INVESTIGATION OF THE POROUS STRUCTURE OF FINELY DIVIDED PLATINUM

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The porous structures of platinized platinum and platinum black (Adams platinum) have been investigated by calibrated porosimetry and by contructing charging curves. The influence of sintering in solutions of electrolytes at a controlled potential on the porous structure of both types of finely divided platinum has been established. A large fraction of micropores comparable in size to the thickness of the electrical double layer has been discovered in the finely divided platinum (especially in platinized platinum), and under certain conditions they should have a significant influence on adsorption (primarily of charged particles) and on the kinetics of electrode processes.

The porous structure of finely divided platinum, which is one of the most widely used electrode materials and catalysts, has a significant influence on the macro- and microkinetics of electrochemical and heterogeneous-catalytic reactions. Nevertheless, in the literature there is a relatively small number of papers on the investigation of the porous structure of platinum catalysts. A significant shortcoming of the investigations carried out in [1] is the narrowness of the ranges of pore radii measured. The application in [2, 3] of the method of forcing in mercury even in the case of a material known to form amalgams, such as platinum [4] was explained on the basis of the fact that mercury porosimetry had for a long time been practically the only method used over a fairly broad range of pore radii. With the aid of calibrated porosimetry [5] it has been shown that the amalgamation of platinum results in strong distortion of the mercury porosimetric curve.

In the present work, the recently developed method of calibrated porosimetry, which makes it possible to measure pore radii over the broad range from $\sim$10 to $\sim 10^7$ Å, was used to investigate the structure of finely divided platinum and the influence of sintering on it. The principles underlying the method and the experimental techniques have been described in a number of reports [6]. Here we shall dwell only on the special features of the method caused by the complexity of the objects of the present investigation. The objects for the measurements were platinized platinum and platinum black (Adams platinum). The methods for obtaining them and the sintering procedure have been described in [7]. The specific surfaces of the samples investigated, which were determined electrochemically from the adsorption of hydrogen (S_{ad}) prior to sintering and after sintering at 75°C in 1 N H_2SO_4 under the potential E_r^{sin} = 300 mV, are presented in Table 1.

One of the main special features was the fact that Pt/Pt is a thin (its total thickness is only several microns) electroplated coating, whose pores can accomodate only a very small volume of measuring liquid, which is insufficient for its determination on an analytical balance. Therefore, in order to increase the volume of the measuring liquid in the pores of the sample, the latter was made up of several (four to eight) disks of a platinized platinum grid (16,000 holes in 1 cm^2) 2 cm in diameter. Because of the crumbling of the deposit, the platinized grid was investigated according to the method usually used for powders, i.e., it was placed at the base of a clamping device and weighed together with it [6]. Due to the high tendency of the samples of Pt/Pt and Pt black to sinter, they were not heated above 50°C in the drying and measuring stages. With the aid of a scanning electron microscope it was established that the surface of a wire in the platinum grid does not have visible roughness with a characteristic dimension less than 10 μ and that the thickness of the coating of platinized platinum is about 4 μ. The samples of the black were molded into tablets with a diameter of 2 cm under a pressure of $\sim$150 MPa.

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TABLE 1. Specific Surfaces of Samples of Finely Divided Platinum Studied

Sample	S_{ad}, m^2/g	S_{por}, m^2/g	Sample	S_{ad}, m^2/g	S_{por}, m^2/g
Platinized platinum	13,8	21,0	Sintered platinized platinum	6,5	5,2
Platinum black	28,6	31,4	Sintered platinum black	17	19,5

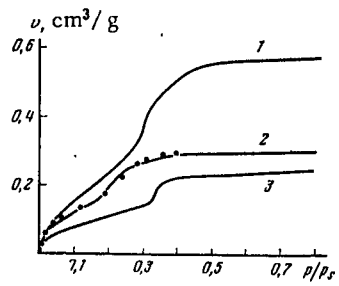

Fig. 1

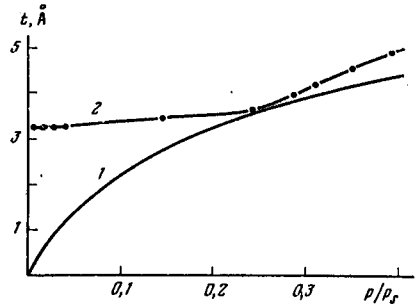

Fig. 2

Fig. 1. Desorption isotherms of adsorbate–silica gel systems: 1) benzene–KSS-4; 2) benzene–ShSM; 3) water–S337.

