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Potentials of Zero Charge

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1. Introduction

The notion of the potential of zero charge (pzc) and the relevant term were introduced 50 years ago.$^{(1)}$ Later, the pzc was proved to be an important electrochemical characteristic of metal and to play a major role in electrocapillary and electrokinetic phenomena, electric double-layer structure, adsorption of ions and neutral organic molecules on the electrode, wetting phenomena, physicochemical mechanics of solids, photoemission of electrons from metal into solution, and in electrochemical kinetics. The introduction of the notion of pzc led to solution of the Volta problem and to rigorous interpretation of the attempts to measure or calculate the "absolute" electrode potential. All this testifies to the fundamental nature of the notion of pzc.

Many hundreds of papers have been devoted to the problem of pzc. The pzc of different metals were first compared by Frumkin.$^{(2)}$ In recent years some reviews have been published in which the pzc values are listed.$^{(3-7)}$ The theoretical validity of various methods of pzc determination and the reliability of experimental data are discussed in detail by Frumkin,$^{(8)}$ where a comprehensive history of the development of the notion of the electrode charge is given and different aspects of the problem of pzc are considered.

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2. The Notion of the Electrode Charge

Before discussing the modern state of the problem of pzc, the notion of the charge of electrode surface will be considered briefly.

The conventional definition of the charge is based on the concept of the electric double layer at the metal/electrolyte interface, and the electrode charge is identified with the charge of the metal side of the double layer, i.e., with the deficiency or excess of electrons in the metal surface layer. This definition dates back to Helmholtz, who in the middle of the last century introduced the double-layer concept. It is evident that such an electrostatic definition postulates the dependence of the charge and hence, of the pzc, on the double-layer model used.

Another, thermodynamic approach to definition of the surface charge was suggested by Lippmann in his early papers.(9) Lippmann laid the foundations for the thermodynamic theory of electrocapillarity by deriving the famous equation

$$\partial\gamma/\partial E = -Q \tag{2.1}$$

where γ is the surface tension at the mercury/electrode-solution interface (for the physical sense of γ in the case of solid metals, see below), E is the electrode potential, and Q is a quantity which Lippmann called "the electric capacity of unit surface at constant potential difference." As follows from this definition, Q denotes the amount of electricity to be supplied to the electrode when its surface increases by unity in order that its potential should remain constant. Here, Lippmann did not use any concept of the electric double-layer structure. However, in his later papers, Lippmann, proceeding from Helmholtz's views, considered the quantity Q as the electrode surface charge, assuming it to be proportional to the potential difference between metal and solution.

The thermodynamic theory of electrocapillarity was developed further by Gibbs(10) and Planck.(11) Gibbs derived the adsorption equation, which was used by a number of authors as a basis in deriving Lippmann's equation.(12–18) According to Gibbs the right-hand side of Eq. (2.1) gives the surface density of adsorbed electrochemically active substance in electric units.†

Planck(11) derived Eq. (2.1) for a completely polarizable electrode ("vollkommen polarisierbare elektrode"), i.e., an electrode whose state is completely determined by the amount of electricity passed through it. He emphasized that this circumstance did not relate the quantity in question to the free charge on both sides of the electrode surface. Thus Planck's formulation clearly shows the difference between the two interpretations of the quantity Q, based on thermodynamics and electrostatics.

Frumkin(12,13) analyzed the electrocapillarity equation derived on the basis of Gibbs adsorption equation:

$$d\gamma = -Q\,dE - \sum_i \Gamma_i\,d\mu_i \tag{2.2}$$

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† For detailed analysis of Gibb's concept on the physical sense of the right-hand side of Eq. (2.1), see Reference 19.

Here, Γ_i's are the Gibbs surface excesses, μ_i's are the chemical potentials of the system components with the exception of that of which the adsorption leads to charging of the surface, and E is the potential measured against a constant reference electrode. This analysis showed that, in a general case, the right-hand side of Eq. (2.1) cannot be equated with the free-charge density of the metal surface, σ. Two relations were obtained which, using the designations proposed by Frumkin *et al.*,(20) can be written as

$$\partial\gamma/\partial E = -\sigma - A_{\mathrm{Me}^+} \tag{2.3}$$

$$\partial\gamma/\partial E = -\sigma + A_{\mathrm{Me}} \tag{2.4}$$

Here, A_{Me^+} is the excess of metal in ionic form in the surface layer at constant metal phase composition, and A_{Me} is the excess of metal in atomic form dissolved in mercury due to formation of amalgam during polarization and at constant $[\mathrm{Me}^+]$ value in the solution bulk. (A_{Me} and A_{Me^+} are expressed in electrical units.) It was shown, as exemplified by Zn amalgam in $ZnSO_4$ solution, that neglect of the second term in the right-hand side of Eq. (2.3) can lead to considerable errors. For a long time, Eqs. (2.3) and (2.4) found no practical use since chief attention of electrochemists was focused on the electric double-layer structure.

Beginning in 1934, in studies on the electrocapillarity theory and the electric double layer, wide use was made of the concept introduced by Koenig,(21) an ideally polarizable electrode, i.e., an electrode on the surface of which no transition of charged particles occurs between the two sides of the electric double layer. In the case of an ideally polarizable electrode, Q proves to be identical with the charge density of the metal side of the electric double layer σ, so that Eq. (2.2) can be rewritten as

$$d\gamma = -\sigma\, dE - \sum_i \Gamma_i\, d\mu_i \tag{2.5}$$

where the subscript i now refers to all system components.

Later, while numerous studies were devoted to electrocapillary phenomena at ideally polarizable electrodes, the electrodes at which charge transfer across the interface occurs and which, using a thermodynamic approach, should be considered as reversible, received relatively little attention. Thus Grahame and Whitney(15) derived an equation for a metal in the solution of its salt MeA (without supporting electrolyte), which in modern notation at $\Gamma_{H_2O} = 0$ is

$$d\sigma = -\Gamma_{\mathrm{A}}\, d\mu_{\mathrm{MeA}} \tag{2.6}$$

A completely similar equation was obtained earlier by Frumkin.(13) It is noteworthy that Grahame and Whitney in deriving this equation did not introduce the notion of charge at all.

Mohilner(18) gave a set of equations for reversible redox systems which reduce to types of relations similar to Eqs. (2.3) and (2.4). Expressing the adsorption in electrical units, Mohilner's equations can be written as

$$(\partial\gamma/\partial E)_{\mu_R} = -(\sigma + \Gamma_O) \tag{2.7}$$

and

$$(\partial\gamma/\partial E)_{\mu_O} = -(\sigma - \Gamma_R) \tag{2.8}$$

These equations differ from Eqs. (2.3) and (2.4) in that in this case, Γ_O and Γ_R are Gibbs adsorptions of oxidant and reducer, respectively. Unlike the ideally polarizable electrode, Mohilner does not give a thermodynamic definition of the charge σ for a reversible electrode.

Further development of the problem of which quantity should be considered as the charge of the metal side of the electric double layer was influenced by the introduction by Lorenz(22) of the concept of a partial charge transfer. Assuming at first that one has to deal with an ideally polarizable electrode, it is of no importance that the side of the double layer, metal or ionic, to which the particle in the adsorbed state should belong is not known. It follows from the electroneutrality principle that

$$Q = \sum \Gamma_{A^-} - \sum \Gamma_{C^+} \tag{2.9}$$

where Γ_{A^-} is Gibbs adsorption of anion and Γ_{C^+} that of cation, expressed in electrical units (as is the case throughout the remainder of this text). According to Lorenz, in the case of the double layer at a mercury or liquid gallium surface, part of the charge of halogen and alkali metal (potassium, cesium) ions due to formation of a covalent bond, is transferred to the metal surface. Lorenz considers the interface between metal and solution from a microphysical point of view. The total charge on the metal side beyond this microphysical boundary is the true electrode charge, and the part of the charge transferred across the interface is expressed by the elementary (or microscopic, true) transfer coefficient λ. The methods of calculating the transfer coefficient λ proposed by Lorenz raise some objections.(23,24) However, in principle, the possibility of such transfer cannot be questioned since it is inevitable in the presence of a covalent bond between ions in the dense part of the double layer and the electrode metal.

The earlier studies of ion adsorption on platinum group metals,(25) and those of recent years, conducted with the use of combined radiochemical, electrochemical, and analytical methods,(26–33) led to the conclusion that in the case in question the adsorption of most ions involves charge transfer. The hydrogen atoms adsorbed on a platinum surface can be formally considered also as hydrogen ions for which the charge transfer coefficient is close to unity, though not equal to it.(20,33,34) Due to the partial charge transfer, the demarcation line between ideally polarizable and reversible electrodes is not clearly defined. However, as the magnitude of partial charge transfer is not known *a priori*, the free charge of an electrode surface, equal to the electron deficiency in the surface layer of metal, cannot be identified with the quantity Q contained in the right-hand side of the Lippmann equation, and determined by Eq. (2.9).

An ambiguity in such a fundamental concept of electrochemistry as the electrode charge made it imperative that it should be analyzed in detail(20); and it has been concluded that, both for an ideally polarizable electrode and for an electrode on which a reversible charge transfer is possible, a thermodynamically valid determination of the surface charge should be based on a refined Lippmann's concept. The electrode charge should be defined as the amount of electricity to be supplied to the electrode when its surface increases by unity with the concentration of the solution components remaining constant. The concentration of the solution components can be held constant by introducing them into solution in the amounts Γ_i (adsorbed amounts according to Gibbs).

A consistent thermodynamic treatment of the adsorption process of electrochemically active components can be based only on the definition of Gibbs adsorption as of the amount of substance to be introduced into the system in order to keep the composition of the bulk phases constant when the interface increases by unity. What happens to this addition subsequently is of no importance: adsorbed substance in an unchanged condition can form part of the equilibrium double layer or participate in the electrochemical reaction with escape or capture of electrons. Thus, e.g., in a hydrogen atmosphere, when the platinum electrode surface increases by unity in NaCl solution, a certain amount of hydrogen, Γ_H, disappears from the gas phase. This amount, however, is not equal to the amount of hydrogen adsorbed on unit surface, as would be the case in the absence of electrolyte solution. Indeed, part of the hydrogen which disappeared from the gas phase undergoes ionization, charging negatively the electrode surface; and the hydrogen ions formed are substituted in the surface layer by Na^+ ions and enter into the solution. When active carbon with a small amount of platinum is used as a hydrogen electrode in alkaline solution, this is what happens to the major part of hydrogen which disappeared from the gas phase.(35) In other words, the surface excess of hydrogen can be very small in spite of its significant Gibbs adsorption.

In the case of an ideally polarizable electrode when the electrode surface increases, the solution composition is kept constant by adding all its components except the solvent. But in the case of a reversible electrode whose potential is determined by the reaction

$$O + ne^- \rightleftarrows R \tag{2.10}$$

with increasing surface, the composition can be held constant by introducing into the system the O component in the amount Γ_O and the R component in the amount Γ_R without supplying electricity from outside. However, an alternative method is possible, viz., the substance participating in the redox process can be introduced in the amount $(\Gamma_R + \Gamma_O)$, adding it entirely as the O form or entirely as the R form. In the first version, in order to keep the solution composition constant, an additional amount of electricity $Q' = -\Gamma_R$ must be supplied to the electrode. In the second version, the respective amount of electricity is $Q'' = \Gamma_O$. For the reversible electrode of type (2.10), two Lippmann's equations are valid:

$$(\partial\gamma/\partial E)_{\mu_O,\mu_i} = -Q' = \Gamma_R \qquad (2.11)$$

and

$$(\partial\gamma/\partial E)_{\mu_R,\mu_i} = -Q'' = -\Gamma_O \qquad (2.12)$$

where subscript μ_i indicates that the chemical potentials of the other system components not participating in the redox process are constant.

In accordance with Eqs. (2.11) and (2.12), Q' and Q'' should be considered as the charges of the reversible electrode corresponding to the two methods of changing its potential: at constant chemical potential of component O and at constant chemical potential of component R. If the chemical potential of one of the components of the redox system is held constant automatically, e.g., in the case of mercury in solution containing a mercury salt, only one of these two equations can be used (in this case, the second). On the basis of an experimental determination of the quantities Γ_R and Γ_O, or for a liquid electrode from a direct determination of the γ, E dependence at constant μ_O or μ_R, it is possible in the case of a reversible electrode to plot electrocapillary curves of two kinds.

The quantities Q' and Q'' can be called *total electrode charges* at constant chemical potential of oxidant or reducer, respectively.(20) This definition of the electrode charge is in keeping with the conventional concept of the charge, used in applied electrochemistry, as the amount of electricity to be obtained from the electrode upon its complete reduction (Q'') or (with opposite sign) upon its complete oxidation (Q'). In this case, however, the reduction and oxidation processes refer to unit surface and not to bulk phase.

The quantities Q' and Q'' by themselves give no indication of the free electricity density, σ, on the electrode surface. In order to relate Q' and Q'' to σ, it is necessary to go beyond the scope of thermodynamics and to use some model of the nature of the solution components in their adsorbed state. Let it be assumed, for example, that the charge transfer of the system components, except that expressed by Eq. (2.10), may be neglected, and the amount of oxidant per unit surface layer be denoted by A_O and the amount of reducer by A_R. (A_O and A_R are the surface excesses for a certain choice of the interface position.) Under these conditions

$$Q' = -\Gamma_R = \sigma - A_R \qquad (2.13)$$

$$Q'' = \Gamma_O = \sigma + A_O \qquad (2.14)$$

and hence

$$(\partial\gamma/\partial E)_{\mu_O} = -\sigma + A_R \qquad (2.15)$$

$$(\partial\gamma/\partial E)_{\mu_R} = -\sigma - A_O \qquad (2.16)$$

Equations (2.15), (2.16) generalize Eqs. (2.3), (2.4) and, at the same time, prove the erroneousness of Eqs. (2.7), (2.8). It follows from Eqs. (2.13) and (2.14) that

$$A_O + A_R = \Gamma_O + \Gamma_R = \Gamma_\Sigma \qquad (2.17)$$

where Γ_Σ is the total extent of adsorption. For simplicity, in Eqs. (2.11), (2.12), (2.15), and (2.16) the potentials are given against a constant reference electrode.

In contrast to the total charge Q' and Q'', the quantity σ can be called the *free charge*. It should be remembered, however, that this name is somewhat conditional since in the derivation of Eqs. (2.15) and (2.16) the possibility of charge transfer, except in the process (2.10), was ignored.

In the case of an ideally polarizable electrode, $A_R = A_O = 0$, and the right-hand sides of Eqs. (2.14) and (2.16) give the free charge (assuming partial charge transfer to be absent).

The refinement of the notion of the electrode charge led to a consistent general phenomenological approach to the description of reversible chemisorption processes involving charge transfer.(34,36)

Thus, in discussing the problem of the pzc, account should be taken of the difference between the total (Q) and free (σ) charges of the electrode surface. Among the systems considered below, this applies directly to platinum group metals and activated carbon. In this case the following designations and terminology shall be used. For Q' the symbol Q shall be retained, and this quantity will be called the total surface charge, neglecting for brevity sometimes the condition $\mu_{H^+} =$ const. Instead of Q'', the symbol Γ_{H^+} shall be used.

3. Methods of Determination of the Potentials of Zero Charge

3.1. Direct Determination of the Value or Sign of the Surface Charge

It follows from the definition of the total charge Q that it can be measured by the amount of electricity flowing in the external circuit, when the electrode surface increases by unity at $E =$ const. In this case the possibility of charges arising on the electrode surface due to interaction with the oxidants or reducers present in solution must be ruled out, and the concentration of all the solution components being adsorbed must be held constant.

In the case of liquid metals, the pzc determination by this method is possible with the use of a dropping electrode, for which pzc corresponds to the zero value of the charging current. Semiquantitative measurements of the Q–E curves were made already in the last century; the first quantitative data obtained by this method are given by Frumkin.(12,14)

The sign of the charge of a liquid metal surface can be determined not only from the current to the growing drop, but also from the electric signal caused by any surface deformation.(37,38) So far these methods have found use in determination of the pzc of mercury. An analog of the vibrating mercury surface method is a technique based on the application of the audio–electrochemical phenomena.(39)

Two versions of the determination of the pzc of solid metals were suggested which can be considered as analogs of those used for liquid metals and considered above.

In the elastic charging method developed by Gokhshtein,(40) it is the

Table 1

Recommended Potential of Zero Charge Values (against N.H.E.)

Metal	Solution	pzc	Reference
	Liquid metals		
Hg	NaF	−0.193	16
Ga	$HClO_4$ and HCl at $c \rightarrow 0$	−0.69 ± 0.01	61
Ga + In (16.7%)	0.001 *N* $HClO_4$	−0.68 ± 0.01	110
Tl amalgam (41.5%)	1 *N* Na_2SO_4	−0.65 ± 0.01	1
In amalgam (64.6%)	1 *N* Na_2SO_4	−0.64 ± 0.01	110
	Solid metals not adsorbing hydrogen		
Bi (polycrystalline)	0.002 *N* KF	−0.39	89
Bi(111)	0.01 *N* KF	−0.42	90
Cd	0.001 *N* NaF	−0.75	91
In	0.003 *N* NaF	−0.65	92
Pb	0.001 *N* NaF	−0.56	93
Sb	0.002 *N* $KClO_4$	−0.15	94
Sn	0.002 *N* K_2SO_4	−0.38	95
Tl	0.001 *N* NaF	−0.71	96
Ag(111)	0.001 *N* KF	−0.46	85, 86
Ag(100)	0.005 *N* NaF	−0.61	87
Ag(110)	0.005 *N* NaF	−0.77	85
Au(110)	0.005 *N* NaF	0.19	88

Metal	Solution	$E_{\sigma=0}$	$E_{Q=0}$
	Platinum metals[a] (31)		
Pt	0.3 *M* HF + 0.12 *M* KF (pH 2.4)	0.185	0.235
Pt	0.5 *M* Na_2SO_4 + 0.005 *M* H_2SO_4	0.16	0.20
Pt	0.5 *M* Na_2SO_4 + 0.01 *M* NaOH	—	−0.25
Pd	0.05 *M* Na_2SO_4 + 0.001 *M* H_2SO_4 (pH 3)	0.10	0.26
Rh	0.3 *M* HF + 0.12 *M* KF (pH 2.4)	−0.005	0.085
Rh	0.5 *M* Na_2SO_4 + 0.005 *M* H_2SO_4	−0.04	0.03
Ir	0.3 *M* HF + 0.12 *M* KF (pH 2.4)	−0.01	—
Ir	0.5 *M* Na_2SO_4 + 0.005 *M* H_2SO_4	−0.06	0.10

[a] The pzc of metals adsorbing hydrogen depends on solution pH. Here, the values for pH = 2–3 and pH = 12 only are given.

magnitude of the potential fluctuations arising upon periodic stretching of a metal tape immersed in solution which is measured. In this case the elongations are small enough to lie within the limits of elastic deformation. From the fluctuations of the tape potential, it is possible to determine the value of $Q + (\partial Q/\partial \ln s)_E$, where s is the electrode area. In the case of a solid metal, the value of $(\partial Q/\partial \ln s)_E$, generally speaking, is not zero, which limits the possibilities of determining the pzc by this method.†

Jakuszewski and Kozlowski developed and widely used the immersion method(41) based on the determination of the potential at which the direction of the current between a stationary electrode and an electrode newly immersed in solution changes. In this case it is assumed that current is consumed only in charging the electric double layer arising upon immersion in the solution. The prerequisite of the fulfillment of this condition is a complete absence on the metal surface before its immersion of adsorbed oxygen or oxides as well as of adsorbed hydrogen. However, the fulfillment of these conditions in real systems presents considerable difficulties and cannot always be controlled. Therefore all attempts at refining the immersion method were directed to improvement of the surface preparation of solid electrodes.(42,43)

3.2. Development of Electrodes with Zero Charge

The methods of developing electrodes with zero charge are similar to those considered above.

