solution practically ceases (0.002 mm/yr), which provides the opportunity for anodic protection of titanium VT I-0 in this process.

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ELECTROCHEMICAL PROPERTIES OF THE PLATINUM METALS IN NONAQUEOUS SOLVENTS. ELECTRIC DOUBLE-LAYER CAPACITY OF RENEWABLE PLATINUM AND PALLADIUM ELECTRODES IN $LiClO_4$ SOLUTIONS IN ACETONITRILE

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In [1, 2] we measured differential-capacity curves of the electric double layer (e.d.l.) in acetonitrile (AN) solutions. It was shown [2] that in $NaClO_4$ solutions in AN, the values of e.d.l. capacity are low (on the order of 3 $\mu F/cm^2$ of true surface area) and depend little on electrode potential over a potential range of more than 2 V. It was concluded that a layer of adsorbed solvent molecules forms on the platinum surface. In the present work the measurements of differential-capacity curves are continued at renewable Pt and Pd electrodes in $LiClO_4$ and $NaClO_4$ solutions in acetonitrile. By using electrodes that can be renewed under the working solution one can avoid the complications associated with their prior history.

The procedure of solvent purification and the measuring procedure have been described before [1, 2]. The Pt electrode used in the work had a roughness factor of 3.9. This was determined from hydrogen adsorption in aqueous 1 N H_2SO_4 solution [3]. The palladium electrode, which was the end of a wire of 0.8 mm diameter that was pressed into Teflon [PTFE], had a roughness factor of 3.2. This was determined from impedance measurements following the method of [4]. All values of electrode capacity are reported in terms of true surface area in the present work.

Lithium perchlorate was purified by twofold recrystallization from distilled ethyl alcohol, and dried in vacuum over P_2O_5 at boiling-benzene temperature.

The potentials, E, were measured relative to an aqueous silver—silver chloride electrode (Ag/AgCl) was connected to the working solution via a salt bridge containing 0.05 N base-electrolyte solution in AN and had a potential of —0.34 V relative to the reference electrode: Ag/0.1 N $AgNO_3$ in AN.

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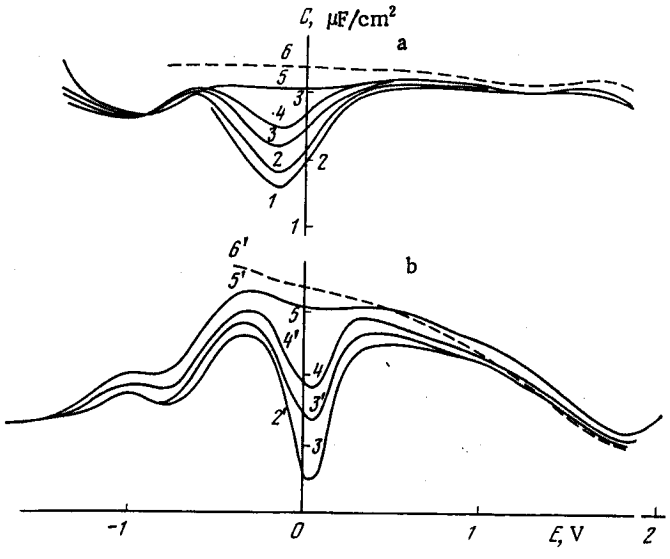

Fig. 1

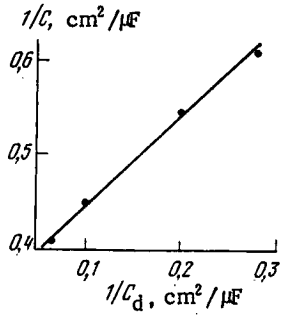

Fig. 2

Fig. 1. Differential capacity curves recorded at Pt (1-6) and Pd (2'-6') in acetonitrile with different concentrations of $LiClO_4$: 1) $5 \cdot 10^{-4}$ N, 2) and 2') 10^{-3} N, 3) and 3') $4 \cdot 10^{-3}$ N, 4) and 4') 10^{-2} N, 5) and 5') $5 \cdot 10^{-2}$ N, and with 10^{-3} N $NaClO_4$ (6, 6').

Fig. 2. A plot of $1/C$ against $1/C_d$ at the potential of the minimum in the C vs E curves for the Pt electrode in $LiClO_4$ solutions in acetonitrile.