Fig. 2. Desorption isotherms of the following systems: 1) benzene–Pt/Pt; 2) benzene–Pt black; 3) water–Pt/Pt; 4) benzene–sintered Pt/Pt; 5) benzene–sintered Pt black.

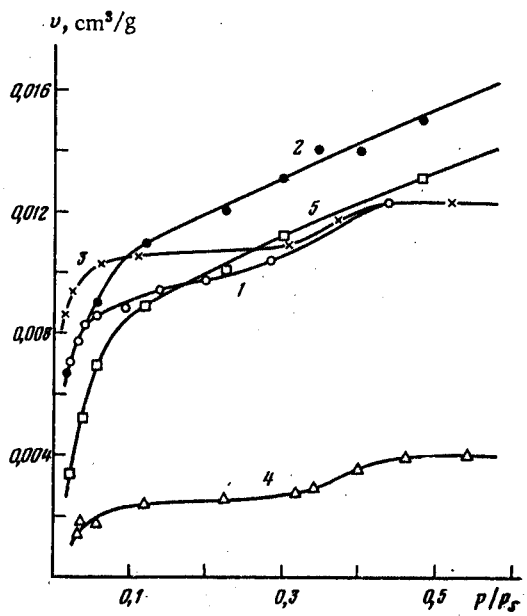

Fig. 3. Desorption isotherms of benzene (t curves): 1) universal on siliceous adsorbents; 2) experimental on platinum.

Metalloceramic nickel disks with ranges of pore radii from ∿1 to 100 and from ∿0.005 to 1 μ served as the standards [6]. As a working liquid we first used decane, which is most often used in the range of pores with r ≈ 0.01 to 100 μ, because of its low volatility at room temperature. However, the measurements taken after the vaporization of decane did not demonstrate the presence in Pt/Pt of pores with a radius above 0.01 μ (with the exception of the cells and the sites of intersection of the wires of the grid with effective radius greater

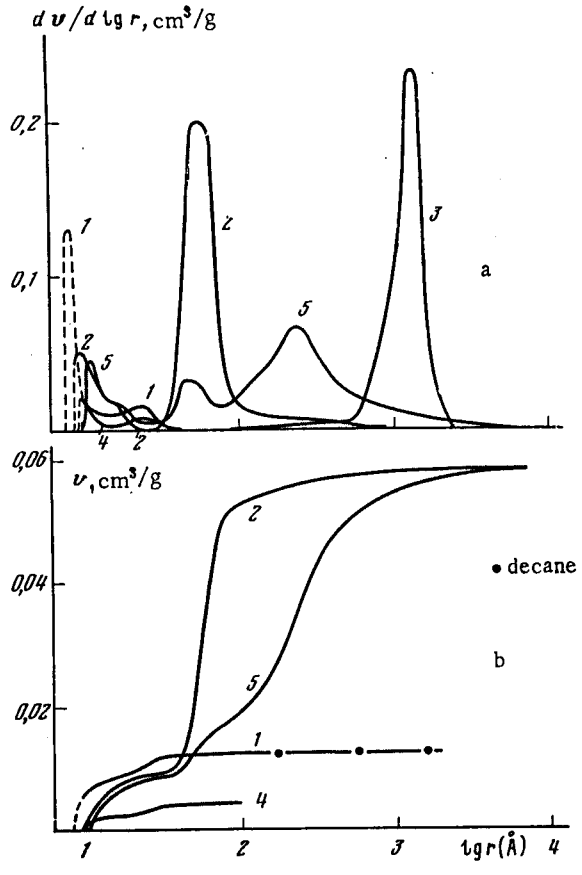

Fig. 4. Differential (a) and integrated (b) distribution curves of the volumes of pores with respect to their radii: 1) Pt/Pt; 2) Pt black tablet; 3) sintered Pt black tablet for determining the t curve on platinum; 4) sintered Pt/Pt; 5) tablet of sintered Pt black.