In the case of liquid metals, use can be made of dropping or streaming electrodes, which was already pointed out by Helmholtz. In principle, surface increase allows a decrease of the charge density to negligible values and permits the direct determination of the pzc if the initial potential difference value is not restored due to interaction between metal and solution. The efficiency of a dropping electrode can be enhanced by increasing rapidly the surface (Paschen) and/or in a more modern version, by removing carefully the traces of depolarizers (oxygen, mercury salts) from solution and eliminating the possibility of its contamination by traces of difficulty-soluble mercury salts from the reference electrode or from the walls of vessels. The dropping (or streaming) electrode method was widely used for determination of the pzc of mercury by Grahame(44) and also for determination of the pzc of indium amalgams by Butler.(45) If the pzc lies in the potential range in which an amalgam electrode can be considered with good approximation to be an ideally polarizable one, the pzc values obtained by the streaming electrode method can be considered as being the values of the potential of zero free charge. If, however, equilibrium is established on the freshly formed amalgam surface between metal dissolved in mercury and

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† Some primitive attempts to determine the surface charge from the direction of the current passing in solution from a stationary metal wire to a wire subjected to stretching were made in 1809 by Kroichkoll.

its ions, the pzc determined by means of the streaming electrode is the potential of zero total charge at constant reducer concentration, i.e., the metal concentration in amalgam.

While the problem of preparing an ideally polarizable electrode with a zero charge is solved by increasing the surface, the method of zero solutions, in which the vanishing of the charge density is ensured by changing the solution composition, is more suitable for a reversible electrode. The zero solutions method, the idea of which was suggested by Nernst at the beginning of this century, was developed by Palmaer, Smith, and Moss. Palmaer measured the current flowing between a streaming electrode and a stationary mercury surface in the same solution and varied the composition in such a manner that the strength of this current should be zero. He believed that thus the potential reached the "absolute zero." Frumkin and Cirves(46) used the zero solutions method for determination of the pzc of thallium and cadmium amalgams. The potential difference between amalgam and solution was varied by adding to solution the corresponding metal salt. An attempt was made to extend the zero solutions method to sodium amalgams,(47) but in that case the results seemed to be affected by chemical interaction of amalgam with solution.

The zero solutions method was used more than once in combination with the immersion method for determination of the pzc of solid metals.(48) However, the difficulties associated with the possibility of the double-layer formation due to ionization of adsorbed gases or discharge of solution ions upon immersion of a solid electrode were overcome only for degassed activated carbon,(49) which has a large surface. The absence of any changes in the solution composition in such cases showed that no electric double layer was formed at the immersed electrode.

By means of the zero solutions method, some authors obtained for a number of metals the pzc lying in the range 0.4–0.5 V (N.H.E.). This potential, independent of the metal nature, was called "the Billitzer (Billiter) zero potential." However, a critical analysis(4,8,50) of the data on Billitzer potentials shows that they are partly erroneous (for a mercury electrode) and partly applicable (for solid metals) to metals with oxidized surface.

Instead of introducing into solution an electrode with a clean surface from the outside, it is possible to obtain a clean surface of the solid electrode immediately in the solution by mechanical treatment. Andersen, Anderson, Perkins, and Eyring(51–53) measured the potential of an electrode the surface of which was renewed by scraping or cutting with the use of a rotating blade from a hard material (scrape potential). If one assumes that, in spite of continuous renewal, there has been time for equilibrium to be established between metal surface and solution, in the general case the scrape potential should correspond to the potential of zero total charge. In many cases the obtained pzc values are actually close to the optimum values of the zero total charge.(31,54)

The scraping method, however, is not free of some drawbacks. The surface arising during scraping or cutting has a higher chemical activity due to the appearance on it of a large number of dislocations,(55) which facilitate chemical interaction between metal and solvent. Possibly, the characteristics of this surface differ somewhat from those of a "normal" surface. In the case of platinum group metals, whose pzc depends on solution pH, the adsorption phenomena attending the formation of an equilibrium surface layer can lead to a change in the pH value when the surface increases rapidly in nonbuffer solutions. This change could be responsible for the appearance of a plateau on the curves expressing the dependence of the pzc of platinum group metals, obtained by the scrape method, on pH in the range of medium pH values,(52) which was not observed in other studies. Finally, the crystallographic characteristics of the surface arising as the result of mechanical treatment are uncertain; however, as will be shown below, the dependence of the pzc on face index has been conclusively established for a number of cases.

Noninski and collaborators(56) determined the pzc of electrodes from the change of the sign of the current passing through a "self-cleaning" rotating electrode in an inert atmosphere. Basically, this method should yield the same results as the determination of the scrape potentials.

3.3. Electrocapillary Methods

Up to now the classic measurement of electrocapillary curves, i.e., the determination of the dependence of surface tension on potential, remains a widely used method for determination of the pzc of liquid metals. According to what has been said above, the position of the maximum of the electrocapillary curve gives the potential of the zero total charge of the electrode ($E_{Q=0}$). It is necessary, however, to elucidate the physical sense of surface tension. This term is usually understood to mean the work expended under reversible conditions in increasing the interface by unity, e.g., by 1 cm^2. This increase can be achieved in different ways, e.g., by stretching, or splitting in the case of a solid, which must be carried out reversibly. In the case of a liquid surface, the work expended in the two cases is the same. This is not so with a crystalline solid body. Thus, if one stretches reversibly a solid crystal face, the work dW expended in stretching by ds generally depends on the direction of stretching. Therefore, the quantity $\gamma^* = \partial W/\partial s$ is a vector, while the reversible work γ necessary for formation of the unit surface is a scalar. The physical sense of the difference between γ^* and γ, which was pointed out already by Gibbs,(10) is associated with the fact that the surface formed by stretching, in the case of a solid, is not identical with an unstretched surface. The thermodynamic equations, which are a particular case of the general Gibbs adsorption equation, e.g., the Lippmann equation, contain the quantity γ, which becomes identical with the surface tension γ^* in the case of liquids. Unfortunately, there is as yet no generally accepted term for γ in electrochemical literature. γ shall be called the reversible work of formation of the unit surface,(57) and the dependence of γ on E both for liquids and solids, the electrocapillary curve.

The electrocapillary curves of liquid metals are measured by a capillary electrometer, which was suggested by Lippmann and improved by Gouy.(58) This capillary electrometer measures the pressure p necessary for forcing the liquid metal down to a certain point of a conical capillary wetted by electrolyte solution. Under the assumption that the capillary walls are completely wetted by electrolyte solution, $p = 2\gamma/r$, where r is the capillary radius at the meniscus level. Generally, the quantity r is not determined experimentally, and the capillary is calibrated by means of the solution for which the value of γ was determined by the sessile or hanging drop methods.

Grahame and collaborators(44) carried out precision determinations of the pzc by means of a capillary electrometer. A capillary electrometer was used also for the pzc determination for thallium(1) and indium(59) amalgams, gallium and its alloys(60,61) (Table 1). Figure 1 shows the electrocapillary curves of indium amalgams of different concentration, on which the influence of indium concentration on the pzc of amalgam is clearly evident. In view of the possibility of metal sticking to glass and partly for other reasons, attention of research workers is centered on the methods of determination of the γ, E curves from the sessile drop profile, the time of formation, weight, and volume of the detaching drop, and the maximum pressure when the drop grows at the tip of a turned-up capillary (for more detail see Reference 8). The latter method seems to be very promising. Drop methods can easily be made automatic.

The electrocapillary measurements give the potential values of the zero total charge, which, in the case of an ideally polarizable electrode, are identical with the potential of the zero free charge ($E_{\sigma=0}$) if Lorenz partial charge transfer is ignored. When the ideal polarizability condition is not fulfilled, the pzc can be assessed by determining the equilibrium γ, E dependences at constant chemical potentials of the oxidized and reduced forms, respectively, i.e., the electrocapillary curves of the first and second kind.(62)

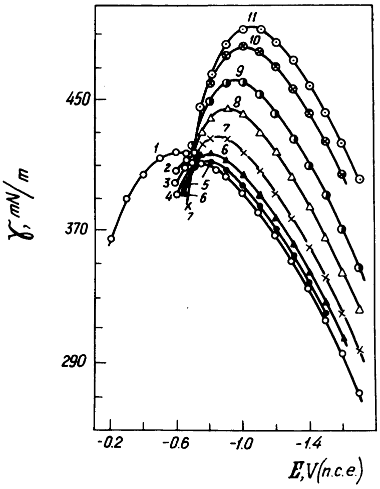

Figure 1. Electrocapillary curves of indium amalgam in 1 M KBr + 0.005 M H_2SO_4. Indium content in amalgam: 1, 0; 2, 0.19; 3, 0.85; 4, 1.97; 5, 3.50; 6, 7.80; 7, 16.70; 8, 30.40; 9, 43.10; 10, 62.20; 11, 70.30 wt %.(59)

Numerous attempts were made to extend the electrocapillary methods to solid electrodes. Gokhshtein(63,64) developed the method of determination of estance—the dependence of surface tension γ^* on electrode charge $\partial\gamma^*/\partial Q$. This quantity is related to the derivative of surface tension with respect to potential by the equation

$$\frac{\partial\gamma^*}{\partial Q} = \frac{\partial\gamma^*}{\partial E} \cdot \frac{\partial E}{\partial Q} = \frac{1}{C} \cdot \frac{\partial\gamma^*}{\partial E} \tag{3.1}$$

where C is the differential capacity of the electrode.

In Gokhshtein's device the electrode is in the form of an L-shaped plate, the bottom face of which is in contact with the electrolyte. Periodic changes of the electrode potential at a definite frequency lead to fluctuations of the surface tension force on this face. The resulting bending vibrations of the electrode are transferred to the piezoelectric cell connected to it, and thence, as an electric signal they come to the input of a selective amplifier. The oscillograms "surface tension amplitude $\Delta\gamma^*$–electrode potential" are taken at a fixed amplitude of the charge density of the electrode ΔQ, which allows consideration of these dependences when plotted as $|\partial\gamma^*/\partial Q| - E$. In the case of a solid body, it can be easily shown that

$$\partial\gamma^*/\partial E = -Q - (\partial Q/\partial \ln s)_E \tag{3.2}$$

It follows from (3.1) and (3.2) that the measurement of $\partial\gamma^*/\partial Q$ can be used as a method for the pzc determination if the second term in the right-hand side of Eq. (3.2) is small as compared to the first term. In the case of liquid metals, $(\partial Q/\partial \ln s)_E = 0$ since when the liquid surface is stretched, it remains identical with itself. For solid metals the quantity $(\partial Q/\partial \ln s)_E$ depends on the metal nature. The contribution of this term is comparatively small for Pb, Bi, Tl, and Cd. In these cases the estance measurements characterize correctly the influence of the anion on the pzc (Figure 2). However, for Pt the second term in Eq. (3.2) can be much larger than the first term. Due to the existence of the term $(\partial Q/\partial \ln s)_E$,

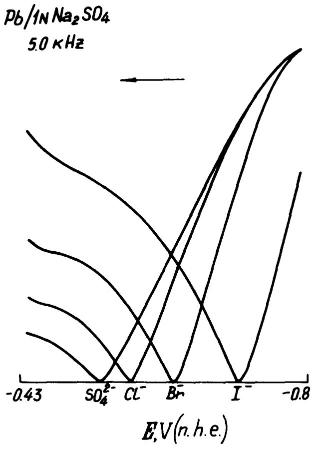

Figure 2. Influence of surface-active anions on the position of the estance zero on a lead electrode in 0.5 M H_2SO_4 with 0.15 M NaCl, NaBr, and NaI additions.(64)

the estance measurements by alternating current of different frequency give information on the properties of the double layer which cannot be obtained by any other methods.(64) However, for the pzc determinations in the case of solid electrodes, the estance measurements can be used only if there are reasons to suppose that $(\partial Q/\partial \ln s)_E \ll Q$.

Some other methods of determining the quantity $\partial\gamma^*/\partial E$ were proposed. Thus Beck observed the change in the length of a stretched metal tape with changing potential.(65) By means of a laser-optical system, Bockris and coworkers measured the dependence on potential of the bending of a thin glass strip metallized on one side and fastened from one end.(66,67) The pzc of carbon was determined by Soffer and Folman(68) from the relationship between surface tension and the linear dimensions of a rigid porous body.

The dependence of the value of γ on the solid metal potential can be assessed from the change of the contact angle θ at the electrode/gas/solution interface according to the equation

$$\gamma_{12} + \gamma_{23} \cos \theta = \gamma_{13} \tag{3.3}$$

where γ_{12}, γ_{13}, and γ_{23} are the values of γ for the interfaces metal/solution, metal/gas, and solution/gas, respectively. The dependence of θ on E was first measured by Möller in 1908. Reproducible data were obtained in 1932.(69)

A direct measurement of the contact angle can be substituted by measuring the liquid rise in a metal capillary,(70) or by measuring the rise of the solution meniscus at a vertical metal surface(71,72) or a wire. The determination of the θ–E curve in the case of mercury points to the dependence of γ_{13} on potential. Hence, at the metal/gas interface under equilibrium conditions there exists a thin wetting solution film.(69) The main obstacle in using this method is the difficulty of determing the equilibrium values of θ in the case of solid interfaces.

According to Rehbinder's theory, the quantity γ determines the work expended in brittle breakdown or plastic deformation of solids. This concept was used as a basis for developing some methods of the pzc determination from the potential dependence of hardness, inverse creep rate, and yield point.(73,74) These parameters characterizing the strength of a solid reach their maximum value at the pzc (Figure 3). In spite of the fact that the work expended in real

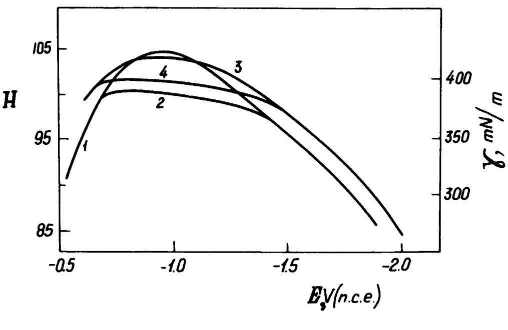

Figure 3. Dependence of the hardness (H) of thallium on the potential in the solutions 0.5 M Na_2SO_4 (1) and 0.5 M Na_2SO_4 + 0.185 M *iso*-$C_5H_{11}OH$ (2), and electrocapillary curves for 41.5% thallium amalgam in solutions of 0.5 M Na_2SO_4 (3) and 0.5 M Na_2SO_4 + 0.175 M *iso*-$C_5H_{11}OH$ (4).(73)

conditions differs from the reversible work γ, the methods developed by Rehbinder and his school lead to reasonable pzc values. The determination of the dependence on potential of the breakdown of a metal under the action of ultrasound and hydroabrasion gives also reasonable approximate values.(75)

Bockris and collaborators suggested a method for determining the pzc from the maximum on the curve of the dependence of external friction on potential.(76,77) The decrease of external friction observed when rubbing surfaces are charged is explained by repulsion between two diffuse double layers arising on base metal and on the sliding contact.(77) When investigating hardness by means of Herbert's pendulum, Rehbinder and collaborators(78) showed that when the pendulum exerts a heavy pressure on the bearing causing it to break, at the pzc the damping decrement of pendulum oscillations is minimal since the pzc corresponds to maximum hardness. When the pressure of the pendulum on the bearing decreases, external friction plays a dominant role in the damping of pendulum oscillations, and at the pzc the damping decrement becomes maximal since the pzc corresponds to maximum external friction. (For interpretation of the experiments with a pendulum, see also References 8 and 50.)

3.4. Adsorption Methods

If, during formation of the electric double layer, the Gibbs adsorption of a certain component Γ_i is not compensated by its supply from outside, its content in the electrolyte solution changes; and in the case when a conductor of the first class in equilibrium with the solution has a variable composition, its composition also changes. In the case of gas electrodes (hydrogen, oxygen), changes in composition also occur due to the double-layer formation. Therefore, basically, the determination of the changes in the composition of the solution or the gas phase can be used for investigation of the double-layer structure and for finding the pzc.

The adsorption effects associated with the electric double-layer formation were first observed at the beginning of this century by Palmaer and Billitzer. The importance of the adsorption methods became evident when they were applied to disperse platinum(25) and activated carbon.(79) It was assumed that the surface charge is caused by ionization of adsorbed hydrogen and oxygen to form H^+ and OH^- ions or by discharge of the latter, and is accompanied by a change in the solution acidity. In the case of electrodes with developed surfaces, the acidity change can be established by usual analytical methods, which make it possible to find Γ_{H^+} or Γ_{OH^-}. If the interface position is chosen so that $\Gamma_{H_2O} = 0$, $\Gamma_{H^+} = -\Gamma_{OH^-}$, and it will be sufficient to consider only Γ_{H^+}. As was shown earlier, this quantity characterizes the total charge of the second kind at $\mu_H = \text{const}$.

In experiments with platinum metals in determining Γ_{H^+}, the value of $\Delta\Gamma_{H^+}$ was found when passing from the reversible hydrogen potential to the given value of the potential E_H. (E_H is the electrode potential measured against

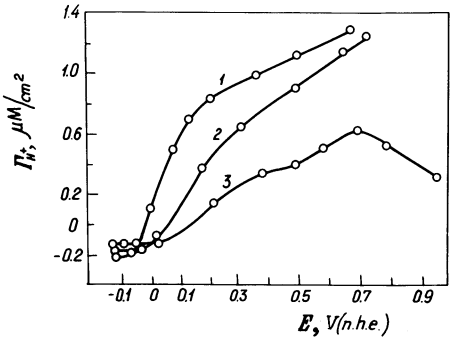

Figure 4. Dependence of Γ_{H^+} on potential on a Pt/Pt electrode in acidified solutions of salts. Initial composition of solutions: 1, 1 M NaBr + 0.01 M HBr; 2, 1 M NaCl + 0.01 M HCl; 3, 0.5 M Na_2SO_4 + 0.005 M H_2SO_4.(25)

a normal hydrogen electrode in the same solution.) Then, the value of Γ_{H^+} at $E_H = 0$ was determined in an experiment in which a dry electrode was introduced into the initial solution in a hydrogen atmosphere. After determination of Γ_{H^+} at $E_H = 0$, it was possible to plot the Γ_{H^+}–E_H curve.(25,28)

Figures 4 and 5 show the dependences of Γ_{H^+} on E_H at a Pt/Pt electrode in acidified and alkalized salt solutions.(25,80) These dependences allow one to find the potentials at which the condition $\Gamma_{H^+} = 0$ is valid, i.e., to determine the potentials of zero total charge (pztc) of the second kind. The measurement of the dependence of Γ_{H^+} on the alkali metal cations concentration showed that when these are present in sufficient excess, the H^+ ions are completely displaced from the ionic side of the electric double layer ($A_{H^+} = 0$), and the quantity Γ_{H^+} proves to be equal to the free surface charge σ(30) [see Eq. (2.4)]. For this reason pztc of the second kind was called the potential of zero free charge (pzfc).

Figures 4 and 5 clearly show the specific features of the σ, E_H curves, typical of platinum metals and responsible for the difference of their behavior from that of a mercury electrode, viz., slight dependence of σ on E_H at small E_H, decrease of σ with increasing E_H when adsorbed oxygen appears on the surface in acid solutions containing no halogen anions, and weak dependence of σ on E_H in alkaline solutions in the absence of surfactant anions. These specific features are associated with the adsorption of hydrogen and oxygen on platinum and with their influence on the adsorption of the solution ions.

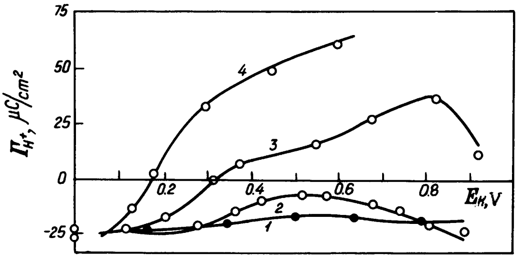

Figure 5. Dependences of Γ_{H^+} on potential on a Pt/Pt electrode in solutions: 1, 0.01 M KOH; 2, 0.01 M KOH + 1 M KCl; 3, 0.01 M KOH + 1 M KBr; 4, 0.01 M KOH + 1 M KI. The values of Γ_{H^+} are referred to true electrode surface.(33)

It follows from the definition of Γ_{H^+} and the electroneutrality condition that

$$\Gamma_{H^+} = \Gamma_{A^-} - \Gamma_{C^+} \tag{3.4}$$

Thus pztc's of the second kind can be defined also as the potential at which $\Gamma_{A^-} = \Gamma_{C^+}$. Such a method of determining the pzc with the use of tracers for finding Γ_{A^-} and Γ_{C^+} was proposed by Balashova.(26) The most accurate measurements of Γ_{A^-} and Γ_{C^+} were made by means of the technique proposed by Kazarinov.(81) Figure 6 illustrates the determination of pzfc by means of the tracer technique. Curve 1 gives the dependence of cation adsorption and curve 2 that of anion adsorption on potential. The abcissa of their point of intersection determines pzfc; at this point curve 3, giving the dependence of $\Gamma_{H^+} = \sigma$ on E_H, passes through zero.