The impedance components were measured with an X-206 automatic instrument developed in the Institute of Physicochemical Fundamentals of Minerals Processing, Siberian Branch, Academy of Sciences of the USSR (IFKhIMS SO AN SSSR) [5]. All results are reported for an ac frequency of 210 Hz. The frequency dependence was within 12% over the frequency range from 20 to 2000 Hz in 0.01 N $LiClO_4$, and within 15% in 10^{-3} N $LiClO_4$. The dependence of capacity on ac frequency can be attributed to solvent chemisorption on the platinum surface, to an asymmetric disposition of working and auxiliary electrode, and to the roughness present at the test electrodes. As a test for the region of ideal polarizability we also measured potentiodynamic I vs E curves.

Curves showing the differential capacity of the renewable Pt electrode as functions of potential for different $LiClO_4$ concentrations are reported in Fig. 1a. In 0.05 N $LiClO_4$, the potential dependence of capacity is minor; the same is found for $NaClO_4$ solutions at the Pt electrode. At higher dilutions of the $LiClO_4$ solutions, a minimum appears in the C vs E curves; the potential of this minimum (-0.14 ± 0.02 V vs Ag/AgCl) does not change with the salt concentration. A similar minimum is not displayed in the C vs E curves of the renewable Pt electrode in $NaClO_4$ solutions in AN (curve 6 of Fig. 1a). The reasons for this difference in the behavior of Li^+ and Na^+ ions are not clear. It can be attributed to some measure of specific adsorption of the Na^+ ions, which in AN are less solvated than Li^+.

To examine the nature of the minimum we used the method of [6] to analyze plots of $1/C$ against $1/C_d$, where C_d is the diffuse-layer capacity calculated from the Gouy–Chapman theory. A value of 38 was used for the dielectric permittivity (D) in the diffuse layer; this corresponds to the value of D in the bulk of AN [7]. The plot of $1/C$ against $1/C_d$ at the potential of the minimum is a straight line (Fig. 2). This result indicates that the minimum is caused by diffuseness of the e.d.l. A slope close to unity found for the straight line of Fig. 2 indicates that the roughness factor of the Pt electrode was determined correctly from hydrogen adsorption in aqueous 1 N H_2SO_4 solution, and that D in the diffuse layer corresponds to the bulk value of D. That the potential of the minimum remains constant while the $LiClO_4$ concentration is varied is an indication that specific adsorption of the base-electrolyte ions does not occur.

The e.d.l. capacity of the Pt electrode depends little on potential. Hence, despite the polycrystalline nature of the electrode, one has reasons to believe that the minimum corresponds to the potential of zero charge (p.z.c.) of polycrystalline Pt rather than to that of

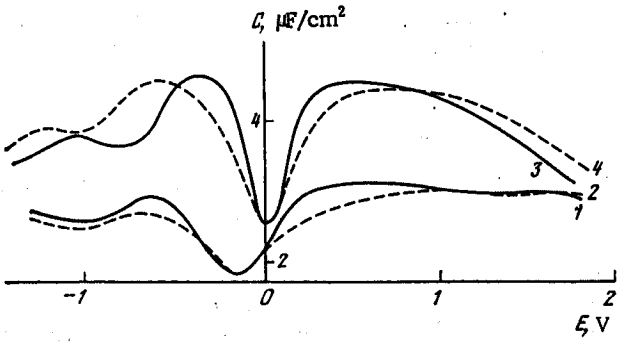

Fig. 3

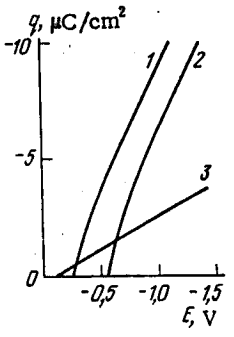

Fig. 4

Fig. 3. Experimental (1, 3) and calculated (2, 4) differential-capacity curves of the Pt (1, 2) and Pd (3, 4) electrode in 10^{-3} N $LiClO_4$ solution.

Fig. 4. Charge density q as a function of potential E at Hg (1) and Ga (2) [11] in 0.1 N $LiClO_4$ solution in acetonitrile, and at Pt (3) in 0.05 N $LiClO_4$ solution in acetonitrile.

the individual single-crystal face with the most negative p.z.c., as found in [8] for the Ag electrode in aqueous solutions.