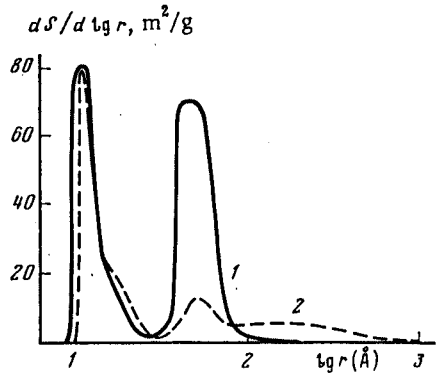

Fig. 5. Distribution of the specific surface of pores with respect to their radii for unsintered (1) and sintered Pt black (2).

than 1 μ). The measurements in the range of pore radii below 100 Å were carried out relative to specially prepared compact standards made from ShSm, KSS-4, and S-337 powdered silica gels, which have known isotherms for the desorption of benzene [8, 9] (Fig. 1). For greater accuracy measurements with the vaporization of benzene were carried out simultaneously relative to two standards made from different silica gels. In Fig. 1 the points denote the desorption

isotherm of benzene from silica gel ShSm, which we obtained relative to silica gel KSS-4 by calibrated porosimetry. The good fit between the curves obtained by the direct sorption method (curve 2, solid line) and by calibrated porosimetry (curve 2, points) points out the correctness of using the latter even at low values of the relative pressure and in the construction of distribution curves of pores with respect to their radii up to the limit of the micropore range.

Before the measurements all the samples were subjected in turn to anodic and cathodic polarization in a 1 N H_2SO_4 solution. Such electrochemical treatment was needed not only before the recording of the charging curves, but also before the porosimetric measurements, since it made it possible to completely remove any organic molecules from the platinum surface and to thereby free the tiniest pores, which might otherwise have been filled by irreversibly adsorbed molecules and might therefore have been inaccessible to the measurements. The samples were then thoroughly washed in doubly distilled water and dried in a vacuum first at room temperature and then at 50°C to constant weight.

As is seen from Fig. 2, the desorption isotherms have different shapes both in the case of different platinum samples and in the case of different adsorbates (benzene and water). According to their shape, the desorption isotherms of benzene may be classified (according to Brunauer's classification [10]) as type IV both in the case of Pt/Pt (curve 1) and in the case of Pt black (curve 2). The distribution curves of the mesopores with respect to their radii can be calculated and the volume of the micropores can be determined from desorption isotherms of this type [10]. The desorption isotherm of the platizined platinum–water system is similar in shape to the isotherms of type I and, therefore, cannot be used for calculating the distribution curve of the volume of the pores with respect to their radii [10].

The construction of distribution curves of pores with respect to their radii from desorption isotherms requires taking into account the thickness t of the adsorption film on the surfaces of the pores not filled by the liquid. A t curve is usually used for this purpose. This curve is a desorption isotherm recalculated in t versus p/p_s coordinates and measured for a nonporous sample (more precisely, for a sample not having pores with a radius comparable to the thickness of the adsorption film) which has a known specific surface and is chemically similar to the porous sample under investigation. So-called universal t curves, which are obtained by averaging for a large number of adsorbents [10], are often used instead of an experimental curve. Figure 3 presents the universal t curve on siliceous adsorbents (curve) taken from [11] for benzene. However, the chemisorption activity of platinum and the possibility of a specific interaction with the adsorbates called for the direct measurement of the t curves for platinum, since we were not able to find them in the literature. These measurements were carried out on a porous tablet with $S_{ad} = 0.85$ m^2/g, which was obtained from platinum black with a specific surface $S_{ad} = 8.2$ m^2/g by molding it at 150 MPa and sintering it at 450°C in a hydrogen atmosphere for 120 min.

From the porosimetric curve of the resultant sample (curve 3 in Fig. 4a) it follows that in this sample there are no pores with a radius $r < 100$ Å, i.e., in the range of p/p_s values of interest to us the platinum surface was smooth. The measurement of the t curve was carried out on this sample by calibrated porosimetry with simultaneous measurement of the desorption isotherms for Pt/Pt and Pt black. Before measurement, the tablet was subjected to the standard preparation procedure. The t curve obtained for benzene is shown in Fig. 3 (curve 2). As is seen from a comparison of curves 1 and 2, the thickness of the adsorbed film of benzene on platinum is close to the usual value of 3–4 Å [10, 11] for other materials. However, unlike the universal t curve (1), which characterizes the reversible physical adsorption, the t curve obtained has a plateau at small values of p/p_s, which corresponds approximately to monolayer filling of the platinum surface. According to [12] this is evidence of the strong irreversible adsorption of benzene on platinum. This finding called for the preliminary electrochemical cleaning of the samples before each measurement of the porograms. Thus, the method of calibrated porosimetry makes it possible to investigate adsorption on nonporous materials.