The pztc's of the first kind at which $\Gamma_H = 0$ can be determined in principle by direct measurement of the potential assumed by the previously carefully degassed electrode when it is immersed into solution. This method was successfully used for activated carbon;(49) but so far it has not been possible to apply it to platinum metals, owing to the difficulty of preparing degassed electrodes with developed surfaces. For this reason, for determination of pztc of the first kind, a nonthermodynamic method is used, based on the equation $\Delta\Gamma_H = \Delta A_H - \Delta\Gamma_{H^+}$, where ΔA_H is the change in the amount of adsorbed hydrogen per cm^2 surface. The substance of the method is illustrated by Figure 7, in which curves 1 and 2 represent the dependences $\Delta\Gamma_H - E_H$ and $\Gamma_{H^+} - E_H$, respectively. The origin of the abcissa corresponds to the zero value of σ, so that the abcissa of each point of curve 2 gives the value of Γ_{H^+}. Curve 3 is the dependence of E_H on ΔA_H, which was found by subtracting Γ_{H^+} from $-\Delta\Gamma_H$. At $E_H > 0.4$ V, the ΔA_H, E_H curve rises vertically, i.e., A_H no longer depends on E_H. It is natural to suppose that here begins the double-layer region of the charging curve, which extends up to the point at which oxygen deposition starts. (The oxygen region is not shown in Figure 7.) The point of intersection of curves 1 and 3 corresponds to the potential of zero free charge. The tangent to curve 3 in its

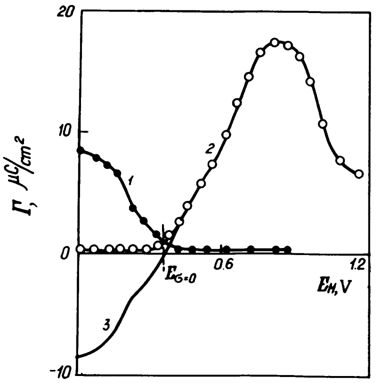

Figure 6. Dependences of the adsorption of Na^+ cations (1), SO_4^{2-} anions (2) and of the free surface charge (3) on the potential of a Pt/Pt electrode in solution: 5×10^{-4} M H_2SO_4 + 1.5×10^{-3} M Na_2SO_4.(111)

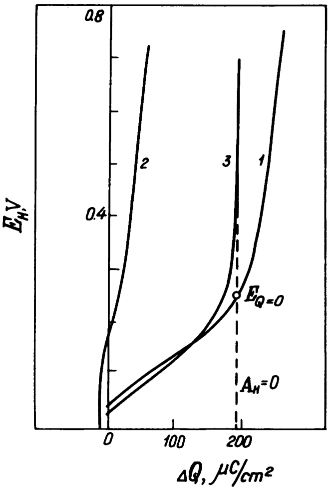

Figure 7. Dependences of the total (1) and free (2) surface charges and of the amount of adsorbed hydrogen (3) on potential on a Pt/Pt electrode in the solution 1 *M* KCl + 0.01 *M* HCl.(111)

vertical portion, as shown in the figure, intercepts on the abcissa a point corresponding to the zero value of A_H. The distance between any point of curve 3 and the straight line $A_H = 0$ is equal to A_H, and the horizontal distance between curves 1 and 3 is equal to σ. Therefore the length of the section of the straight line, parallel to the abscissa and drawn through the point of intersection of the straight line $A_H = 0$ and curve 1, between curves 1 and 3, determines simultaneously the values of A_H and σ on curve 1. Hence, at the point of intersection of curve 1 and the straight line $A_H = 0$, the quantity $\Gamma_H = A_H - \sigma$ vanishes. Thus the pztc of the first kind can be found.

The described method of determination of pztc of the first kind can be used only in the presence of an ideal double-layer region, which is the case only in solutions containing surface-active anions, e.g., in acidified solutions of chlorides or bromides or in alkalized solutions of iodides.(31) However, if the value of the total charge in a certain solution is known, then the dependence of Γ_H on the electrode potential can be obtained and, hence, pztc of the 1st kind determined for the same electrode in other solutions by measuring the shift of the electrode potential upon substitution of one solution by another at constant total charge value $Q = -\Gamma_H$. This condition is fulfilled if the potential shift is measured on an isolated electrode, and the possibility of molecular hydrogen and oxygen or some other oxidants or reducing agents, except H^+ and OH^- ions, getting into solution is ruled out.

The dependences of Γ_{H^+} on E_H can be calculated if one knows the values of the potential shifts with changing solution pH at constant total charge Q,(28) i.e., under the so-called isoelectric conditions. In fact, the Gibbs adsorption equation for a reversible system formed of the components H, CA, and HA at $\Gamma_{H_2O} = 0$ is as follows(29):

$$d\gamma = -\Gamma_H \, d\mu_H - \Gamma_{HA} \, d\mu_{HA} - \Gamma_{CA} \, d\mu_{CA} \qquad (3.5)$$

where Γ_{HA} and Γ_{CA} are the Gibbs adsorptions, and μ_{HA} and μ_{CA} are the chemical potentials of acid and salt. If [CA] $\gg$ [HA], so that it can be assumed that $\mu_{CA} = \text{const}$, taking into account the relations $\Gamma_{HA} = \Gamma_{H^+}$, $d\mu_H = -dE_H$ and $\Gamma_H = -Q$, from Eq. (3.5), the following is obtained:

$$(\partial\Gamma_{H^+}/\partial E_H)_{\mu_{HA},\mu_{CA}} = -(\partial E_H/\partial\mu_{HA})_{Q,\mu_{CA}}(\partial Q/\partial E_H)_{\mu_{HA},\mu_{CA}} \tag{3.6}$$

or

$$(\partial\Gamma_{H^+}/\partial E_H)_{\mu_{H^+},\mu_{CA}} = -(\partial E_H/\partial\mu_{H^+})_{Q,\mu_{CA}}(\partial Q/\partial E_H)_{\mu_{H^+},\mu_{CA}} \tag{3.7}$$

The derivative $(\partial E_H/\partial\mu_{H^+})_{Q,\mu_{CA}}$ gives the value of the potential shift for as small a change in the solution composition as possible under isoelectric conditions. The technique of measurement of this quantity was developed by Frumkin *et al.*(28) The second factor in the right-hand side of Eq. (3.7) represents the slope of the charging curve of the first kind in the HA + CA solution. Thus, from Eqs. (3.6) and (3.7), the value of $\partial\Gamma_{H^+}/\partial E_H$ for the solution of given composition can be found; and hence, one can determine the dependence of Γ_{H^+} on E_H from a single value of this coefficient found in the experiment. The calculated dependences of Γ_{H^+} on E_H were compared with those found experimentally for Pt, Rh, Ir, Pd, and Ru electrodes with developed surfaces in acidified and alkalized Na_2SO_4, KCl, and KBr solutions and in KI and KOH solutions.(28–33) The comparison proved the validity of Eqs. (3.6) and (3.7) and, hence, of Eq. (3.5) and allowed determination of the areas of its practical applicability. At the same time, this comparison of calculation and experiment revealed the reliability of the pzc determination by adsorption methods.

3.5. Methods Based on the Dependence of the Properties of the Diffuse Part of the Double Layer on the Surface Charge

Several methods of determination of the potential of zero free charge are based on the influence of the surface charge σ on the space distribution of potential within the diffuse part of the electric double layer.

3.5.1. Differential Capacity Minimum

The most important of the methods under consideration is the determination of the position of the minimum on the curve showing the dependence of the differential capacity C on the electrode potential, E. This method was proposed by Vorsina and Frumkin.(82)

It follows from the Gouy–Chapman theory that the diffuse layer thickness in the case of symmetrical electrolyte is maximal at $\sigma = 0$ and is inversely proportional to $c^{1/2}$, where c is the electrolyte concentration. The dependence of the diffuse layer thickness on concentration leads to a decrease of its capacity with dilution of the solution, which in sufficiently diluted solutions affects the total electrode capacity. As a result, a minimum appears on the C–E curves, whose potential in diluted solutions of surface-inactive electrolytes approaches pzfc.

Grahame(16) proposed to model the electric double layer by means of two capacitors with the capacities C_1 and C_2 connected in series, which leads to the relation

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \tag{3.8}$$

where C_1 is the dense layer capacity and C_2 is the diffuse layer capacity. According to Grahame, in the absence of specific adsorption, the value of C_1 should not depend on the electrolyte concentration, which makes it possible to find, using the diffuse double-layer theory, the C–E dependence for an arbitrary concentration if the C_1–E dependence has been determined from experimental C values and calculated C_2 values for any one concentration. These conclusions were verified by Grahame for the case of aqueous NaF solution. It was shown that they extend to systems with weak specific adsorption.(83)

It follows from Eq. (3.8) that at constant C_1, a linear dependence of $1/C$ on $1/C_2$ with the slope equal to unity should be valid (Parsons–Zobel criterion).†

The differential capacity measurements afford reliable data on the pzc only if certain conditions are fulfilled. First of all, it is necessary that the electricity supplied to the electrode/electrolyte interface should be expended only in charging the double layer. A criterion of the fulfillment of this condition is the absence of the frequency dependence of the capacity component of impedance which is being measured. Another criterion is a good fit of the measured capacity values at different solution concentrations to Eq. (3.8).

The method of the pzc determination from the capacity minimum was used, apart from mercury, for other liquid metals: thallium and indium amalgams, gallium, gallium–indium, and gallium–thallium alloys. The capacity measurements of the electric double layer for determination of the pzc of solid electrodes were carried out for the first time by Borisova, Ershler, and Frumkin in 1948. However, considerable time was needed to improve sufficiently the technique of preparation of the solution and of the solid electrode surface, so that the C–E curves satisfying the conditions pointed out above could be obtained. A significant contribution to the development of these techniques was made by Leikis and co-workers, Bagotskaya, Grigoryev, and by Past and Palm in USSR. Quite satisfactory C–E curves with respect to their shape and the dependence on the electrolyte concentration were obtained at an early stage of development of these studies by Randles in England. A further step in the development of the technique of these measurements was the transition from polycrystalline surfaces to faces of single crystals (Budewski and co-workers).

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† The deviation of the slope from unity in the case of solid electrodes can be associated with the difference between true and apparent electrode surface and also with crystallographic inhomogeneity of the solid electrode surface. Such deviation is observed also, however, for liquid gallium.(84) It was suggested by Frumkin *et al.*(84) that it may be indicative of a difference in the dielectric constant of water in the diffuse layer and in the solution bulk.

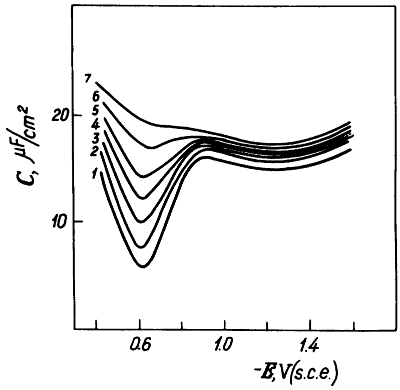

Figure 8. Differential capacity curves of a bismuth electrode in KF solutions: 1, 0.001 M; 2, 0.002 M; 3, 0.005 M; 4, 0.01 M; 5, 0.02 M; 6, 0.05 M; 7, 0.1 M.(89)

At present reliable data on the pzc have been obtained by the capacity minimum method for the following metals: Ag (111),(85,86) Ag (100),(87) Ag (110),(85) Au (110),(88) Bi (polycrystalline),(89) Bi (111),(90) Cd,(91) Ga,(60,61) In,(92) Pb,(93) Sb,(94) Sn,(95) Tl.(96) As an illustration of the determination of the pzfc from the capacity minimum, some data for a Bi electrode are given in Figure 8.

In the pzc determination solutions of alkali metal fluorides were used for most electrodes, due to the low adsorbability of the F^- ion. However, on tin the fluorine ion proves to be surface active, and optimum results are obtained with perchlorates. In unsymmetrical surface-inactive electrolytes, the minimum on the C–E curves shifts in the direction of more negative σ values in the case of a higher anion charge and in the positive direction in the case of a higher cation charge.

The C–E curves of polycrystalline and single-crystal silver electrodes have been compared, and an attempt was made to describe the C–E curve of a polycrystal as an additive sum of the C–E curves of individual faces of a single crystal(97):

$$C = C_{(111)}\theta_{(111)} + C_{(100)}\theta_{(100)} + C_{(110)}\theta_{(110)} \qquad (3.9)$$

where $C_{(111)}$, $C_{(100)}$, and $C_{(110)}$ are the capacities on individual faces of a single crystal and $\theta_{(111)}$, $\theta_{(100)}$, and $\theta_{(110)}$ are the fractions of these faces on the surface of a polycrystalline electrode. As can be seen from Figure 9, the calculated curve roughly corresponds to the experimental one. It appeared that, since the C–E curves of the single-crystal faces of silver, as with other electrodes, are unsymmetrical, when they are added in compliance with Eq. (3.9), the minimum on the total capacity curve lies closer to the minimum of the C–E curve of the face whose pzc has the most negative value. This means that the minimum on the C–E curve of polycrystalline silver does not correspond to its pzc, i.e., the potential at which

$$\sigma = \sigma_{(111)}\theta_{(111)} + \sigma_{(100)}\theta_{(100)} + \sigma_{(110)}\theta_{(110)} = 0 \qquad (3.10)$$

but is located more negatively than this potential.

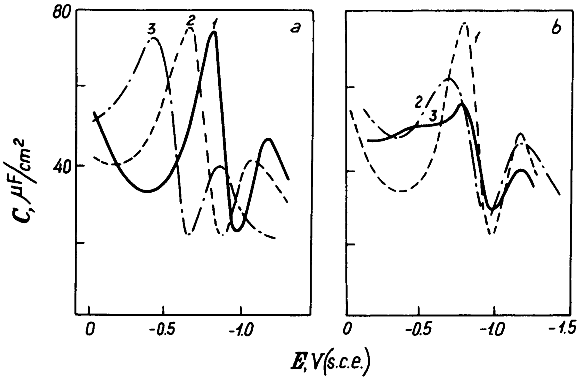

Figure 9. Differential capacity curves of a silver electrode in 0.01 M NaF: (a) for the faces {110} (1); {100} (2) and {111} (3) of Ag single crystal. (b) for the face {110} (1), for polycrystalline silver (2), and the curve calculated by means of Eq. (3.9) (3) at $\theta_{(110)} = 0.31$, $\theta_{(100)} = 0.23$, and $\theta_{(111)} = 0.46$.[97]

In principle, this complication caused by crystallographic inhomogeneity of the surface extends to all polycrystalline electrodes. A significant difference between the pzc and the potential of the minimum of the C–E curve of a polycrystalline electrode is to be expected only in the case when the pzc of individual faces differ by some tenths of a volt. In the case of Bi and, probably, Pb, Cd, In, Sn, Tl, and Sb, the potential of the minimum on the C–E curve of a polycrystal can be roughly equated with the pzc of the metal.

In the case of metals of the VIII group of the Periodic System, the interpretation of the C–E curves, apart from the difficulties associated with the crystallographic surface inhomogeneity, is further complicated by the fact that the double-layer capacity is superimposed by the pseudocapacity of the adsorbed hydrogen ionization and by ionization of the metal itself (in the case of the iron group metals). Nevertheless, repeated attempts to determine the pzc's of these metals are reported in the literature.[8,27] The data on the capacity minimum for platinum cannot be considered conclusive as yet. The C–E curves for an iron electrode satisfying the above criteria have been obtained.[98] But in order to draw definitive conclusions, it is necessary to perform measurements on individual faces of an iron single crystal.

The electrolyte concentration at which a minimum appears on the C–E curve, caused by the double-layer diffuseness at the pzc, depends on the ratio between the first and the second terms in the right-hand side of Eq. (3.8). It is the higher, the larger is C_1. (For example, for mercury the concentration is $\sim 10^{-2}$ M and for Ga $\sim$ 10^{-1} M.) The sensitivity of the signal being measured to a change in the differential capacity of the diffuse layer can be considerably increased by applying to an electrochemical cell two sinusoidal currents of the same amplitude and similar frequencies ω_1 and ω_2.[99] The voltage amplitude of the vibrations arising in the circuit is recorded as a function of the difference

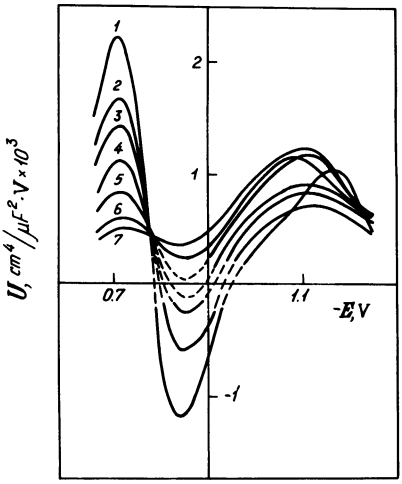

Figure 10. Dependence of U on potential on cadmium in NaF solutions: 1, 0.026 M; 2, 0.04 M; 3, 0.06 M; 4, 0.09 M; 5, 0.13 M; 6, 0.20 M; 7, 0.30 M.(100)

frequency ($\omega_1 - \omega_2$). The value of the amplitude of these vibrations U at the cell terminals is

$$U = \text{const}\,(1/C^3)(dC/dE) \tag{3.11}$$

Using Grahame's model it is possible to show that the U–E curves measured in electrolytes of different concentration must intersect at the pzc. This conclusion was confirmed by measurements on mercury and cadmium(100) (Figure 10).

3.5.2. Electrokinetic Phenomena

When a tangential electric field is applied to the interface between two phases at which an electric double layer exists, pondermotive forces arise at this interface which set into motion, depending on experimental conditions, the particle present in the liquid (electrophoresis) or the bulk of the liquid (electro-osmosis). On the other hand, any motion along the interface between two phases gives rise to potential differences, for example, when solid particles are falling in liquid (sedimentation potential) or when a liquid is forced through a diaphragm (streaming potential). These phenomena can be considered to be the reverse of electrophoresis and electro-osmosis. The velocity of electrokinetic motion of a particle of an arbitrary shape in liquid medium in a uniform electric field of the strength X is given by the equation(101)

$$v_{\mathrm{E}} = \tfrac{1}{4}\varepsilon\zeta X/\pi\eta \tag{3.12}$$

where ε is the dielectric constant of the solution, η is its viscosity, ζ is a certain effective potential difference within the electric double layer, the so-called electrokinetic (or zeta) potential. Equation (3.12) is applicable to a particle from a hard metal, if the polarizability of the metal/solution interface is large enough.

Billitzer was the first to use the electrokinetic phenomena to find the pzc (which Billitzer thought was the absolute zero of potential) from the reversal of the zeta-potential sign. This was determined from the direction of the electrophoresis of metal suspensions, from the deviation of wires or of a small suspended metal sphere in the electric field and from the potentials arising when metal particles are falling in a vertical tube filled with electrolyte (silver, gold, platinum, iron). The experimental part of Billitzer's studies raised some objections, but the reversal of the sign of ζ at very positive potentials ($+0.4 - +0.5$ against N.H.E.) is undoubtedly a real fact. As was shown by Balashova and Frumkin,(102) under appropriate experimental conditions, the electrokinetic measurements in the case of platinized platinum lead to pzc values comparable to those obtained from the adsorption measurements. If follows from these experiments that, in the absence of surface oxidation and specific ion adsorption, the electrokinetic methods can afford information on the potential of zero free charge.

An electric field in electrolyte solution causes a liquid metal drop to move. This phenomenon, discovered by Christiansen in 1903, can be observed on a sessile or on a free-falling mercury drop. Its mechanism is essentially different from electrophoretic motion of solid particles. The electric field in solution sets up a potential difference and, hence, a difference in the surface tension between different points of the interface. As a result, the interface starts to perform tangential motion, which push the mercury drop away from the surrounding medium. According to the quantitative theory of these phenomena developed by Frumkin and Levich(103,104) and experimentally proven by Frumkin and Bagotskaya, the potential of the drop at which velocity of tangential motion of its surface vanishes, coincides with the potential of the electrocapillary curve maximum. The studies on electrocapillary phenomena do not provide new information on the pzc, but are of independent interest, especially in connection with the problem of polarographic maxima.