The p.z.c. of the Pt electrode in acetonitrile solutions is more positive than the p.z.c. of mercury [9], bismuth [10], gallium [11], and In–Ga alloy [9] in the same solutions.

Below we report the changes in the p.z.c. of $LiClO_4$ solutions in acetonitrile ($\Delta E_{q=0}^{Me-Pt}$) and the work-function changes (ΔW^{Me-Pt}) found to occur in going from other metals to platinum:

	$-\Delta E_{q=0}^{Me-Pt}$, V	$-\Delta W^{Me-Pt}$, V
Hg	0.12	1.20 [12, 13]
Bi	0.27	1.41 [12, 13]
Ga	0.41	1.41 [12]
In-Ga	0.52	

We see that the p.z.c. changes found to occur in going from other metals to platinum do not correspond to the changes in the metal–vacuum electronic work functions. This is an indication for strong chemisorption of AN on the platinum electrode.

The differential capacity of the renewable Pd electrode was measured (Fig. 1b). The minimum in the C vs E curves which corresponds to the p.z.c. of the polycrystalline Pd electrode in $LiClO_4$ solutions occurs at 0.04 ± 0.02 V. The potential dependence of the e.d.l. capacity of the Pd electrode is more pronounced than that of the Pt electrode, and the actual capacity values are higher, which can be attributed to a somewhat different chemisorption of AN on these two metals. As with the Pt electrode, diffuseness of the electric double layer in $NaClO_4$ solutions in AN remains without effect at the Pd electrode (curve 6 of Fig. 1b).

We used Grahame's method [14] to calculate C vs E curves for the Pt and Pd electrode. The capacity in 0.05 N $LiClO_4$ solution was taken as the compact-layer capacity. The results of the calculation are reported in Fig. 3 together with the experimental data for 10^{-3} N $LiClO_4$ solution. The best agreement between calculated and experimental differential-capacity curves is found at potentials close to the p.z.c. This agreement between calculation and experiment indicates that the Gouy–Chapman theory applies quantitatively to Pt and Pd electrodes in $LiClO_4$ solutions in AN at low surface charge densities.

The q vs E curves for Hg, Ga [11], and Pt electrodes in $LiClO_4$ solutions in acetonitrile are compared in Fig. 4. The essentially different shape of the charge density curves indicates that AN chemisorption on mercury is different in nature from that on the platinum metals; this difference is retained throughout the potential range accessible to measurements.

Thus, the capacity minimum corresponding to maximum e.d.l. diffuseness near the p.z.c. could be observed for the first time in the present work at platinum-group metals in acetonitrile solutions.

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CONVECTIVE DIFFUSION IN PITS.

STARTING EQUATIONS

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The processes of mass and charge transport in pits are important, since the solution components are actively involved in the elementary act, so that their distribution inside the pit will influence the electrochemical kinetics. In theory, this has the effect that the general relation for the dissolution current density i_a obtained in [1] contains functions $c_s(t)$ and $c_{ss}(t)$, which represent the boundary values of concentrations $c(x, t)$ and $c_s(x, t)$ of the ionic components and the solvent. They can only be found from the general mass transfer problem; the solution of this problem is the subject of the present work.

The specific features of this problem are determined — as was ascertained in [1] — by the large size of i_a, the rapid increase of $c(x, t)$, and the associated decrease in the solvent concentration (dehydration). Hence the methods of ordinary diffusion kinetics where one assumes that $c(x, t) \ll c_s(x, t)$ and where the mutual influence of the components is disregarded are inadequate in the case of local corrosion, and Onsager's general theory of transport processes [2] must be used. For an m component solution this is formulated as a system of equations linking the statistical average velocities, $\vec{V}_k$, of the particles to the gradient of electrochemical potential, $\mu_i = \mu_i^{(o)} + z_i F\varphi + RT \ln (\gamma_i c_i/c_o)$

$$\frac{\bar{c}}{RT}\nabla\mu_i = \sum_{k=1}^{m}\left(\frac{c_k}{D_{ik}}\right)(\vec{V}_k - \vec{V}_i), \quad \sum_{k=1}^{m} c_k \nabla\mu_k = 0, \quad \bar{c} = \sum_{k=1}^{m} c_k, \tag{1}$$

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