The integrated and differential distribution curves of the pores with respect to their radii in Fig. 4 were calculated from the curves in Fig. 2 and curve 2 in Fig. 3. This calculation was carried out according to the procedure described in [13]. However, inasmuch as the objects investigated contain a large fraction of very small pores, the curvature of the cylindrical film was also taken into account in the calculation of its volume v_f:

$$v_f = 2t\int_{r_K}^{\infty}\frac{dv}{r_K} + t^2\int_{r_K}^{\infty}\frac{dv}{r_K^2} = \frac{2t}{2.3}\sum_i\frac{\Delta v_i}{\Delta \lg r_K^i}\left(\frac{1}{r_K^i} - \frac{1}{r_K^{i-1}}\right) + \frac{t^2}{4.6}\sum_i\frac{\Delta v_i}{\Delta \lg r_K^i}\left(\frac{1}{r_{K,i}^2} - \frac{1}{r_{K,i-1}^2}\right), \quad (1)$$

where $r_K = r - t$ is the pore radius appearing in the Kelvin equation

$$r_K = \frac{2\sigma v_m \cos\theta}{RT\ln p/p_s}, \quad (2)$$

where σ, v_m, and θ are the surface tension, the molar volume, and the contact wetting angle of the adsorbate. Next, taking into account that the real volume of the pores filled by the liquid is equal to the experimentally measured value minus the volume of the film, we obtained the distribution curves of the pore volume v with respect to the radii r in Fig. 4. The porosimetric curves obtained were used to calculate the specific surfaces of the samples S_{por} from the equation

$$S_{por} = 2\int_r^{\infty}\frac{dv}{r} = \frac{2}{2.3}\sum_{(i)}\frac{\Delta v_i}{\Delta \log r_i}\left(\frac{1}{r_i} - \frac{1}{r_{i-1}}\right). \quad (3)$$

Table 1 compares the values of S_{por} with the corresponding values of S_{ad}. According to the table, the values of S_{por} and S_{ad} are close to one another in the case of the last three samples, in which the volume of the micropores is relatively small and to which, therefore, the Kelvin equation (2) is applicable over practically the entire range of existing pore radii. Consequently, calibrated porometry makes it possible to determine the values of the specific surface with sufficient accuracy for highly dispersed materials. In the case of Pt/Pt, the fit is poorer, but this may be attributed to the fact that the large volume of micropores, for which the Kelvin equation (2) was applied on a purely formal basis to calculate the distribution with respect to their radii, is significant in Pt/Pt.

Thus, according to Figs. 2 and 4, Pt/Pt is a typical microporous adsorbent like activated charcoals, silica gels, etc. More than half of the volume of all the pores in it is made up of micropores ($r \leq 10$ Å), and the radius of most of the remaining pores does not exceed 30 Å. The distribution of the volume of the micropores with respect to their radii, which is denoted in Fig. 4 by a dashed line, was formally calculated according to the method described above. Taking into account the porosity of the deposit (~20%), we may postulate that the platinum crystallites have radii significantly exceeding the pore radii of the pores. The calculation of the mean diameter of the crystallites $\bar{d}$ from the data on the specific surface with the aid of the equation [10]

$$\bar{d} = 6/\rho S_{ad}, \quad (4)$$

where ρ is the density of platinum, yields $\bar{d} \approx 200$ Å for Pt/Pt. This value is approximately an order of magnitude greater than the mean size of the pores. The narrow spectrum of the pore radii, the absence of a secondary structure, and the small porosity provide some basis to assume that the pores are formed by surfaces of the crystallites and have a length which significantly exceeds their transverse dimension. It is possible that Pt/Pt has an ordered porous structure. The size of the crystallites is in good agreement with the x-ray diffraction data obtained in [14].