3.5.3. Photoemission of Electrons from Metal into Solution

Photoemission of electrons from a metal into the electrolyte solution is among relatively new phenomena in electrochemistry which could be used for pzfc determination. Photoemission of electrons occurs when a metal electrode is illuminated by light, the quantum energy of which exceeds the work function in the metal/solution system.(105) The emitted electrons are thermalized and solvated (at distances from the electrode of the order of 10–100 Å), and then enter into reaction with the electron acceptors specially added to the solution (e.g., H_3O^+, N_2O, NO_3^-, etc.). Cathodic polarization of the electrode decreases the work function and therefore increases the photoemission rate.

In the case of relatively diluted solutions, when the de Broglie wavelength of an emitted electron λ is less than the thickness of the diffuse part of the double

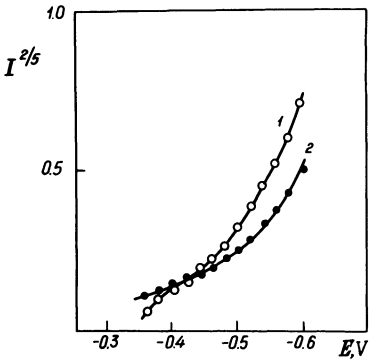

Figure 11. Dependences of $I^{2/5}$ on potential in 10^{-3} M HCl (1) and 10^{-3} M HCl + 9 × 10^{-3} M KCl (2) on a mercury electrode. Potentials are referred to SCE.(106)

layer, a theoretical analysis of the photoemission process(106) leads to the following relation for the photoemission current:

$$I = A[\hbar\omega - \hbar\omega_0 - e_0(E - \psi_1)]^{5/2} \tag{3.13}$$

where A is a constant, $\hbar\omega$ is the light quantum energy at the frequency ω, $\hbar\omega_0$ is the work function in the metal solution system at the potential $E = 0$, measured against some reference electrode, and ψ_1 is the potential at the point which is at the distance of the order of λ from the electrode. The correction for the ψ_1 potential is similar to that introduced into the equation of electrochemical kinetics to take account of the diffuseness of the electric double layer. At pzfc, $\psi_1 = 0$, and the photocurrent–potential curves for electrolyte solutions of different concentration should intersect (Figure 11).

The described method was used to determine the pzc of some metals (Pb, Bi, Cd, In, Hg), which proved to be in good agreement with the independent measurements from the differential capacity minimum.(106) A possible error in these determinations is about 0.02–0.03 V.

3.5.4. Interaction of Two Double Layers

The presence of the diffuse electric double layer leads to repulsion between two charged surfaces. As was shown by Deryaguin, Voropaeva, and Kabanov,(107) this effect can be utilized for finding the pzc. The quantity to be determined experimentally is the force barrier which is necessary to surmount in order that two threads crossed at an angle of 90° should come into contact. The force barrier was measured by means of a torsion balance with a vertical suspension; one of the threads acted as the weight lever. The second thread could be brought close to the first thread or drawn away from it. The contact between the threads, which was evidenced by the disappearance of ohmic resistance between them, arose when the suspension was twisted to an angle depending on the barrier height. At the pzc, the Coulomb portion of the force barrier disappears; at the distance from the pzc greater than 0.15–0.2 V, it reaches the limiting value in accordance with the theory of repulsion between diffuse layers.(107) Also, in agreement with the theory, the Coulomb portion of the force barrier disappears with increasing electrolyte concentration. The method under consideration was used for Pt, Au, and Fe, the greatest attention being given to Pt.(108) However, the solution purification seemed to be insufficient (especially in the case of Pt) to ensure the cleanliness of the small surface in contact with a relatively large solution volume. Moreover, it is difficult to compare the data with the results obtained by other methods due to the absence of information on the pH of the test solution. It would be desirable if this method, which has a serious theoretical basis and elegant equipment at its disposal, should be verified under more carefully elaborated electrochemical conditions of the experiment.

It should be stressed that the results of all the methods based on the diffuse layer properties are affected by the crystallographic surface inhomogeneity. Therefore, with the use of these methods, it is possible to obtain reliable data on the pzc only for single-crystal electrodes.

4. Influence of Metal Nature, Solution Composition, and pH on the Potentials of Zero Charge

Numerous studies carried out with the use of the methods described above revealed the dependence of the pzc on a large number of factors: metal nature, solution composition, solvent nature, temperature, and, in the case of hydrogen- and oxygen-adsorbing metals, on the pH of the medium. It seems reasonable to attempt elucidation of the role of each of these factors separately.

The influence of the metal nature can be followed if one examines the behavior of different metals in the same solvent at constant temperature and considers only the electrolyte solutions in which the interaction of their ions with the electrode metal is determined by electrostatic forces alone. Such ions are assumed to be adsorbed nonspecifically. When nonspecifically adsorbable ions approach the electrode surface, they retain their hydration sheath. When this condition is not fulfilled, specific adsorption results. Specific adsorption can be the result of the interaction of ion with electrode metal, which is accompanied by partial loss of the hydration sheath (according to Lorenz, also by partial charge transfer) as well as loss of ion expulsion from the water bulk, especially in the case of large organic ions.

Practically all ions to a greater or lesser degree show specific adsorbability at the electrode/solution interface. However, in the presence of weak specific adsorption, the shift of the pzc often proves to be less than 0.1 mV, i.e., less than the present accuracy of determination of this quantity.(83) To weakly adsorbable ions belong the cations of alkali and alkali–earth metals; their adsorbability decreases with the crystallographic radius. Among the anions the specific adsorbability is the least pronounced for F^-, HF_2^-, BF_4^-, and PF_6^- ions and also for some doubly charged anions, such as SO_4^{2-} or CO_3^{2-}. The structure of the double layer near the pzc is the less distorted by specific ion adsorption, the lower is solution concentration; and the independence of the found pzc value of the electrolyte concentration in a sufficiently wide concentration range indicates that the influence of specific adsorption has been eliminated. Thus, determining the pzc with sufficiently diluted electrolyte solutions whose ions do not show appreciable specific adsorbility, or extrapolating to infinite dilution, one obtains the pzc values depending only on the nature of the metal and the solvent. Presently, at ordinary temperatures a reliable set of pzc values is available, primarily for aqueous solutions. If the solution composition to which a particular pzc value refers is not specially indicated, it is understood that the pzc value of a metal was obtained in aqueous solutions at ordinary temperatures and, as far as possible, not distorted by specific adsorption. For this value Antropov suggests the term "zero point of metal" and recommends to differentiate between the notions "zero point" and "potential of uncharged surface."(129) However, in the absence of specific adsorption of ions or neutral surface-active substances as well, one must take into account the potential difference resulting from the orientation of solvent molecules,(7,12–14) which to a considerable extent eliminates the difference between the pzc in the presence or absence of specific adsorption.

From a short review of the methods proposed for the pzc determination, it follows that for liquid metals it is possible to use equally well the electrocapillary measurements, a dropping electrode, and the determination of the potential of the differential capacity minimum of the diffuse layer. In the case of solid metals, the most reliable results are obtained by adsorption measurements, and in the case of ideally polarizable electrodes, the determination of the position of the differential capacity minimum of the diffuse layer yields the most reliable results. In the latter case the obtained values are simultaneously the potentials both of zero free ($E_{\sigma=0}$) and zero total ($E_{Q=0}$) charges. However, in the case of hydrogen-adsorbing metals, the quantities $E_{Q=0}$ and $E_{\sigma=0}$ do not coincide. In Table 1 are given the data for various metals, which can be considered as recommended pzc values. These data relate to the temperature about 25°C, except gallium (32°C). They give an idea of the dependence of the pzc on the nature of the metal.

The influence of solution composition on the pzc was studied by many authors. Figure 12 shows the electrocapillary curves of mercury in equimolar NaF, NaCl, NaBr, and NaI solutions.(111) The specific anion adsorption shifts the pzc in the negative direction; the shift increases with rising surface activity of anions in the sequence $F^- < Cl^- < Br^- < I^-$. Specifically adsorbed cations, e.g., Tl^+ cations, shift the pzc in the positive direction.(112)

Esin and Markov,(113) and also Iofa, Ustinsky, and Eiman,(114) were the first to study quantitatively the influence of the surface-active anion concentration on the pzc of mercury. It was found that when the activity of an electrolyte containing surface-active anions changes by an order, the shift of the pzc in the negative direction is ~100–200 mV; whereas, from the double-layer theory, assuming the charge of specifically adsorbed anions to be uniformly diffuse, one-half of that would be expected. On Grahame's suggestion an abnormally

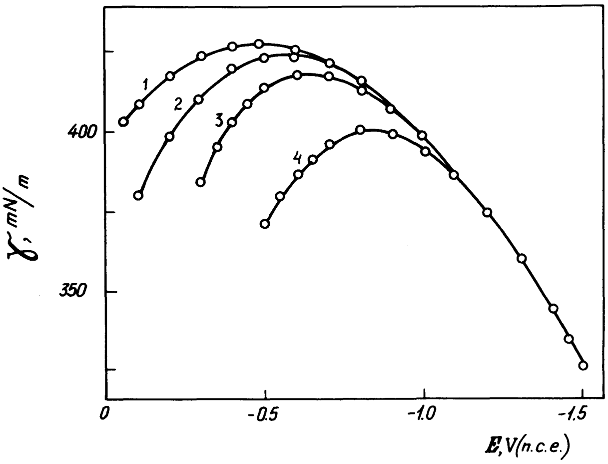

Figure 12. Electrocapillary curves of a mercury electrode in solutions: 1, 0.9 *M* NaF; 2, 0.9 *M* NaCl; 3, 0.9 *M* NaBr; 4, 0.9 *M* NaI.(111)

large pzc shift was called the Esin–Markov effect. To explain the shift of the pzc observed in the presence of surface-active anions, Frumkin's concept of the discrete nature of adsorbed ions was used. This concept formed the basis of the model theories of the Esin–Markov effect developed in numerous papers.(111,115)

From the basic electrocapillarity equation, in the case of an ideally polarizable electrode, Frumkin and Parsons(116,117) have shown that it is possible to obtain a thermodynamic relation for the dependence of the potential of constant free charge on electrolyte concentration, which in a particular case of 1,1-valent electrolyte is of the form

$$(\partial E/\partial \ln a_\pm)_\sigma = -(RT/F)[\partial(\Gamma_{C^+} + \Gamma_{A^-})/\partial\sigma]_{a_\pm} \qquad (4.1)$$

At $\sigma = 0$ this relation describes the dependence of the pzc on $\ln a_\pm$. It is clear from Eq. (4.1) that the Esin–Markov effect should be observed in cases when the adsorption both of anions and cations increases with σ. Under this condition the Esin–Markov effect is observed not only at $\sigma = 0$, but also at any constant σ.

The studies carried out by the adsorption methods and by the isoelectric potential shifts method showed that on platinum metals pztc of the first and second kinds shift in the negative direction in the presence of specifically adsorbed anions and in the positive direction in the presence of specifically adsorbed cations.(31) By virtue of the presence of two total charges, Q and $\Gamma_{H^+} = \sigma$, for platinum metals it is necessary to introduce two Esin–Markov coefficients, $(\partial E/\partial \ln a_\pm)_{Q,\mu_{H^+}}$ and $(\partial E/\partial \ln a_\pm)_{\sigma,\mu_{H^+}}$. The following thermodynamic relations were obtained for these quantities(29,31):

$$(\partial E/\partial \ln a_\pm)_{Q,\mu_{H^+}} = -(RT/F)[\partial(\Gamma_{C^+} + \Gamma_{A^-})/\partial Q]_{a_\pm,\mu_{H^+}} \qquad (4.2)$$

$$(\partial E/\partial \ln a_\pm)_{\sigma,\mu_{\mathrm{H}^+}} = -(RT/F)[\partial(\Gamma_{\mathrm{C}^+} + \Gamma_{\mathrm{A}^-})/\partial\sigma]_{a_\pm,\mu_{\mathrm{H}^+}} - 2\frac{(\partial A_{\mathrm{H}}/\partial \ln a_\pm)_{E,\mu_{\mathrm{H}^+}}}{(\partial\sigma/\partial E)_{a_\pm,\mu_{\mathrm{H}^+}}} \qquad (4.3)$$

These relations become identical with each other and with relation (4.1) for an ideally polarizable electrode when $A_{\mathrm{H}} = 0$ and $Q = \sigma$. The direct determinations of Esin-Markov coefficients on a platinized platinum electrode in the double-layer region showed(29–33) that, unlike mercury, in the case of adsorption of Cl^- ion on a positively charged platinum surface, the discreteness is not evident: when the HCl concentration increases by an order, $E_{\sigma=\mathrm{const}}$ shifts in the negative direction only by ~58 mV. The disappearance of discreteness points to the covalent nature of the bond between metal and specifically adsorbed anions, leading to transition of a major portion of the adsorbed anion charge to the metal surface.

The suggestion that the ions adsorbed on indifferent electrodes pass into adatomic state before the reversible potential is established in the relevant system was first made by Haissinsky in 1933. The comparison of the extent of adsorption of surface-active anions and cations on platinum metals with their contribution to the potential difference between metal and solution led to a convincing conclusion about the charge transfer and an essentially covalent nature of the bond in the case under consideration.(27) The measurements of the superequivalent cation adsorption on a positively charged platinum surface carried out in 0.003 *M* NaA + 0.001 *M* HA solutions, where *A* is $\mathrm{SO_4}^{2-}$, Cl^-, Br^-, or I^-, clearly demonstrated the dependence of the degree of polarity of the bond on the anion nature(31) (Figure 13). The cation adsorption was determined by the tracer technique. In sulfate solutions of the above concentration, superequivalent cation adsorption is not observed due to small surface activity of the $\mathrm{SO_4}^{2-}$ ion. In chloride solutions there exists superequivalent adsorption of Na^+, even if small, still measurable, which is nearly independent of potential; this is responsible for the absence of the Esin–Markov effect. In bromide solutions superequivalent

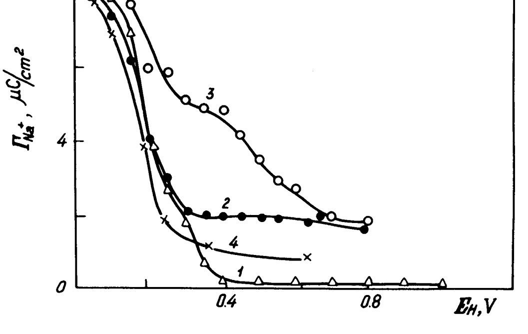

Figure 13. Dependences of the adsorption of Na^+ cations on the potential of a Pt/Pt electrode in solutions: 1, 5×10^{-4} *M* $\mathrm{H_2SO_4}$ + 1.5×10^{-3} *M* $\mathrm{Na_2SO_4}$; 2, 10^{-3} *M* HCl + 3×10^{-3} *M* NaCl; 3, 10^{-3} *M* HBr + 3×10^{-3} *M* NaBr; 4, 5×10^{-4} *M* $\mathrm{H_2SO_4}$ + 3×10^{-3} *M* NaI.(111)

Na^+ adsorption reaches an appreciable value, but drops with increasing potential due to the strengthening of the anion bond with the surface when its positive charge increases. In iodide solutions, in spite of a high adsorbability of I^- ion, superequivalent adsorption is very small, which points to the transition of I^- ion into the atomic state in the case of adsorption on platinum.

These conclusions are supported by the comparison of the dependences of the adsorption of anions on their concentration c, which is given by the logarithmic isotherm

$$\theta = \text{const} + (1/f) \ln c \tag{4.4}$$

where θ is the coverage and the coefficient f is an empirical constant approximately summing the influence of surface inhomogeneity and the effect of the repulsive forces. According to Bagotzky *et al.*(118) the value of f for smooth platinum in the case of neutral molecules is 14–15 and for the HSO_4^- ion ~77, for Cl^-, Br^-, and I^- ions ~18, 15, 14, respectively. In other words, as the surface activity increases, the behavior of anions approaches that of uncharged particles. The covalent nature of the bond of specifically adsorbed anions on platinum metals is consistent with the slow establishment of equilibrium, and exchange can be followed by means of tracers.(26,27,33) The rate of exchange of the Br^- ion on platinum and palladium drops appreciably with increasing E_H, which testifies to an increase of covalence of the bond when passing to more positive potentials.

When the strength of the bond between specifically adsorbed ions and the platinum surface increases, the concept of the pzc itself becomes ambiguous. This is clearly illustrated by the data obtained by tracer techniques on electrodes previously covered with strongly adsorbed iodine or thallium atoms.(31) Thus an electrode was kept in KI or Tl_2SO_4 solution. After it had been removed from solution and washed several times with water to eliminate the weakly bound ions and to determine the amount of strongly bound ones, it was immersed in an acidified Na_2SO_4 solution to measure the adsorption of Na^+ and SO_4^{2-} ions. The results of these measurements are given in Figures 14 and 15. The conclusions about the value of the pzc depend on which part of the double layer one considers the charge of strongly adsorbed ions to belong. If one ascribes it to the metal charge, the position of the pzc is determined by the condition $\Gamma_{Na^+} = \Gamma_{SO_4^{2-}}$, which corresponds to the point of intersection of the curves 1–4, on the one hand, and of the curves 1′–4′, on the other, in Figures 14 and 15. Under this assumption, the adsorption of I^- shifts the pzc toward more positive (Figure 14) and the adsorption of Tl^+ toward more negative (Figure 14) potential values, i.e., the signs of the shift of the pzc prove to be opposite to those which are usually ascribed to these ions. If, however, the charge of chemisorbed ions is considered to belong to the ionic side, the pzc should be determined from the conditions $\Gamma_{Na^+} = \Gamma_{SO_4^{2-}} + \Gamma_{I^-}$ or $\Gamma_{Na^+} + \Gamma_{Tl^+} = \Gamma_{SO_4^{2-}}$, respectively. As can be seen from the position of curves 5 in Figures 14 and 15, with such approach, the adsorption of Tl^+ leads to the shift of the pzc to more positive

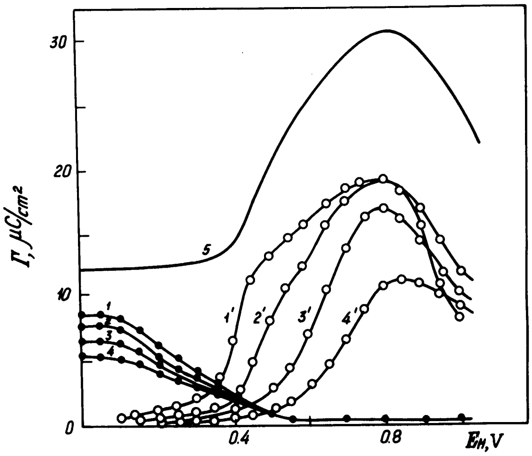

Figure 14. Dependences of the adsorption of Na^+ cations (1–4) and SO_4^{2-} anions (1'–4') on the potential of a Pt/Pt electrode with iodine ions preadsorbed on its surface in the amounts: 1,1'—0; 2,2'—12; 3,3'—26; 4,4'—38 μC/cm². Curve 5—the dependence of $\Gamma_{I^-} + \Gamma_{SO_4^{2-}}$ on E_H at $\Gamma_{I^-} = 12$ μC/cm².(33)

values; and the adsorption of I^- should lead to a shift of the pzc to very negative values, which, however, is not realized experimentally. The first assumption, probably, approaches more closely the real picture, since under experimental conditions, the adsorption of iodine and thallium to a large extent occurs in the atomic form with formation of a dipole bond between the metal and adsorbed atoms. In the case of iodine, the negative dipole end and, in the case of thallium, the positive end, is turned toward the solution. The question as to whether the chemisorbed particle charge should be ascribed to solution or to the metal side of the double layer arose first when the influence of the oxidation of a Pt electrode on its adsorption properties was considered.(25)

The assumption that strongly chemisorbed anions shift the pzc of metal in the direction of more positive values was used in the interpretation of the action of corrosion inhibitors of iron.(119,120)

