ion to adion, $\overleftarrow{K}_1$ for the inverse process; and $\vec{K}_2$ and $\overleftarrow{K}_2$ for the transitions (forward and inverse) from adion to lattice ion in the growth site. These constants depend on the zero selected for the potential scale; up to this point we shall assume that the zero potential is arbitrary but constant (so long as the equilibrium potential has not been defined). We stress that addition to the growth site here is regarded, not as a subsequent (or, for the anodic process, preceding) chemical step but as an electrochemical step the rate of which, generally, depends on potential. It does not matter whether the adions represent incompletely discharged metal atoms, intermediates of the discharge of complex ions, or other species; it is only important that these intermediates do exist in the adsorbed state on the surface, and that they will form metal ions which are added to the lattice when, by diffusion, they reach growth sites. Thus, metal deposition in general is regarded as a two-step process, and the steps are separated by a diffusion process. In addition to the rate constants, transfer coefficients will be introduced for each step: α_1 and β_1, α_2 and β_2.

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