The porous structure of Pt black (curve 2 in Fig. 4), unlike that of Pt/Pt, has a pronounced bidisperse character. Besides the narrow pores with r equal to 10 to 15 Å forming the primary structure, there is also a significant volume of pores with r equal to 60 to 100 Å, and there is a smaller number of pores with r equal to 100 to 300 Å, which form a secondary structure. The clear boundary between the primary and secondary structures made it possible to calculate the porosity in each of them with some approximation: in the primary structure it is 16%, and in the secondary structure it is 47%. The specific surfaces are $S_{por_1} = 15$ m^2/g and $S_{por_2} = 17$ m^2/g, respectively, when $S_{tot} = S_{por_1} + S_{por_2}$. The mean diameter of the crystals calculated for $S_{ad} = 28.6$ m^2/g is ~100 Å, and that for the secondary agglomerates is ~200 Å, under the assumption that $\bar{d} = 6v_{ag}/S_{por_2}$, where v_{ag} is the total volume of the secondary particles, which includes the volume of the solid phase of platinum and the volume of the primary pores.

Comparing the porous structures of the different types of finely divided platinum, we should note that the primary structure of the black is similar to the structure of Pt/Pt both with respect to the range and with respect to the volume of the pores. The main dif-

ference between them is the small fraction of micropores ($r \leqslant 10$ Å) in the primary structure of the black and the presence of a secondary structure in Pt black.

In the present work we also studied the influence of sintering in a 1 N H_2SO_4 at E_r^{sin} = 300 mV [7] on the structure of finely divided platinum. Figure 2 presents the desorption isotherms of benzene for sintered Pt/Pt (curve 4) and Pt black (curve 5), and Fig. 4 presents the corresponding distribution curves of the pores with respect to their radii. As a result of the sintering, the porosity of Pt/Pt decreased to less than half, and the mean diameter of the crystallites increased to ∿400 Å. In the case of Pt black, the bidisperse nature of its structure was preserved and even enhanced. The mean diameter of the primary particles increased to ∿160 Å, and that of the secondary particles increased to ∿550 Å.

As follows from the porosimetric curves, the sintering process takes place differently for the two types of finely divided platinum. In the case of Pt/Pt, it may be assumed that all, but primarily the micropores were sintered, causing a decrease in the total pore volume. In the case of Pt black, the volumes of the pores in the two structures changed slightly, but intense consolidation of the secondary pores and reduction of the surface in the secondary structure did not occur, as is graphically seen from Fig. 5, which presents the differential distribution of the specific surface of the pores with respect to their radii calculated from Eq. (3). This difference in the nature of the sintering is apparently attributable to the presence in Pt black of a secondary structure, whose specific surface amounts to more than half of the total specific surface, as well as the strength of the skeleton of the molded sample. This somewhat unexpected nature of the change in the porous structure of Pt black upon sintering, i.e., the decrease in the volume of the pores with radii in the vicinity of 100 Å to a greater extent, is confirmed by the literature data in [1]. As a whole, this question calls for additional investigations.

In [7] a definite difference between the rates of sintering of Pt/Pt and Pt black was observed, and, in addition, the dependence of the degree of sintering on the potential for Pt black was characterized by a curve with a considerably more diffuse maximum than is Pt/Pt. This may be attributed to the broader spectrum of the pores in Pt black.

The most important result of the present work is the establishment of the presence of a large fraction of micropores with $r \leqslant 10$ Å in finely dispersed platinum, and especially in platinized platinum. The fact is that the size of these pores is comparable to the thickness δ of the electric double layer (with the exception only of very concentrated solutions), as well as to the size of many molecules (a), especially organic molecules. In our opinion, both these factors must influence the adsorption processes and the kinetics of the electrode reactions, as was shown in [6]. When $r \lesssim \delta$, as well as, of course, when $r \lesssim a$, the specific catalytic activity (per unit of true surface) should, all other conditions being equal, generally be smaller than the specific catalytic activity of the corresponding smooth electrocatalyst. A comparison of the porograms for the two types of finely divided platinum studied indicates that this effect should be stronger for the type of platinzed platinum investigated, despite the fact that the specific surface of the latter is approximately half of that of platinum black. In the literature the possibility of an influence due to changes in the properties of the solution in the small pores, particularly changes in the structure of the electric double layer, is usually not taken into account, and the effect of the dispersity of the catalyst on its specific catalytic activity known from experimental studies is usually (except in cases of relatively large reactant molecules) attributed to the influence of the dispersity on the physical properties of the catalyst itself: its electronic structure, the number of atoms with free valences, the predominant crystallographic orientation, the concentration of crystal defects, etc. [15]. It has been established experimentally in a fairly large number of studies that the rates of different electrocatalytic processes as calculated per unit of true surface drop upon the transition from smooth to platinized platinum.