It follows from the above data that pzc of platinum metals depend on

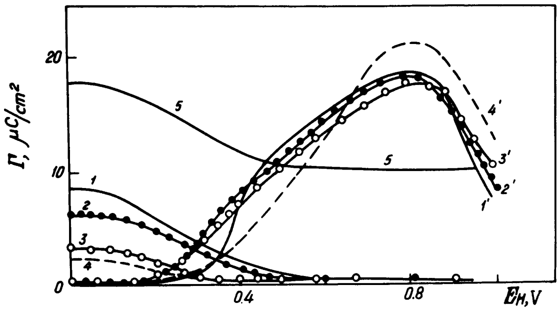

Figure 15. Dependences of the adsorption of Na^+ cations (1–4) and SO_4^{2-} anions (1'–4') on the potential of a Pt/Pt electrode with thallium ions preadsorbed on its surface in the amounts: 1,1'—0; 2,2'—10; 3,3'—26; 4,4'—53 μC/cm². Curve 5—the dependence of $\Gamma_{Tl^+} + \Gamma_{Na^+}$ on E_H at $\Gamma_{Tl^+} = 10$ μC/cm².(33)

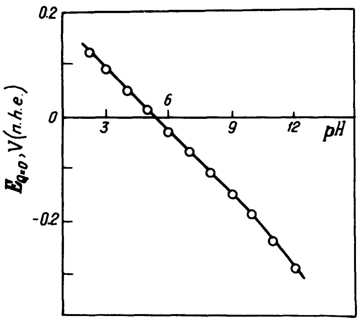

Figure 16. Dependence of the potentials of zero total charge on the solution pH for a Pt electrode in 0.1 *M* KCl.(123)

solution pH. This phenomenon was first detected by Šlygin *et al.*(25) In recent years the studies of Kheifets and Krasikov(121) have given impetus to the investigation of the pH dependence of the pzc. To obtain a complete picture of the dependence of the pzc on solution pH, a method of potentiometric titration at constant total surface charge Q was developed.(122) This titration is carried out with the use of an electrode with its developed surface in an inert-gas atmosphere at open circuit. Previously, the electrode is kept for a long time at a given E_H value so that after breaking the circuit, E_H of the electrode remains constant. The electrode potential must comply with the condition $E_H \geqslant 0.04$ V. The pH value is determined by means of a glass electrode. The composition of solutions is chosen so that the supporting electrolyte concentration should always be higher than that of the H^+ or OH^- ions and practically should not change during titration. Under these conditions, $\Gamma_{H^+} = \sigma$. The potentiometric titration under the conditions specified above gives the dependence of E on pH, corresponding to the value of Q preset at the initial pH. In particular, if $Q = 0$, the $E_{Q=0}$–pH dependence can be directly determined. Such dependence is shown in Figure 16 for a Pt/Pt electrode in 0.1 *N* KCl. Its slope is 40–45 mV per unit pH in the pH range 2–10 and ~55 mV in the pH range 10–12.(123)

It follows from Eqs. (2.13) and (3.5) that

$$(\partial E/\partial \mathrm{pH})_Q = -2.3(RT/F)[1 - (\partial\sigma/\partial A_H)_{\mathrm{pH}}]^{-1} \tag{4.5}$$

In acidified solutions in the pH range studied, the pztc of the first kind lies within the hydrogen region, in which $(\partial\sigma/\partial A_H)_{\mathrm{pH}}$ has a small negative value; in alkaline solutions it is close to zero due to the slight dependence of σ on E_H, which leads to the observed dependence of $E_{Q=0}$ on pH. The physical sense of this conclusion is quite clear since the value of Q in the hydrogen region is determined primarily by the term $-A_H$, and the dependence of A_H on E_H varies comparatively little with the solution pH. As a result $Q = -\Gamma_H$ vanishes at the E_H values varying relatively little with the solution pH.

With the use of the titration method at constant Q, it is possible to obtain not only $E_{Q=0}$–pH dependence, but also that of $E_{\sigma=0}$ on pH. For this purpose the E, pH curves corresponding to different Q values are used. Figure 17 shows a set of such curves for a Pt/Pt electrode in 0.1 *N* KCl. The vertical sections on

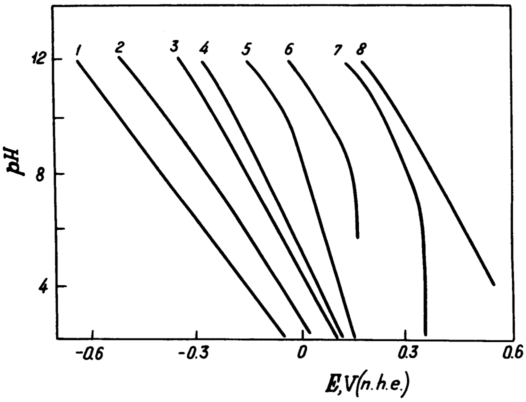

Figure 17. Dependences of the potential E of a Pt/Pt electrode on the solution pH in 0.1 M KCl under isoelectrical conditions at different Q: 1, -152; 2, -82.5; 3, -10; 4, 0; 5, 13; 6, 25; 7, 38; 8, 60 μC/cm².(123)

the curves correspond to the passage of the electrode through the double-layer region within which $E_{Q=\mathrm{const}}$ does not depend on pH. By means of the E–pH dependences from the charging curves of the first kind (Q–E curves) measured in acidified (pH = 2.5) and alkalized (pH = 12) solutions, the charging curves of the first kind were plotted at intermediate pH. Then, by means of Eq. (3.7), from the slopes of the E–pH dependences and the Q–E curves, the derivatives $(\partial\sigma/\partial E_{\mathrm{H}})_{\mathrm{pH}}$ were calculated. By integration of the $(\partial\sigma/\partial E_{\mathrm{H}})_{\mathrm{pH}}$–$E_{\mathrm{H}}$ curve, it is possible to find the σ, E_{H} dependence. The integration constant was determined from the values of $\Gamma_{\mathrm{H}^+} = \sigma$ at $E_{\mathrm{H}} = 0$, obtained by potentiometric titration at the atmospheric pressure of hydrogen.(31)

The results of the calculation of the σ–E_{H} curves are shown in Figure 18. The points of intersection of these curves with the abscissa give the pzfc values,

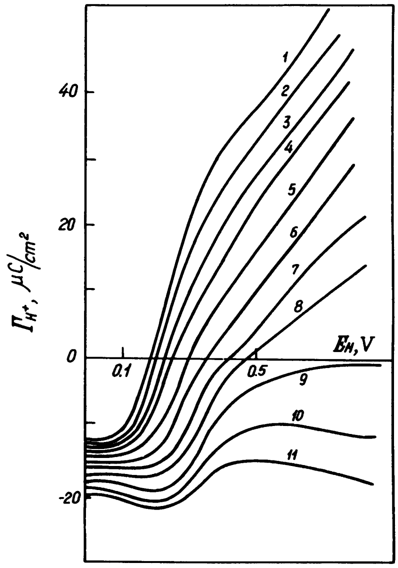

Figure 18. Dependences of the free surface charge of a Pt/Pt electrode on E_{H} in 0.1 M KCl at different pH: 1, 2.3; 2, 3; 3, 4; 4, 5; 5, 6; 7, 8; 8, 9; 9, 10; 10, 11; 11, 12.(123)

$(E_H)_{\sigma=0}$. It is clear from Figure 18 that as pH increases a transition occurs to the surface negatively charged in the measurable E_H range. To explain this phenomenon it is necessary to take into account a simultaneous action of two factors. First, when pH increases, the potential range in which the measurements are performed shifts in the negative direction relative to the constant reference electrode, which should lead to an increase of the negative charge at constant E_H and hence to an increase of the cation adsorption. Secondly, with increasing pH desorption of adsorbed hydrogen becomes difficult if the Pt–H dipole is turned with its negative end toward the solution and oxygen deposition is facilitated. The arising hydrated oxide groups are slightly acid. As a result, the adsorption of cations in the form, say, $PtOK^-$, becomes possible, which leads to desorption of anions from the platinum surface. Thus, in alkaline solutions a transition takes place from the adsorption of cations caused by ionization of adsorbed hydrogen atoms and decreasing with increasing E_H, to the adsorption of cations by the surface oxide groups, increasing in a certain E_H range. At pH = 10 in a relatively large E_H range, the conditions are established when the Pt surface practically does not carry a free charge.

Figure 19 gives the dependence of $E_{\sigma=0}$ on solution pH in 0.1 N KCl. In the pH range 2.3–5.0, the potential $E_{\sigma=0}$ shifts in the cathodic direction by 35 mV when pH increases by a unit. In the pH range 5–9, the shift of $E_{\sigma=0}$ proves to be small; at pH > 7, $E_{\sigma=0}$ begins to shift in the positive direction with increasing pH. A complex shape of the $E_{\sigma=0}$–pH curve is due to the circumstance that $E_{\sigma=0}$ shifts from the hydrogen region to the double-layer region and, then, to that of adsorbed oxygen deposition.

From Eqs. (2.14) and (3.5) by some simple transformations, it is possible to obtain the relation

$$(\partial E/\partial \mathrm{pH})_{\sigma,\mu_{\mathrm{CA}}} = -2.3(RT/F)(\partial A_H/\partial\sigma)_{E_H}[(\partial A_H/\partial\sigma)_{E_H} - 1]^{-1} \qquad (4.6)$$

At the potentials corresponding to $\sigma = 0$, anion adsorption and hydrogen adsorption are mutually antagonistic. This is associated with the polarity of the $Pt\text{–}H_{ads}$ bond whose negative end is turned toward the solution. Therefore, the quantity $(\partial A_H/\partial\sigma)_{E_H}$ is negative, and in absolute value it increases with rising

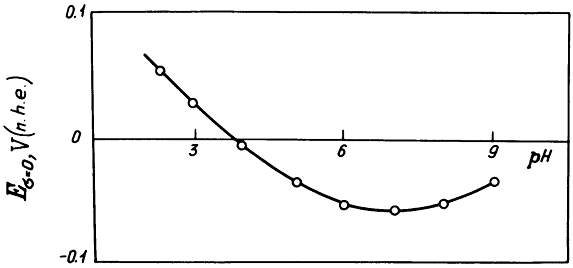

Figure 19. Dependence of the potential of zero free charge of a Pt/Pt electrode in 0.1 M KCl on the solution pH.[123]

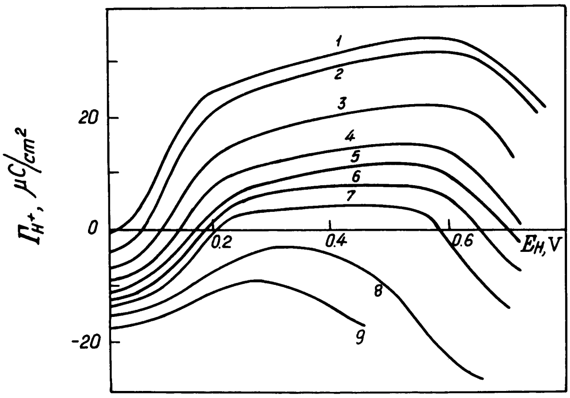

Figure 20. Dependences of the free surface charge of a Rh electrode on E_H in 0.1 *M* KCl at different pH: 1, 3; 2, 4; 3, 5; 4, 6; 5, 7; 6, 8; 7, 9; 8, 10; 9, 11.(124)

specific adsorbability of the anion. As a result, according to Eq. (4.6), $E_{\sigma=0}$ decreases with increasing pH with the slope which at small pH approaches 2.3 RT/F per unit pH when the adsorbability of the anion rises. These considerations apply to the hydrogen region. In the double-layer region, $A_\mathrm{H} = 0$ and, hence, $(\partial E/\partial \mathrm{pH})_{\sigma=0} = 0$. At pH ≈ 7, $E_{Q=0} = E_{\sigma=0}$, which is natural since these values of E lie within the double layer of Pt in 0.1 *N* KCl, where $Q = \Gamma_{\mathrm{H}^+} = \sigma$. It is possible, however, that the overlapping of hydrogen and oxygen regions is important here also since at more positive E_H, the derivative $(\partial A_\mathrm{H}/\partial\sigma)_{E_\mathrm{H}} < 1$ and $E_{\sigma=0}$ shifts into the positive direction with increasing pH.

Figure 20 gives a set of the σ–E_H curves for a rhodium electrode in 0.1 *N* KCl at different pH.(124) At $E_\mathrm{H} \approx 0.6$ V, these curves show a decay associated with oxygen adsorption and similar to that on the σ–E_H curves of Pt in sulfate solutions (Figure 4). In the case of Pt in chloride solutions, such decay is absent (Figure 18). The curve for rhodium, owing to its great oxidizability, shows a decay in chloride medium as well. When pH rises, the beginning of the decay shifts in the direction of less positive potentials. In the pH range 6–9, the σ–E_H curves cut the abcissa twice, ie., there are two conditional pzfc lying in the hydrogen and oxygen regions, respectively. The distance between them is 0.4–0.6 V. At pH > 9, the rhodium surface carries a negative charge at all E_H values.

While in the hydrogen region the experimental values of $(\partial E/\partial \mathrm{pH})_{\sigma=0}$ vary within 0–50 mV depending on solution composition and nature of the metal, in the oxygen region the values of this derivative are much larger. For example, in the case of a rhodium electrode in 0.1 *N* KCl, the shift in the negative direction of the pztc lying in the oxygen region per unit pH is ~180 mV. By substituting $-A_\mathrm{OH}$ for A_H, Eq. (4.6) yields

$$(\partial E/\partial \mathrm{pH})_\sigma = 2.3(RT/F)(\partial A_\mathrm{OH}/\partial\mu_{\mathrm{OH}^-})_{E_\mathrm{H}}(\partial\sigma/\partial\mu_{\mathrm{OH}^-})_{E_\mathrm{H}}^{-1} \times [(\partial A_\mathrm{OH}/\partial\mu_{\mathrm{OH}^-})_{E_\mathrm{H}}(\partial\sigma/\partial\mu_{\mathrm{OH}^-})_{E_\mathrm{H}}^{-1} + 1]^{-1} \quad (4.7)$$

It is evident that $(\partial E/\partial \mathrm{pH})_\sigma$ can be less than $-2.3RT/F$ if $(\partial A_{\mathrm{OH}}/\partial \mu_{\mathrm{OH}^-})_{E_\mathrm{H}} > 0$, and $(\partial \sigma/\partial \mu_{\mathrm{OH}^-})_{E_\mathrm{H}} < 0$.

It follows from the above that, for evaluation of the quantity $(\partial E/\partial \mathrm{pH})_{\sigma=0}$, it is very important to know the effective polarity of the Pt–$\mathrm{H_{ads}}$ and Pt–$\mathrm{O_{ads}}$ bonds. One can get an idea of the polarity of the Pt–$\mathrm{H_{ads}}$ bond by comparing the quantities $X = (\partial E/\partial A_\mathrm{H})_\sigma$ and $Y = (\partial E/\partial \sigma)_{A_\mathrm{H}}$. The calculations of the values of X and Y have been performed and analyzed.(27,30)

Using Eqs. (2.11) and (2.12) for the redox system, H, $\mathrm{H^+}$, when the $\mathrm{H^+}$ and $\mathrm{OH^-}$ ion concentrations are small compared to those of other system components, the following relations are obtained:

$$(\partial \gamma/\partial E)_{\mu_{\mathrm{H}^+}} = \Gamma_\mathrm{H} = -Q \tag{4.8}$$

and

$$(\partial \gamma/\partial E)_{\mu_\mathrm{H}} = (\partial \gamma/\partial E)_{E_\mathrm{H}} = -\Gamma_{\mathrm{H}^+} = -\sigma \tag{4.9}$$

Integration of Eq. (4.8) gives the electrocapillary curve of the first kind of platinum accurate to the integration constant. The value of Q is found from the charging curves if the potential of zero total charge $E_{Q=0}$ is known. Since the absolute value of γ for platinum is not known, the result of integration can be most conveniently represented in the form of $\Delta\gamma, E$ curves, where $\Delta\gamma = \gamma - \gamma_0$, and γ_0 is the value of γ at the platinum/solution interface at the maximum of the electrocapillary curve of the first kind for any arbitrary solution. Frumkin and Petrii(31) used the solution 10^{-2} N $\mathrm{H_2SO_4}$ + 1 N $\mathrm{Na_2SO_4}$. With such a choice $\Delta\gamma \leqslant 0$ (except with fluoride solutions(125)). For integration of Eq. (4.9) leading to the $\Delta\gamma$–E curves of the second kind, the data on the dependence of σ on E at constant E_H is essential and can be determined by comparing the σ–E_H curves obtained at different pH.

Figure 21a gives the electrocapillary curves of platinized platinum of the first and second kind for platinized platinum borrowed from Frumkin and Petrii.(31) Curve 1 has been obtained from the charging curve for a

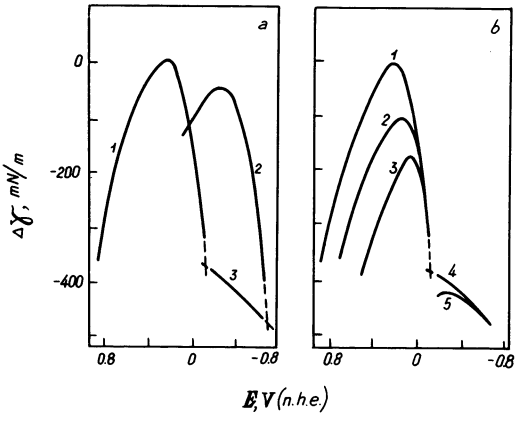

Figure 21. Electrocapillary curves of a Pt/Pt electrode: (a) curves of the first kind in 5×10^{-3} M $\mathrm{H_2SO_4}$ + 0.5 M $\mathrm{Na_2SO_4}$ (1), 10^{-2} M NaOH + 0.5 M $\mathrm{Na_2SO_4}$ (2) and a curve of the second kind in 0.5 M $\mathrm{Na_2SO_4}$ at $E_\mathrm{H} = 0$ (3); (b) curves of the first kind in 5×10^{-3} M $\mathrm{H_2SO_4}$ + 0.5 M $\mathrm{Na_2SO_4}$ (1), 10^{-2} M HCl + 1 M KCl (2), 10^{-2} M HBr + 1 M KBr (3) and curves of the second kind at $E_\mathrm{H} = 0$ in 0.5 M $\mathrm{Na_2SO_4}$ (4), in 0.1 M KI (5).(31)

10^{-2} N H_2SO_4 + 1 N Na_2SO_4 solution and extrapolated to $E_H = 0$. From the value of $\Delta\gamma$ in this solution, it is possible to pass to its value in a 10^{-2} N NaOH + 1 N Na_2SO_4 solution at $E_H = 0$ by means of the electrocapillary curve of the second kind (curve 3, Figure 21a), which allows one to determine the position of the curve of the first kind of the second solution (curve 2). In Figure 21b, the electrocapillary curves of the first and second kind for platinum in solutions containing different anions are compared.(31) The position along the vertical line of the maxima of the electrocapillary curves of the first kind in acidified KCl and KBr solutions was chosen in such a way to ensure the coincidence of the $\Delta\gamma$–E dependences at such E_H values at which the anion nature no longer affects the values of Q and σ. The position of the $\Delta\gamma$, E curves of the first kind of acidified salt solutions with different anions resembles that for mercury. But the slope of both branches of the electrocapillary curves of platinum is greater than in the case of mercury since the quantities A_H and A_{OH} in their absolute values are significantly larger than σ. A distinctive characteristic of the behavior of the two metals is the dependence of the position of the electrocapillary curves of the first kind on solution pH. In Figure 21b, the maximum on the curves of the second kind, i.e., the potential of zero conditional free charge at $E_H = 0$, can be observed only in the NaI supporting electrolyte ($E_{\sigma=0} = -0.31$ V). In the case of SO_4^{2-}, Cl^-, and Br^- anions in the pH range accessible to investigation at $E_H = 0$, $\sigma < 0$.