A predominant influence of the steric factors should be expected in the case of the adsorption and electrooxidation of the uncharged organic compounds, since the rate-limiting steps in these processes are chemical in nature (dehydrogenation, interactions of adsorbed particles with OH_{ads}, etc.) the intermediates are also uncharged, and sufficiently concentrated solutes of a supporting electrolyte ($\geqslant$1 N) are used. This may account for the fact that in the case of organic compounds with small molecules (CH_3OH, HCOOH, C_2H_5OH, etc.), smaller specific rates of chemisorption and electrooxidation have been found on Pt/Pt than on smooth Pt; however, the ratio between the rates does not exceed 10, according to most studies. Nevertheless, the presence of a "true" catalytic effect cannot be ruled out, since the dif-

ferences between the rates of electrooxidation on smooth Pt and Pt/Pt have also been found for processes which do not include the supply of the substance from the bulk of the solution (electrooxidation of a product of the strong chemisorption of CO with CO present in the solution [16]). At the same time, considering the complexity of the removal of the intermediates from the narrow pores in the case of multistep reactions, we may expect differences in the composition of the final products on smooth and finely divided Pt. This makes it possible to account for the difference between the final oxidation products of CH_3OH on smooth Pt and Pt/Pt [17]. Although the inaccessibility of a considerable portion of the surface of finely divided Pt to the fairly large molecules of organic compounds has been postulated in a number of studies, the experimental material obtained in the present work will make it possible in the future to more correctly and quantitatively take into account the influence of this factor in work with finely divided platinum.

With respect to the establishment of the influence of the comparability of the values of r and δ on the rate of electrocatalytic processes, attention should be focused on the processes with the participation of ions. In this sense the studies in [18, 19], in which the rates of the isotope exchange of ions on smooth and platinized platinum were investigated, are of special interest. For example, the ratio between the rates for the Tl^+ ion on smooth Pt and Pt/Pt is $\sim$50 [18], and that for the exchange of Br^- ions is up to 10^3 [19]. Changes may also be expected in the values of the electrostatic adsorption of ions (as calculated per square centimeter of true surface) with variation of the dispersity of Pt and primarily upon the transition from smooth Pt to Pt/Pt (especially in dilute solutions). Displacement of the point of zero free charge as Pt/Pt is sintered was noted in [20].

Attention should also be focused on the fact established in the present work that the mean radius of the primary pores in finely divided platinum is an order of magnitude lower than the mean radius of its particles. This underlines the need to take into account the changes in the composition of the solution in the electrical double layer (in comparison to the case of smooth platinum) in explaining the influence of the dispersity of platinum on its catalytic activity.

Moreover, the possibility of an additional decrease in the effective diffusion coefficients of the molecules and ions due to the comparability of their dimensions and the dimensions of the pores, which, in turn, can result in reinforcement of the internal-diffusion restrictions on the rates of the corresponding reactions, cannot be ruled out.

Thus, it should be assumed that the comparability of the dimensions of the micropores in finely divided platinum, the thickness of the electric double layer, and the dimensions of the molecules of many substances especially organic compounds, established in the present work may be responsible to a considerable extent for the dependence of the specific catalytic activity on the dispersity for a number of electrocatalytic processes.

LITERATURE CITED

1. K. Kinoshita, K. Routsis, J. A. S. Bett, and C. S. Brooks, Electrochim. Acta, 18, 953 (1973).
2. A. V. Dribinskii, M. R. Tarasevich, and R. Kh. Burshtein, Élektrokhimiya, 7, 1144 (1971).
3. I. G. Abidor, Ya. B. Shimshelevich, G. V. Shteinberg, A. P. Baranov, and V. S. Bagotskii, Élektrokhimiya, 9, 366 (1973).
4. M. Hansen and A. Anderko, Constitution of Binary Alloys, McGraw-Hill, New York (1958).
5. V. E. Sosenkin and Yu. M. Vol'fkovich, Article deposited in the All-Union Institute of Scientific and Technical Information of the Academy of Sciences of the USSR, No. 181-77, January 17, 1977; Élektrokhimiya, 13, 1090 (1977).
6. Yu. M. Vol'fkovich, V. S. Bagotskii, V. E. Sosenkin, and E. I. Shkol'nikov, Élektrokhimiya, 16, 1620 (1980).
7. B. I. Podlovchenko and T. D. Gladysheva, J. Electroanal. Chem., 103, 375 (1979).
8. O. G. Larionov, K.V. Chmutov, and M. D. Yudilevich, Zh. Fiz. Khim., 41, 1011 (1967).
9. O. M. Dzhigit, Dissertation for the Degree of Canditate of Chemical Sciences, Moscow (1957).
10. S. Gregg and K. Sing, Adsorption, Surface Area, and Porosity, Academic Press, New York (1967).
11. A. A. Isirikyan and A. V. Kisilev, Dokl. Akad. Nauk SSSR, 119, 731 (1958).
12. V. E. Kazarinov, A. N. Frumkin, E. A. Ponomarenko, and V. N. Andreev, Elektrokhimiya, 11, 860 (1975).

13. Yu. M. Vol'fkovich and E. I. Shkol'nikov, Élektrokhimiya, 14, 404 (1978).
14. Yu. D. Gamburg, R. P. Petukhova, B. I. Podlovchenko, and Yu. M. Polukarov, Élektrokhimiya 10, 751 (1974).
15. V. S. Bogotskii (editor), Problems in Electrocatalysis [in Russian], Nauka, Moscow (1980).
16. M. W. Breiter, J. Electroanal. Chem., 101, 329 (1979).
17. R. P. Petukhova, V. F. Stenin, and G. I. Podlovchenko, Élektrokhimiya, 14, 755 (1978).
18. V. E. Kazarinov and V. N. Andreev, Élektrokhimiya, 11, 1482 (1975).
19. V. N. Andreev and V. E. Kazarinov, Élektrokhimiya, 12, 224 (1976).
20. O. A. Petrii and A. V. Ushmaev, Élektrokhimiya, 17, 1154 (1981).

NONSTATIONARY EFFECTS IN ELECTRODIFFUSION PROCESSES

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The nonstationary effects appearing in electrolytes upon sudden alteration of the boundary conditions have been investigated in this work. The one-dimensional case, in which the electrolyte is enclosed between two impermeable walls, has been considered. The external perturbation acting on the system has been simulated by changes in the potential difference of the external field or by means of the mechanical displacement of the walls. It has been shown that electrical parameters of the solutions in the transition periods can differ significantly from steady-state parameters and that when a rectangular voltage pulse is supplied to the walls, the electrical signals within the electrolyte have a totally different form.

Electrodiffusion processes in solutions have been studied in the context of various phenomena in physics, chemistry, and biology [1-4]. However, the exact solutions of the electrodiffusion equations are used only for stationary conditions which are limiting with respect to time.

Nevertheless, there is some basis to assume that in some cases (for example, when the boundary conditions or the physicochemical properties of the solution are suddenly altered) just these effects determine the main features of the phenomena under study. For example, the process of the formation of crystallization potentials (10 to 10^2 V) could be explained only after rejecting the stationary conditions [3], but the solution was obtained at the cost of knowingly making the problem less exact.

In the present work the nonstationary effects in an electrolyte have been investigated by numerical solution of the electrodiffusion equations.

FORMULATION OF THE PROBLEM. PRINCIPAL EQUATIONS, INITIAL CONDITIONS, AND BOUNDARY CONDITIONS

We shall restrict ourselves to the one-dimensional case of the process in an electrolyte enclosed between two plates which are impermeable to ions. We shall stimulate the external perturbation by applying an assigned potential difference to the plates or by mechanically moving them.

In order to reveal the effects caused by the nonstationary nature of the boundary conditions, we shall use the following simplified model. We assume that the electrolyte contains only two kinds of singly charged ions taken in equal numbers. At the initial moment in time the ions are distributed uniformly, and there is no electric field within the electrolyte. Furthermore, motion of the ions occurs only under the action of electric forces and diffusion. The effects at the walls due to the presence of Helmholtz layers, as well as the dimensions of these layers themselves, are negligibly small, and the ions are completely reflected from the walls.

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