A more complete picture of the dependence of γ on solution pH can be obtained from the electrocapillary curves of the first and second kind in Figure 22 (Pt in 0.1 N KCl), plotted with the use of the results of potentiometric

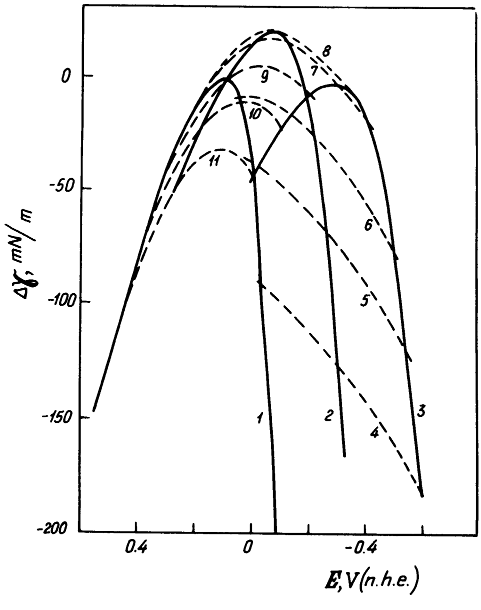

Figure 22. Electrocapillary curves of the first kind (1–3) and of the second kind (4–11) of a Pt/Pt electrode in 0.1 M KCl solution with pH 2.3 (1); 7 (2); 12 (3) and at $E_H = 0.10$ (4); 0.15 (5); 0.20 (6); 0.30 (7); 0.40 (8); 0.50 (9); 0.60 (10); and 0.70 (11) V.(33)

titration at constant charge. As can be seen from Figure 22, in acidified solutions the values of γ at the maximum of the electrocapillary curves of the first kind are higher than in alkaline solutions. This is due to the fact that, at $E_{Q=0}$ in acid solution, the surface coverage by ions and atoms is less than in the alkaline one. The decrease of Cl^- adsorption when passing from pH 2.3 to pH 7 leads to increase of γ at the maximum of the electrocapillary curve of the first kind. With further increase of pH, the hydrogen and oxygen adsorption regions begin to overlap, which decreases γ. The fact that curves 2 and 8 of Figure 22 practically coincide in a certain range of E is a consequence of the equality $Q = \sigma$, since these sections of the curves lie in the double-layer region.

The existence of two types of electrocapillary curves for platinum metals is accounted for by the fact that the reversible work of surface formation γ is a function of two variables μ_H and μ_{H^+}, and hence when plotted in the coordinates γ, μ_H and μ_{H^+}, it represents a certain surface. The section of this surface by the plane $\mu_{H^+} =$ const gives the electrocapillary curve of the first kind, and its section by the plane $\mu_H =$ const gives the electrocapillary curve of the second kind.

In the experiments described above, the values of $E_{Q=0}$ and $E_{\sigma=0}$ were obtained for electrolytic deposit of platinum metals under the conditions of maximum approach to equilibrium between solution and electrode. Bockris and coworkers(126) studied the pH dependence of the pzfc of smooth platinum free of adsorbed hydrogen. For this purpose a platinum electrode, reduced in hydrogen by heating for a short time to 400°C, was kept at 450°C in an argon atmosphere and, after cooling, was introduced into the solution at the potential $E_H > 0.4$ V to avoid hydrogen adsorption. Then, for the electrodes thus prepared, the C–E curves were plotted. In sufficiently diluted solutions these curves showed a minimum, which disappeared when the overall solution concentration increased. The C–E curves did not exhibit any marked frequency dependence, but their shape and position at different concentrations were other than those generally observed in the case of mercury or "mercurylike" metals. The dependence of the potential of the minimum $E_{\min}$ (N.H.E.) on pH was expressed by the relation

$$E_{\min} = 0.56 - 2.3(RT/F)\text{pH} \tag{4.10}$$

A short cathodic polarization of the electrode down to $E_H = 0.2$ V led to a shift of $E_{\min}$ in the direction of more negative potentials on the subsequently plotted C–E curve. Bockris and co-workers interpreted the obtained values of $E_{\min}$ as the pzc of platinum free of adsorbed hydrogen. They explained the dependence of pH by specific adsorption of the hydroxyl ion obeying a logarithmic isotherm.

The thermodynamic interpretation of these results, however, is not clear. The coefficient 59 mV in the $E_{\sigma=0}$–log C_{OH^-} dependence on the surface free of adsorbed gases should point to a practically complete transfer of the adsorbed anion charge to the metal, as was discussed earlier. In other words, it is the

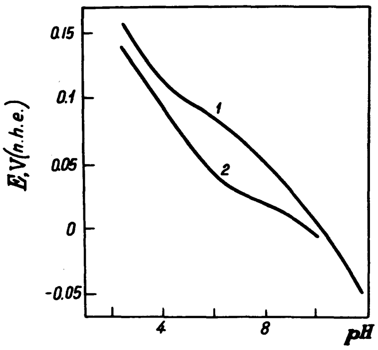

Figure 23. Dependences of pztc (1) and pzfc (2) on pH in 0.05 M K_2SO_4 for a carbon black electrode.(127)

chemisorption of the radical OH which would be in question, rather than the specific adsorption of the OH^- ion. Without the assumption of the presence of strong chemisorption, it also would be impossible to explain the adsorption of OH^- in acid solutions. Thus the interpretation of the above-mentioned authors leads to the conclusion that, if the differential capacity minima observed in their experiments really point to the zero free charge, it must be the zero charge of the oxidized surface. It should be noted that in the case of strong specific adsorption of OH^- ions, as with other ions, the capacity minimum method cannot give the pzc of the surface free from adsorbed material.

The dependences of $E_{Q=0}$ and $E_{\sigma=0}$ on pH have also been obtained for electrodes from activated sugar carbon and carbon black (containing 0.2% Pt/g) by potentiometric titration at constant total charge.(127) The values of σ for carbon adsorbents, as for Pt metals, at all E_H decreases with increasing pH. In Figure 23, the dependences of $E_{Q=0}$ and $E_{\sigma=0}$ on pH for a carbon black electrode are compared. In plotting the $E_{Q=0}$, pH curve, it was assumed that, at pH = 2.4 in acidified 0.1 N K_2SO_4 solution, $E_{Q=0} = +0.16$ V (N.H.E.). The mean shift of the pztc in the pH range 2.4–10 is ~20 mV per unit pH. The shift of $E_{\sigma=0}$ is ~30 mV per unit pH in the pH range 2.4–6, and in the neutral region (pH = 6–8), only ~10 mV per unit pH. For interpretation of these results, the relations (4.5) and (4.6) considered above were used.

5. Potentials of Zero Charge and the Adsorption of Organic Compounds on Electrodes

The discussion of this important problem shall begin with the consideration of the relation between the pzc and the potentials of the adsorption–desorption peaks on the differential capacity curves in the presence of organic compounds. So far the adsorption–desorption peaks have been obtained for different liquid and solid electrodes: Hg, Bi, Pb, Sb, Zn, Cd, Sn, In, Tl, Ag, liquid and solid Ga, and In + Ga and Ga + Tl alloys. (The relevant references are given in Chapter 8 of this volume.) With the exception of mercury, bismuth, and silver, only cathodic adsorption–desorption peaks could be observed for the metals listed above since in other cases anodic peaks fall within the region of anodic dissolution of the metal. The similarity in the behavior of adsorption of organic compounds on these metals suggests that the position of the cathodic adsorption–desorption peak permits one to draw some quantitative conclusions about the pzc of the metal adsorbent. It can be shown, however, that in the general case this conclusion is erroneous, and the adsorption behavior of the metal is determined not only by its pzc value, but also by its hydrophilic properties.(7,8) Therefore, in principle, the difference between the pzc and the cathodic adsorption–desorption potential (E_d) at a certain concentration of organic substance and surface-inactive supporting electrolyte solution can be used as a criterion of the hydrophilic properties of metals: the stronger are the hydrophilic properties of a metal, the less is ($E_d - E_{\sigma=0}$). This criterion is, however, only a qualitative one since the position of E_d depends not only on the free energy gain upon substitution of water molecules by those of organic substance, but also on some other parameters characterizing the adsorbed layer.

In Table 2, the values of $E_d - E_{\sigma=0}$ and of the charges σ_d, corresponding to E_d in a supporting electrolyte solution and in the presence of an organic substance (0.1 M n-$C_5H_{11}OH$), are compared for different metals.(7) The data on the dependence of ($E_d - E_{\sigma=0}$) on the nature of the metal are also illustrated in Figure 24.

As can be seen from Table 2, in spite of large differences between the values of $|E_d - E_{\sigma=0}|$ for different metals, the values of $|\sigma_d|$, both in pure electrolyte solution and in the presence of an organic substance, depend little on the nature of the metal. (On the average in the supporting electrolyte solution, $|\sigma_d| \approx 13.1$ $\mu C/cm^2$; and in the solution with 0.1 M n-$C_5H_{11}OH$ addition, $|\sigma_d| \approx 9.1$ $\mu C/cm^2$.) This result permits approximate evaluation of the pzc on the basis of the C–E curves measured in 0.1 N solution of a surface-inactive electrolyte and in

Table 2

Maxima of Adsorption and Potentials of Zero Charge

Metal	$\|E_d - E_{\sigma=0}\|$ (V)	$\|\sigma_d\|$ ($\mu C/cm^2$) Supporting electrolyte solution	$\|\sigma_d\|$ ($\mu C/cm^2$) Supporting electrolyte solution + n-$C_5H_{11}OH$	Electrolyte
Ga	0.32	13.0	8.0	0.1 M $NaClO_4$
In + Ga	0.45	12.4	9.4	0.05 M Na_2SO_4
In	0.51	13.2	9.2	0.05 M Na_2SO_4
Cd	0.55	14.3	9.5	0.1 M KF
Sn	0.63	13.2	9.3	0.05 M Na_2SO_4
Pb	0.67	12.8	9.4	0.05 M Na_2SO_4
Bi	0.71	12.5	9.0	0.05 M K_2SO_4
Hg	0.74	13.3	9.3	0.1 M NaF

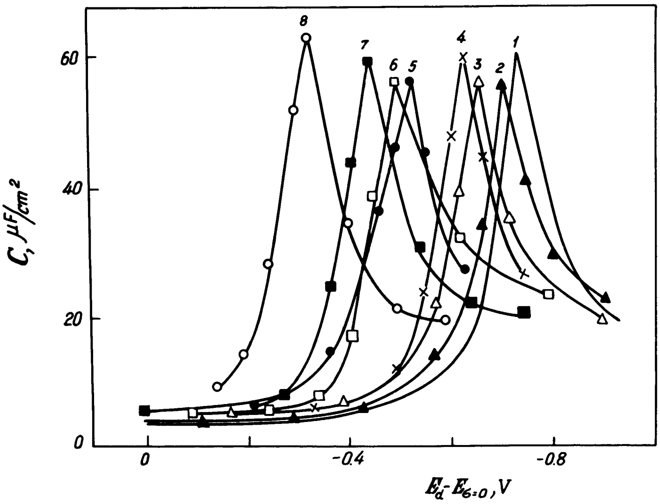

Figure 24. Cathodic sections of the differential capacity curves with an adsorption–desorption peak in 0.1 *M* n-$C_5H_{11}OH$ solution in the presence of 0.1 *M* NaF, KF, $NaClO_4$, and 0.5 *M* Na_2SO_4 supporting electrolytes on different metals: 1, Hg; 2, Bi; 3, Pb; 4, Sn; 5, Cd; 6, In; 7, In + Ga; 8, Ga.(7)

the same solution with *n*-amyl alcohol addition. Indeed, if the electrode charge at E_d is known, it is possible to obtain the value of $E_{\sigma=0}$ by reverse integration of the C–E curves. However, this estimate will be reliable only under the condition that, in the region of sufficiently large negative charges (within which σ_d falls), different metals have approximately the same compact layer density (C_1). Figure 25 shows the C_1–σ curves for electrodes from indium, cadmium, tin, lead, mercury, antimony, and bismuth and also the C–σ curve for a gallium electrode in 0.5 *M* Na_2SO_4 not corrected for the diffuse layer capacity.† As can be seen from this figure, at $\sigma = \sigma_d$ the capacities for different metals differ only slightly, i.e., at $E = E_d$ the differences in the hydrophilic properties smooth over to a considerable extent, which leads to identical conditions of organic substance desorption. If, however, the differences in the hydrophilic properties of a metal are retained in the region of large negative σ, the double-layer capacity will be affected, and the adsorption–desorption peak will not correspond to the constant value of σ_d. Neither will the constant value of σ_d be retained under conditions where an organic substance can interact specifically with the electrode surface.

The differences in the hydrophilic properties observed at the pzc depend on the surface charge values and, hence, to what extent water chemisorption begins to manifest itself. While at sufficiently negative potentials the capacities for different metals (except indium and its alloy with gallium) differ little, at the pzc,

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† The difference of this curve from the C_1, σ dependence should not be large due to the high concentration of the supporting electrolyte solution.

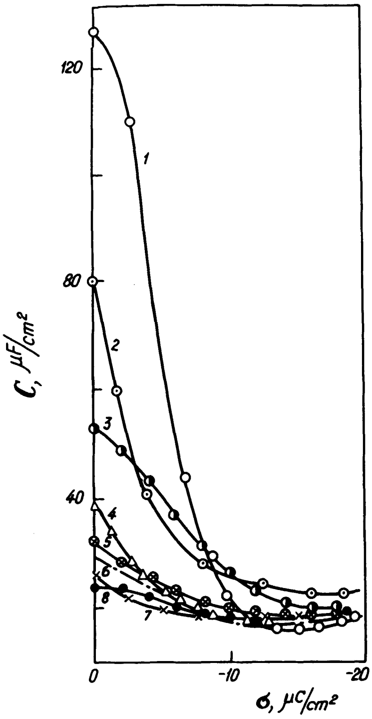

Figure 25. Dependences of the differential capacity of the Helmholtz layer on the surface charge on different metals: 2, In; 3, Cd; 4, Sn; 5, Pb; 6, Hg; 7, Bi; 8, Sb. Curve 1 for Ga is not corrected for the diffuse layer capacity.[7]

the capacity increases markedly in the sequence Bi, Sb < Hg < Pb < Sn < Cd < In < Ga. This sequence nearly coincides with that in which, according to Table 2, the value of $|E_d - E_{\sigma=0}|$ decreases. However, in the case of Bi and Sb, the low capacity values near the pzc can be due to the semiconducting nature of these metals, rather than to their low hydrophilic properties.

The absence of a simple connection between E_d and the pzc, even for mercurylike metals, shows that great care should be taken in extending the results on the adsorption of organic compounds, obtained by means of electrocapillary curves or by some other method for mercury, to solid metals as is done by Antropov[128,129] on the assumption that at equal values of $E - E_{\sigma=0}$ (according to Antropov at equal potential values in the reduced or ϕ scale), the adsorbability of organic compounds, to the first approximation, does not depend on the nature of the metal. This point of view, which is common in electrochemical and corrosion literature, takes an approximate account of the influence of the electric double layer on adsorption, but makes no allowance for the specific character of the interaction of an uncharged metal surface with molecules of water and the organic substance. As will be shown below, the situation becomes even more complicated for metals on whose surface hydrogen and oxygen are adsorbed.

Thus, from the value of E_d measured at a single supporting-electrolyte concentration, it is impossible to deduce quantitatively the value of the pzc. Recently, Damaskin, Batrakov, and Ipatov(130,131) have shown that it is possible to obtain more detailed information from measurements of E_d by determining its dependence on the supporting-electrolyte concentration, c_{el}, over a wide range of its values. At sufficiently low c_{el}, an increase of the supporting electrolyte concentration, leads to an increase of the double-layer capacity and, hence, of its desorbing action, causing E_d to approach the pzc. The shift of the cathodic desorption peak in the direction of more positive potentials is limited, however, by another effect, viz., by the salting out of the organic substance by the supporting electrolyte at sufficiently high concentrations of the latter. This salting out leads to increased activity of the substance being adsorbed, which is equivalent to the increase of its concentration, and hinders desorption. As a result, the dependence of E_d on c_{el} (or on log c_{el}) passes through an inflection (Figure 26). As follows from the theory set forth by Damaskin *et al.*,(130,132) the electrode charge in the supporting-electrolyte solution at the potential E_{ex}, corresponding to the inflection on the E_d–log c_{el} curve, is equal to

$$|\sigma_0| = 2.3kF\Gamma_m\left\{(c_{ext})^{3/2}\left[\frac{4A}{2.3kF\Gamma_m} + (c_{ext})^{1/2}\right]\right\}^{1/2} \tag{5.1}$$

where c_{ext} is the supporting-electrolyte concentration at the inflection of the E_d–log c_{el} curve, k is the salting out coefficient, Γ_m is the limiting adsorption of the organic substance, $A = (\varepsilon RT/2\pi)^{1/2}$, and ε is the dielectric constant of water.

As previously shown,(130) relation (5.1) is valid if the conditions given below are satisfied: the organic substance adsorption on the electrode surface is reversible and localized within one monolayer. The adsorption isotherm is congruent with E in the potential range ~ 100 mV in which E_d depends on c_{el}. At these potentials hydrogen or oxygen atoms are not adsorbed on the electrode surface. The desorption potential corresponds to a definite surface coverage (say, $\theta = 0.5$), and the surface layer properties at the maximum coverage by the organic substance do not depend on c_{el}.

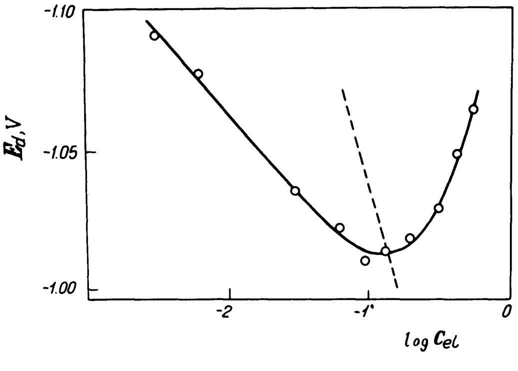

Figure 26. Dependence of the cathodic potential of camphor desorption from the mercury electrode surface on NaF concentration. Camphor concentration 3 × 10^{-4} M.(132)

When these conditions are satisfied (electrodes with a sufficiently high hydrogen overvoltage, an organic substance giving a condensed monolayer upon adsorption, a surface-inactive supporting electrolyte), formula (5.1) permits calculation of the electrode charge in the supporting-electrolyte solution, σ_0, at $E = E_d$.

If the charge value at a definite electrode potential is known, it is possible by means of the C–E dependence to find the pzc. In the case of metals considered at the beginning of this section, such determinations of the pzc are of no practical interest since the value of $E_{\sigma=0}$ can be determined more easily and more accurately from capacity measurements in diluted solutions. This is not the case, e.g., with zinc. The pzc of zinc lies at more positive potentials than the normal potential of a Zn/Zn^{+2} electrode, i.e., it lies in the region of active Zn dissolution. By means of the method described above, it is possible to determine the charge on the Zn surface at potentials at which the Zn electrode can be considered to be ideally polarizable, and, by means of the C–E curve, to continue the determination of σ_0 up to maximum admissable values. Naturally, further approach to $E_{\sigma=0}$ requires extrapolation. Such calculation was performed on the assumption that the values of Γ_m for camphor, which was chosen as a surfactant, are the same for mercury and zinc.(131) The extrapolation (Figure 27) leads to the values of $E_{\sigma=0} = -0.77$ V for the face (0001) and about -0.9 V for a prismatic face. The estimation of the accuracy of this method shows that the error in the determination of the pzc can be ~0.05 V.

The measurement of the dependence of adsorption of an organic substance Γ_{org} on E was used by Bockris and his school for the determination of the pzc by an indirect method.(126,133) The idea of this method is as follows. Since, in the absence of specific ion adsorption, the pzc does not depend on electrolyte concentration, the change of this concentration does not affect the state of the surface at the pzc and should not affect the value of Γ_{org} at the pzc. Thus, by determining the dependence of Γ_{org} on E at different inorganic electrolyte concentrations, it is possible to find the pzc ($E_{\sigma=0}$) from the point of intersection

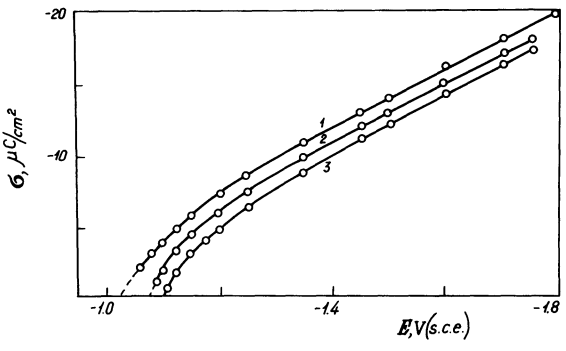

Figure 27. Dependences of the surface charge on potential in 0.1 M KCl (pH = 3.7) for different faces of zinc single crystal: 1, (0001); 2, (1010); 3, (1120).(131)

of the curves giving this dependence. The applicability of this method is based on the assumption that the introduction of the organic substance does not itself lead to a shift of the pzc. If this were so, the adsorption of the organic substance should be a maximum at the pzc, i.e., the common point of the Γ_{org}, E curves at different concentrations should also be the point of maximum adsorption. In a general case, this assumption is not valid (see Chapter 8 of this volume and Bockris and Reddy,$^{(168)}$ where a relation of the potential of maximum adsorption to the pzc is derived). The shift of $E_{\sigma=0}$ during adsorption of organic substances ($\Delta E_{\sigma=0}$) can reach 0.5 V and more; the character of the $E_{\sigma=0}$–θ dependence is determined by the adsorbate nature. In the case of adsorption of aliphatic compounds, the dependence of $E_{\sigma=0}$ on θ is usually monotonic and can be described by means of the two-parallel-capacitor model. In the case of adsorption of aromatic or heterocyclic compounds, the sign of $\Delta E_{\sigma=0}$ may change with an increase in θ, due to the change in the orientation of adsorbed molecules. Under these conditions the dependence of $E_{\sigma=0}$ on θ can be described by the three-parallel-capacitor model.

If $\Delta E_{\sigma=0} \neq 0$, the $\Delta\gamma$–E and the Γ_{org}–E curves measured at different c_{el} also have a common point at the potential of maximum adsorption $E_0 = E_{\mathrm{m}}$$^{(134)}$ (Figure 28a). In the case, the common point of the Γ_{org}–E curves does not coincide with the pzc. However, this conclusion is valid only at sufficiently low electrolyte concentrations, when the salting-out effect can be neglected (e.g., in NaF solutions at $c_{\mathrm{el}} \leqslant 0.05$ *M*). In the presence of the salting-out effect, however, the $\Delta\gamma$–E and Γ_{org}–E curves intersect twice; the intersection points lie on both sides of E_{m} (Figure 28b). In this case one of the intersection points may coincide with the pzc. (It is not possible to predict at what electrolyte concentration this will occur.)

The adsorption of organic substances on iron and platinum group metals is accompanied by a strong chemical interaction with the electrode metal and, probably, by a partial dissociation of the molecules being adsorbed (Chapter 8 of this volume). The experimental determination of the dependence of Γ_{org}

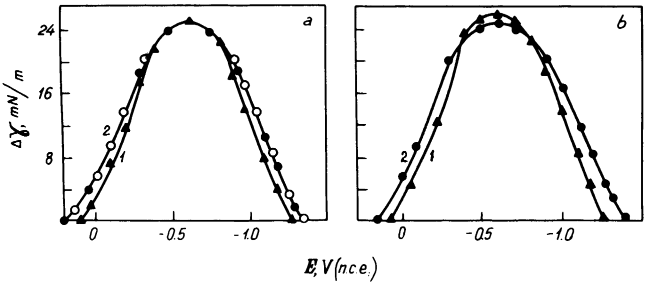

Figure 28. Dependence on potential of the surface tension decrease of mercury caused by ethyl acetate adsorption from its 0.1 *M* solution in the presence of different NaF concentrations. (a) NaF concentrations: 1, 0.05 *M*; 2, 0.07 *M*. Open circles on curve 2—theoretical calculation. (b) NaF concentrations: 1, 0.1 *M*; 2, 0.007 *M*.$^{(134)}$

on E on platinum usually leads to a symmetrical bell-shaped curve, which Bockris and his school interpreted in the same terms as similar curves observed in the adsorption of neutral molecules on mercury.(126) With such an interpretation, E_m could be assumed to lie close to the pzc of platinum. (The degree of deviation is deduced by Bockris and Reddy.(168))

Frumkin(135) gave a different interpretation to the bell shape of the Γ_{org}–E curves on hydrogen- and oxygen-adsorbing metals, according to which the decrease of Γ_{org} with distance from the maximum of the bell-shaped curve is defined primarily by the appearance of adsorbed hydrogen and oxygen on the surface. From this point of view, which explains also the dependence of E_m on solution pH observed by Bockris and co-workers, the potential of the adsorption maximum should be associated with the potential of zero total charge $E_{Q=0}$, rather than with $E_{\sigma=0}$. Some attempts to substantiate the theory developed experimentally by Frumkin(135) failed since no organic substance was found whose adsorption on platinum at ordinary temperatures would be reversible and, thus, could be used to check the conclusions of the thermodynamic theory. The shape of the adsorption vs. potential curve proves to be defined not only by a decrease of adsorbability with distance from E_m, but also by desorption of the organic substance due to its oxidation or hydrogenation. Moreover, the adsorption of these organic substances leads to a deep disturbance of the electric double-layer structure at the platinum/solution interface, which would make it difficult to establish the relationship between the quantities $E_{\sigma=0}$ and E_m even for a reversible adsorption process.

It follows that, though the existence of qualitative relations between the increase of the total charge of a Pt electrode and the decrease of adsorbability of organic compounds is unquestionable,(135) the determination of $E_{\sigma=0}$ and $E_{Q=0}$ of platinum and, probably, of other platinum metals cannot generally be based on that of the dependence of Γ_{org} on potential.

The study of the adsorption of organic compounds on iron leads only to semiquantitative results regarding the position of the pzc of this metal.(8) Of significant interest is a marked change in the adsorption properties of an iron electrode when surface-active halogen anions or the SH^- ion is introduced into solution.(8,119,136) Thus, e.g., in the presence of I^- ions, iron acquires the ability to adsorb $N(C_4H_9)_4{}^+$ ions in the potential range in which the iron surface seems to be positively charged. Probably, chemisorbed I^- ions belong to the metal side of the double layer of iron and not to the ionic side, as in the case of platinum considered above. In the case under consideration, the pzc shifts in the direction of more positive values as compared to $E_{\sigma=0}$ of the uncovered surface, which leads, at a given E = const, to an increase of cation adsorption. Anion chemisorption, however, not only causes $E_{\sigma=0}$ to shift to more positive values, but also makes the iron surface hydrophobic. Therefore, in the presence of halogen ions, an increase is observed in the adsorption not only of cations, but also of neutral molecules, though this effect is less pronounced than in the case of positively charged particles.

6. Potentials of Zero Charge and the Nature of the Medium

Above, the experimental data on the pzc obtained with aqueous electrolyte solutions was considered. It is natural to compare these results with those obtained in different media. This discussion shall begin with the simplest case of the medium being a vacuum.

6.1. Metal/Vacuum Interface

When considering this interface, one encounters the question, which quantity measurable in a vacuum is to be compared with the difference of the pzc of two metals? As was shown(1) this is the Volta (contact) potential arising between the surfaces of two metals in a vacuum when a conducting contact is established between them by means of a conductor of the first kind or as a result of direct contact.

The formulation of the problem of the relationship between the Volta potential and the pzc was preceded by a dispute, which lasted for over a hundred years, as to the extent to which the contact potential arising upon contact of metals, in the absence of chemical interaction, determined the electromotive force of a galvanic cell in which the same metals are used as electrodes. This problem arose at the end of the 18th century and became known as the Volta problem.

As follows from thermodynamics, the Volta potential is equal to the difference of the work functions of metals Me_2 and Me_1 ($W_e^{Me_2}$ and $W_e^{Me_1}$). The Volta potential can also be determined as the potential difference, taken with the opposite sign, which is to be applied to the ends of the circuit (a) in Figure 29 to eliminate the potential drop in a vacuum. On the other hand, evidently, the Volta potential between metals Me_2 and Me_1 is equal to the difference of the surface potentials of these metals χ^{Me_2} and χ^{Me_1}, plus the Galvani potential at the Me_2/Me_1 interface ($\Delta_{Me_2}^{Me_1}\phi$):

$$-\Delta_{Me_2}^{Me_1}\psi = W_e^{Me_1} - W_e^{Me_2} = \chi^{Me_1} - \chi^{Me_2} - \Delta_{Me_2}^{Me_1}\phi \qquad (6.1)$$

Since it is more convenient to compare the potential differences at the ends of the galvani circuit (b), in Figure 29, with the potential difference at the ends of the circuit (a), the quantity $-\Delta_{Me_2}^{Me_1}\psi = \Delta_{Me_1}^{Me_2}\psi$, which figures in the left-hand side of Eq. (6.1), shall be used rather than the Volta potential value $\Delta_{Me_2}^{Me_1}\psi$.

The determination of the pzc gave a correct answer to the question about the relation between the potential difference at the ends of the galvanic circuit and the Volta potential. It is the difference between the pzc of two metals that defines the fraction of the total potential difference which can be compared with the Volta potential in a vacuum. To this fraction must be added the potential differences in the electric double layers at the metal/solution interface.

The analogy between the difference of the pzc of two metals in the absence

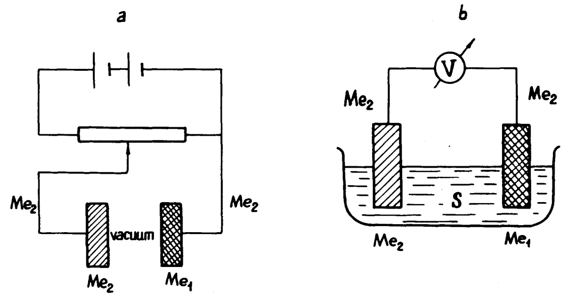

Figure 29. Circuits from two different uncharged metals Me₁ and Me₂, separated by vacuum (a) and solution (b).

of specific adsorption, $\Delta E_{\sigma=0}$, and the Volta potential in a vacuum, $\Delta_{\mathrm{Me}_1}{}^{\mathrm{Me}_2}\psi$, becomes apparent if circuit (a) in Figure 29 is compared with circuit (b) in which the vacuum is substituted by an electrolyte solution; but on both metals $\sigma = 0$. Thus the main difference between the circuit formed by metals in a vacuum and the usual galvanic circuit—the existence of ionic double layers at the metal/electrolyte interface—is not to be found here, but a metal surface in a vacuum is substituted by a metal surface in contact with an electrolyte solution. The determination of the pzc of a concentrated thallium amalgam(1) and of liquid gallium(137) showed that the contribution of the contact potentials to the potential difference at the ends of the galvanic circuit may be quite large.

Taking into account the possibility of a change of the dipole potential jump in the surface layer of water, which was discussed by Frumkin,(138) and also the possibility of a change of the value of χ^{Me} upon contact of an uncharged metal water,(139–141) the expression for $\Delta E_{\sigma=0}$ is obtained from Figure 29:

$$\begin{aligned}\Delta E_{\sigma=0} &= E_{\sigma=0}{}^{\mathrm{Me}_1} - E_{\sigma=0}{}^{\mathrm{Me}_2}\\ &= -\chi^{\mathrm{Me}_2(\mathrm{s})} + \chi^{\mathrm{s}(\mathrm{Me}_2)} - \chi^{\mathrm{s}(\mathrm{Me}_1)} + \chi^{\mathrm{Me}_1(\mathrm{s})} + \Delta_{\mathrm{Me}_1}{}^{\mathrm{Me}_2}\phi\\ &= \Delta_{\mathrm{Me}_1}{}^{\mathrm{Me}_2}\psi - [\chi^{\mathrm{s}(\mathrm{Me}_1)} - \chi^{\mathrm{s}(\mathrm{Me}_2)}] + [\delta\chi^{\mathrm{Me}_1} - \delta\chi^{\mathrm{Me}_2}]\\ &= \Delta W_{\mathrm{e}} - \Delta\chi^{\mathrm{s}(\mathrm{Me})} + \Delta(\delta\chi^{\mathrm{Me}}) \qquad (6.2)\end{aligned}$$

Here, $\chi^{\mathrm{s}(\mathrm{Me})}$ is the potential jump caused by the orientation of the solvent (water) dipoles at the metal/solution interface at the pzc ($\chi^{\mathrm{s}(\mathrm{Me})} > 0$, if the positive dipole end is turned toward the solution). $\delta\chi^{\mathrm{Me}} = \chi^{\mathrm{Me}(\mathrm{s})} - \chi^{\mathrm{Me}}$; χ^{Me} is the surface potential of the metal, and $\chi^{\mathrm{Me}(\mathrm{s})}$ the potential jump in the metal phase at the pzc; $\Delta W_{\mathrm{e}} = W_{\mathrm{e}}{}^{\mathrm{Me}_1} - W_{\mathrm{e}}{}^{\mathrm{Me}_2}$. Equation (6.2) expresses in an analytical form the necessity of introducing corrections into the relation between the difference of the pzc and the Volta potential for the dependence on the metallic nature of the orientation of solvent molecules and for the disturbance of the electron density distribution in the metal as the result of its contact with solvent. This equation can be rewritten also as

$$\Delta E_{\sigma=0} = \Delta W_{\mathrm{e}} + (\Delta_{\mathrm{s}}{}^{\mathrm{Me}_1}\psi)_{\sigma=0} - (\Delta_{\mathrm{s}}{}^{\mathrm{Me}_2}\psi)_{\sigma=0} \qquad (6.3)$$

where $(\Delta_{\mathrm{s}}{}^{\mathrm{Me}}\psi)_{\sigma=0}$ is the Volta potential metal solution at $\sigma = 0$.

Thus for the difference in the pzc of two metals in any solvent to coincide quantitatively with the difference in work functions, it is necessary that the Volta potential between metal and solution at the pzc should not depend on the nature of the metal or should be zero. This is equivalent to equating the quantities $\Delta\chi^{s(\mathrm{Me})}$ and $\Delta(\delta\chi^{\mathrm{Me}})$ to zero, or having them exactly compensate each other. The assumption that the Volta potential between a metal and aqueous solutions at the pzc is equal to zero was used by Jakuszewski and Antropov to prove the exact equality of the quantities ΔW_e and $\Delta E_{\sigma=0}$ (see References 4 and 142). However, neither the lack of dependence of the values of $(\Delta_s{}^{\mathrm{Me}}\psi)_{\sigma=0}$ upon the metal nor their being identified to zero can be proved theoretically, though it is not impossible that in many cases the difference in $(\Delta_s{}^{\mathrm{Me}}\psi)_{\sigma=0}$ in the right-hand side of Eq. (6.3) can be much less than ΔW_e. Were $(\Delta_s{}^{\mathrm{Me}}\psi)_{\sigma=0}$ equal to zero, the Galvani potential at the metal/solution interface at the pzc would have to be the sum of the surface potentials of the metal and water with corresponding signs, an unlikely coincidence. The lack of dependence of this quantity upon the nature of the metal would point to the same deviations from this additivity with changing nature of the metal. The above assumption is proven to be invalid, in particular, by results which point to a change in the work function of xenon during adsorption on different metal surfaces.(143)

Finally, the quantity $(\Delta_s{}^{\mathrm{Me}}\psi)_{\sigma=0}$ can be measured, and a direct measurement shows that it is not equal to zero. The Volta potential measurements performed by Klein and Lange(138) led to the value of $(\Delta_{\mathrm{H_2O}}{}^{\mathrm{Hg}}\psi)_{\sigma=0} = -0.33$ V. More accurate measurements of the Volta potential at the mercury/solution interface made by Randles,(144) in combination with Grahame's value of $E_{\sigma=0}{}^{\mathrm{Hg}} = -0.193$ V, led to the value of $(\Delta_{\mathrm{H_2O}}{}^{\mathrm{Hg}}\psi)_{\sigma=0} = -0.26$ V.

If the value of $(\Delta_s{}^{\mathrm{Hg}}\psi)_{\sigma=0}$ were zero, the difference $(\Delta_{s_1}{}^{\mathrm{Me}}\psi)_{\sigma=0} - (\Delta_{s_1}{}^{\mathrm{Me}}\psi)_{\sigma=0}$ for two different solvents should also be zero. Experimentally, however, this is not the case. Indeed, determining the differences of the potentials ΔE_{I} and ΔE_{II} at the ends of the circuits

NCE	aqueous solution	air	nonaqueous solution (s)	aqueous solution	NCE (I)

and

NCE	aqueous solution	Hg at $\sigma = 0$	nonaqueous solution (s)	aqueous solution	NCE (II)

one can obtain

$$\Delta E_{\mathrm{I}} - \Delta E_{\mathrm{II}} = (\Delta_s{}^{\mathrm{Hg}}\psi)_{\sigma=0} - (\Delta_{\mathrm{H_2O}}{}^{\mathrm{Hg}}\psi)_{\sigma=0} \tag{6.4}$$

Table 3 summarizes the experimental data for some solvents.(145) The last column of this table gives the values of $(\Delta_s{}^{\mathrm{Hg}}\psi)_{\sigma=0}$ calculated by means of Eq. (6.4) under the assumption that $(\Delta_{\mathrm{H_2O}}{}^{\mathrm{Hg}}\psi)_{\sigma=0} = -0.26$ V.

Table 3

Volta Potentials

Solvent	ΔE_{I} (V)	ΔE_{II} (V)	$(\Delta_s^{\mathrm{Hg}}\psi)_{\sigma=0}$ (V)
Water	0	0	−0.26
Methanol	−0.38	−0.13	−0.51
Ethanol	−0.37	−0.20	−0.44
Dimethylformamide	−0.65	−0.24	−0.67
Dimethylsulfoxide	−0.57	−0.15	−0.68
Acetone	−0.57	−0.22	−0.61

As can be seen from the table, the Volta potentials $(\Delta_s^{\mathrm{Hg}}\psi)_{\sigma=0}$ depend significantly on the nature of the solvent, which testifies once more to the fact that the values of the Volta potentials at $\sigma = 0$ are not zero.

Attempts to compare the experimental data on $\Delta E_{\sigma=0}$ and ΔW_e will be considered here. Novakovsky, Ukshe, and Levin(146) found that the data at their disposal fit best the relation

$$E_{\sigma=0} = 1.02W_e - 4.88 \tag{6.5}$$

which is close to the relation

$$E_{\sigma=0} = W_e - 4.78 \tag{6.6}$$

which they deduced assuming $(\Delta_s^{\mathrm{Me}}\psi)_{\sigma=0}$ to be constant.

Later, a similar equation with a somewhat modified constant in the right-hand side was compared more than once with the experimental data, e.g., by Frumkin,(3) where its semiquantitative nature was pointed out

$$E_{\sigma=0} = W_e - 4.72 \tag{6.7}$$

The value of the constant 4.72 was chosen in accordance with the data obtained for mercury.

Argade and Gileadi(147) considered Eq. (6.7) to be valid. A somewhat different relation was derived earlier from the experimental data by Vasenin.(148) According to Vasenin,

$$E_{\sigma=0} = 0.86W_e - 4.25 \tag{6.8}$$

Vasenin explains the difference of the coefficient before W_e from unity by the dependence of the orientation of adsorbed water molecules on the nature of the metal.

A far-reaching attempt to refine the relation between $E_{\sigma=0}$ and W_e was made by Trasatti.(6,149) Having considered the values of W_e which, in his opinion, are most reliable,(150) Trasatti draws the conclusion that the relation of W_e to $E_{\sigma=0}$ cannot be expressed by a linear relation which would cover all metals.(6,149,151) According to Trasatti, for *sp* metals, with the exception of Ga and Zn (Sb, Hg, Sn, Bi, In, Pb, Cd, Tl), an approximate relation is

$$E_{\sigma=0} = W_e - 4.69 \tag{6.9}$$

which is no different from Eq. (6.7); for the transition metals (Ti, Ta, Nb, Co, Ni, Fe, Pd), an approximate relation is

$$E_{\sigma=0} = W_e - 5.01 \tag{6.10}$$

In choosing the values of $E_{\sigma=0}$ in the case of metals not adsorbing hydrogen, Trasatti gives preference to those obtained from the position of the minimum on the *C–E* curve. For platinum metals Trasatti uses the pzc values found by the method suggested by Eyring and co-workers in neutral solutions, assuming that, unlike the pzc values obtained from adsorption measurements, the values thus found refer to metal surfaces free of adsorbed gases. However, the surface renewal without the supply of electricity from outside in the presence of water can at best (if all error sources are eliminated) lead to the disappearance of the total, but not the free, charge.

According to Trasatti, it is possible to derive a relation between $E_{\sigma=0}$ and W_e covering all metals if account is taken of the dependence of $\chi^{H_2O(Me)}$ on the nature of the metal, and the quantity $\delta\chi^{Me}$ is considered to be constant. This relation is

$$E_{\sigma=0} = W_e - 4.61 - 0.40\alpha \tag{6.11}$$

where α is the degree of orientation of water molecules, which, according to Trasatti, increases in the sequence Au, Cu < Hg, Ag, Sb, Bi < Pb < Cd < Ga. The enthalpy of the reaction $Me + \frac{1}{2}O_2 \rightarrow MeO$ also increases in this sequence, which allows one to associate the degree of orientation of adsorbed water molecules and, hence, the quantity $\chi^{H_2O(Me)}$, with the interaction between oxygen atoms and the metal surface.(152) The choice in the above sequence for Cu and Ag does not seem to be fully justified.

Trasatti relates α to the effective electronegativity of the metal surface α_{Me} by the following equation:

$$\alpha = (2.10 - \varkappa_{Me})/0.6 \tag{6.12}$$

The concept of electronegativity as a chemical property characterizing individual atoms was introduced by Pauling. Extending it to the surface of metals, Trasatti considered it necessary to define more accurately Pauling's values of $\varkappa_{Me}$ (Pauling calculates only to the first decimal place) and, in the case of gold, copper and transition metals, to correct them using the empirical relations between the work function and electronegativity. As a result, Trasatti obtains

$$\varkappa_{Me} = 0.50W_e - 0.29 \tag{6.13}$$

for *sp* metals except Ga, Zn, and Al, for which

$$\varkappa_{Me} = 0.50W_e - 0.55 \tag{6.14}$$

It follows from Eqs. (6.11) and (6.12) that

$$E_{\sigma=0} = W_e - 6.01 + 2/3\varkappa_{Me} \tag{6.15}$$

whence, using Eq. (6.13)

$$E_{\sigma=0} = 1.33W_e - 6.20 \tag{6.16}$$

for *sp* metals except Ga, Zn, and Al.

As in Vasenin's papers,(148) the deviation from unity of the slope of the $E_{\sigma=0}$–W_e dependence is associated with the allowance for the change of water orientation with the nature of the metal; but, here, the effect is ascribed an opposite sign. With zero orientation of water (Cu, Au), according to Eq. (6.11)

$$E_{\sigma=0} = W_e - 4.61 \tag{6.17}$$

and with maximum orientation (Al, transition metals, roughly Ga),

$$E_{\sigma=0} = W_e - 5.01 \tag{6.18}$$

The final results of the processing of the experimental data by Trasatti are given in Figure 30. Straight lines corresponding to Eqs. (6.17) and (6.18) bind the region of possible values of W_e as a function of $E_{\sigma=0}$. Straight lines lying within this region give the W_e, $E_{\sigma=0}$ dependence for certain groups of metals which are now combined, but not in the α constancy principle. However, the values of W_e used in plotting this graph in some cases (Tl, and also Cd, Pb) are (following Trasatti's terminology) *electrochemical* values. In other words, they do not represent the result of direct measurements of W_e in a vacuum, but were corrected to bring them into better conformity with the electrochemical behavior of a particular metal.

In spite of the fact that the quantitative calculations of Trasatti are open to objections, his study is noteworthy as an attempt to take into account systematically the influence of the value of $\delta\chi^{H_2O}$ on the relation of W_e to $E_{\sigma=0}$. Quite correct is the Trasatti statement that, at present, for many metals the values of $E_{\sigma=0}$ are much more reliable than those of W_e.

For metals for which there exist reliable pzc values and σ–E dependences, Frumkin and co-workers(7) attempted to compare the values of ΔW_e with

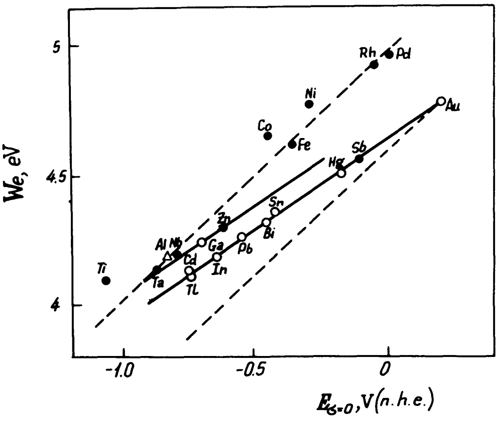

Figure 30. Dependence of the potential of zero charge of metals on the work function. Solid circles—physical work functions; open circle—electrochemical work functions; open triangle—the potential of zero charge value, unavailable experimentally.(149)

those of $\Delta E_{\sigma=q}$, where q has a negative value as large as possible. The comparison is based on the assumption that, at sufficiently negative surface charge, water molecules are oriented similarly and the quantities $\chi_{\sigma=q}{}^{H_2O(Me)}$ and $\delta\chi^{Me}$ can be considered to be independent of the nature of the metal. Such comparison, however, is valid only if the Helmholtz layer capacities are the same for the metals being compared. Otherwise, identical charges will not correspond to identical potential drops in the dense layer. As can be seen from Figure 24, at $\sigma = -18\ \mu C/cm^2$, this condition is satisfied for the whole group of metals under consideration except indium for which a correction is to be introduced based on the similarity of the surface properties of indium and an In + Ga alloy. The quantities $\Delta E_{\sigma=0}$, $\Delta E_{\sigma=q}$ (at $q = -18\ \mu C/cm^2$) and ΔW_e are compared in Table 4.

As can be seen from the table, the differences between the values of the quantities in the first and second columns are large for cadmium and gallium. In Figure 31, plotted from the data of Table 4, the dependences of ΔW_e on $\Delta E_{\sigma=0}$ and on $\Delta E_{\sigma=q}$ are shown. The values of W_e were taken from the first summary table by Trasatti.(6) An exception was made only for Ga, viz., $W_e{}^{Hg} - W_e{}^{Ga}$ was taken to be 0.2. As can be seen from Figure 31, the experimental values of ΔW_e fall somewhat better on the straight line with a slope of 45° if, instead of the values of $\Delta E_{\sigma=0}$, those of $\Delta E_{\sigma=q}$ are plotted on the abcissa, which confirms the necessity of taking account of the quantity $\chi^{H_2O(Me)}$ in considering the relations between the pzc and the work function.

In the light of the foregoing, it is of interest to measure the work functions of metals when water vapors are adsorbed on their surface. If one assumes that the water adsorption layers arising in this case on metal surfaces pretreated in a vacuum behave similarly to a water layer adsorbed from surface-inactive

Table 4

Differences of Potentials for $\sigma = 0$ and $\sigma = -18\ \mu C/cm^2$

Metal	$E_{\sigma=0}{}^{Hg} - E_{\sigma=0}{}^{Me}$ (V)	$E^{Hg}_{\sigma=-18} - E^{Me}_{\sigma=-18}$ (V)	$W_e{}^{Hg} - W_e{}^{Me}$ (eV)
Sb	−0.04	—	−0.06
Bi	0.20	0.17	0.21
Sn	0.19	0.10	0.15
Ga	0.50	0.17–0.18	0.20
In	0.46	0.34 (corr.)	0.42
In + Ga	0.43(CH_3CN)	0.33–0.34 (H_2O, corr.) 0.34–0.35 (CH_3CN)	—
Ga + Tl	0.51	0.40	—
Tl	0.52	—	0.48
Pb	0.37	0.36	0.32
Cd	0.56	0.35	0.38

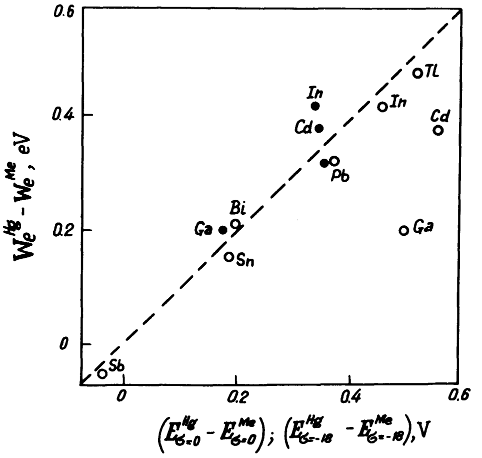

Figure 31. Dependence of $W_e^{Hg} - W_e^{Me}$ on $E_{\sigma=0}^{Hg} - E_{\sigma=0}^{Me}$ (open circles) or $E_{\sigma=-18}^{Hg} - E_{\sigma=-18}^{Me}$ (solid circles).(8)

electrolyte solutions, it is the difference in the work functions in the presence of water vapors $\Delta W_{e(H_2O)}$ which should be primarily compared with the difference of the pzc of respective metals. The most reliable data on the influence of water vapors on W_e(153) show that they practically (within ±0.05 eV) do not affect the W_e of mercury, silver, and lead and cause a decrease of W_e for gallium, iron, and platinum. However, in the latter cases there remains a difference between $\Delta E_{\sigma=0}$ and $\Delta W_{e(H_2O)}$ of the order of 0.1–0.2 V. To find the reasons for these differences requires a more thorough analysis of the phenomena involved in the adsorption of water vapors on metals.

6.2. Metal|Nonaqueous Solution Interface

Gouy(58) and Frumkin(14) were the first to perform accurate measurements of the electrocapillary curves in nonaqueous solvents. Recently, a large number of electrocapillary and capacity measurements have been made in different nonaqueous solvents (alcohols, amides, acetonitrile, ethylene and propylene carbonates, dimethylsulfoxide, liquid ammonia, etc.), mainly at mercury and bismuth electrodes. It is difficult to use the obtained data to elucidate the physical sense of the pzc, since it is impossible to compare unambiguously the potentials measured in two different solvents. Such a comparison is equivalent to the evaluation of the potential difference at the interface between electrolyte solutions in two different solvents, which requires some hypothetical assumptions.(8) Therefore it is expedient to consider only studies in which the pzc has been determined in nonaqueous solvents for two different metals.

In measurements in nonaqueous media, aqueous reference electrodes are often used and give rise in the measuring circuit to an interface between the two solvents. Since this is a nonequilibrium interface, the value of the potential difference established across it depends on the method of the interface formation;

Table 5

The Differences of the Potentials of Zero Charge of Bismuth and Mercury in Different Media

Solvent	$E_{\sigma=0}^{\mathrm{Bi}} - E_{\sigma=0}^{\mathrm{Hg}}$ (V)
Water	-0.19
Methanol	-0.18
Ethanol	-0.19
Dimethylformamide	-0.18
Dimethylsulfoxide	-0.19
Acetonitrile	-0.13

and it is possible to compare the pzc of two metals in the cases when the construction of the interface remains constant in all experiments. The comparison is more correct if, after measuring the pzc of the metal being investigated in the same cell, the pzc of a streaming mercury electrode is measured.

A large number of pzc determinations were carried out by Jakuszewski and co-workers,(154) but they used the immersion method for this purpose, which makes it necessary to exercise caution in handling their data.

In recent years reliable data have been obtained on the pzc of bismuth in different solvents, from which it is possible to find the differences of the pzc of bismuth and mercury. The results of this comparison(8) are given in Table 5. As it follows from the table, the difference of the pzc of bismuth and mercury for a number of solvents remains practically constant. In acetonitrile this difference is less than in other media; the reason for this phenomenon is not clear. Possibly, it is connected with the different structure of the interface between

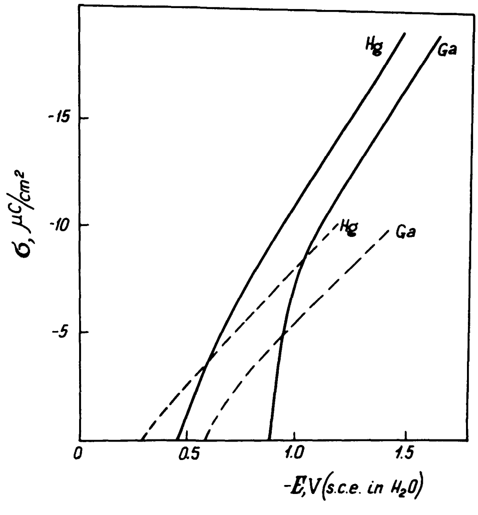

Figure 32. Dependences of the surface charge of mercury and gallium in 0.5 M Na_2SO_4 in water (solid curves) and in 0.1 M $LiClO_4$ in acetonitrile (dashed curves).(155)

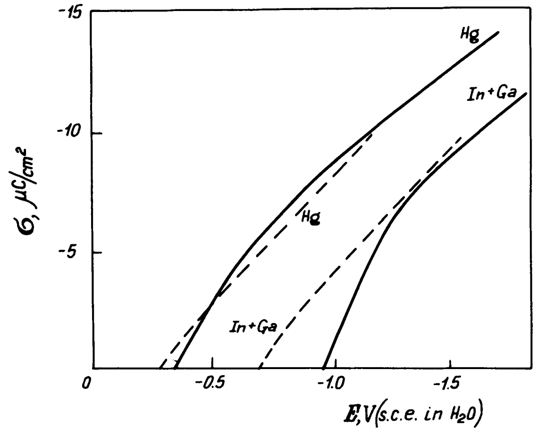

Figure 33. Dependences of the surface charge of mercury and an indium–gallium alloy in 0.1 *M* $LiClO_4$ in dimethylsulfoxide (solid curves) and in acetonitrile (dashed curves).(155)

nonaqueous and aqueous solutions in the reference electrode circuit in the pzc measurements of Bi and Hg. Similar circumstances could affect the values of $\Delta E_{\sigma=0}$ in the case of other solvents, and therefore, the data in the table need verification.

Frumkin and co-workers(155) compared the behavior of mercury, gallium, and eutectic indium–gallium alloy in water, acetonitrile, and dimethylsulfoxide. The pzc values were found from the position of the differential capacity minimum in dilute solutions and with the use of a streaming electrode.

The differential capacity curves were used to calculate the dependences of the electrode surface charge on potential in different solvents (Figures 32 and 33) and to determine the values of $E_{\sigma=q}{}^{\mathrm{Me}_2} - E_{\sigma=q}{}^{\mathrm{Me}_1}$.

Table 6, in which the obtained results are summarized, shows that the values of $E_{\sigma=0}{}^{\mathrm{Ga}} - E_{\sigma=0}{}^{\mathrm{Hg}}$ and $E_{\sigma=0}^{\mathrm{In+Hg}} - E_{\sigma=0}{}^{\mathrm{Hg}}$ depend strongly on the nature of the solvent; the difference in the pzc increases in the sequence acetonitrile < water < dimethylsulfoxide in accordance with the increase in this sequence of the chemisorption interaction between the metal surface and the

Table 6

Differences of Potentials for σ = 0 and σ = q in Various Solvents

$\mathrm{Me}_1 - \mathrm{Me}_2$	Solvent	$E_{\sigma=0}{}^{\mathrm{Me}_2} - E_{\sigma=0}{}^{\mathrm{Me}_1}$ (V)	$E_{\sigma=q}{}^{\mathrm{Me}_2} - E_{\sigma=q}{}^{\mathrm{Me}_1}$ (V)
Ga − Hg	Acetonitrile	0.29	0.23
	Water	0.50	0.17
	Dimethylsulfoxide	0.71	—
(In + Ga) − Hg	Acetonitrile	0.42	0.37
	Water	0.48	(0.34)[a]
	Dimethylsulfoxide	0.63	0.43

[a] In the case of aqueous solutions, the value of $E_{\sigma=q}{}^{\mathrm{Hg}} - E_{\sigma=q}^{\mathrm{In+Ga}}$ could be determined only approximately.

solvent molecules. At the same time the solvent affects less the difference of potentials of the same negative charge, which is determined by the difference of the work functions of the respective metals.

6.3. Metal|Electrolyte Melt Interface

For molten electrolytes the scope of the experimental data on the dependence of the pzc on the nature of the metal is larger than for nonaqueous solvents. Here, the main method of pzc determination is that of the measurement of electrocapillary curves. The first attempts at such measurements were made by Luggin, Hevesy, and Lorenz. Later, many systems were studied by Karpachev, Stromberg and co-workers, Kuznetsov and co-workers, and Smirnov and co-workers. In making electrocapillary measurements in molten electrolytes, it is necessary to keep in mind two possible error sources: the nonideal polarizability of metals in salt melts, and the wetting of glass capillary walls by liquid metals.

Along with electrocapillary measurements, the differential capacity measurements are of great importance for the investigation of the metal–melt interface. Randles and White(156) were the first to measure the capacity of mercury in mixtures of low-temperature molten electrolytes. Ukshe and co-workers carried out systematic studies of the electrode–melt interface by means of this method.(157) It was found that the *C–E* curves for liquid and solid electrodes show a well-defined minimum. Often, these curves are of an almost symmetrical and nearly parabolic form (Figure 34), but in the case of some systems, inflections or steps arise on the branches of the parabola. The appearance of steps is associated with adsorption processes, the nature of which, however, is not clear. The capacity measured in molten halides depends on the ac frequency, which is associated with faradaic processes. However, at a frequency of 20 kcps and

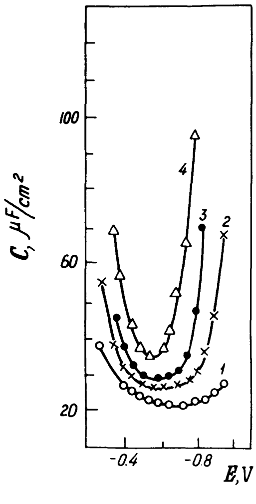

Figure 34. Differential capacity curves of a lead electrode in KCl + LiCl melt (1:1) at different temperatures: 1, 450°C; 2, 600°C; 3, 700°C; 4, 800°C. Reference electrode—Pb/KCl + LiCl (1:1), 2.5 mol % $PbCl_2$.(157)

higher, the difference of the capacity being measured from the double-layer capacity is no more than 10%–15%. The availability of the data on the double-layer capacity in electrolyte melts made it possible to compare the measured electrocapillary curves with the results of the double integration of the *C–E* curves.(157,158) The data thus obtained for Pb in chloride melts are given in Figure 35. In integrating, the value of $E_{\sigma=0}$ found from the electrocapillary measurements was used. It practically coincides with the potential of the minimum of the differential capacity curve. Good agreement between the calculated and experimental electrocapillary curves proves that capacity values obtained at high frequencies do represent the electric double-layer capacity, and the readings of the capillary electrometer do give correctly the dependence of interfacial tension on potential.

The minimum on the *C–E* curve of salt melts lies at potentials close to the potential of the maximum γ, though in some cases a scatter is observed, probably associated with the errors committed in comparing the potentials of the reference electrodes used in different studies. A fairly complete picture can be seen in Table 7.(8,157) All potentials are given against a reference electrode Pb/2.5 wt % $PbCl_2$, LiCl + KCl.

The data obtained in electrolyte melts cannot be explained in terms of the concepts of the double-layer structure generally used in interpretation of the phenomena in electrolyte solutions. A double-layer structure involving layers of ions of alternating sign is more probable, as first pointed out by Esin.(159) Such a picture was considered and theoretically substantiated by Dogonadze and Chizmadjev.(158,160)

The present state of the theory of electrolyte melts at the interface with metals does not permit one to draw definite enough conclusions regarding the coincidence of the pzc and $E_{\min}$, especially for the general case in which the radii and polarizability of cations and anions are different. Therefore, generally speaking, unlike the situation with diluted electrolyte solutions, a similarity between the potential of the minimum on the *C–E* curve and the pzc in melts can be considered only as an empirically established fact.

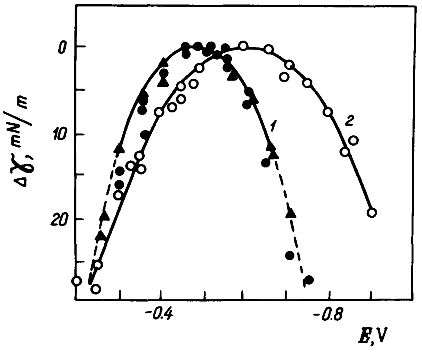

Figure 35. Electrocapillary curves of lead in NaCl (curve 1) and KCl (curve 2) melts at 820°C. The curves were obtained by integration of the capacity curves. Points—experimental data.(157)

Table 7

Potentials of Zero Charge for Metals in Contact with Molten Salts

	LiCl + KCl at 450°C		LiCl + KCl and NaCl + KCl at 700°C	
Me	Electrocapillary curves, $E_{\sigma=0}$ (V)	Capacity minimum, $E_{\sigma=0}$ (V)	Electrocapillary curves, $E_{\sigma=0}$ (V)	Capacity minimum, $E_{\sigma=0}$ (V)
Pb	0	0	0	0
Tl	−0.18	−0.22^a	−0.11	−0.32
	−0.10			
Cd	−0.16	—	—	−0.25
	−0.09	—	—	—
	−0.17	—	—	—
Ag	—	—	+0.08^b	+0.06
In	−0.07	−0.05	−0.06	−0.23
	−0.04	−0.22	−0.17^d	—
Zn	−0.08	—	—	—
	−0.05	—	—	—
	−0.15	—	—	—
Ga	+0.07	+0.05	+0.11	−0.06
	+0.13^c	−0.10	—	—
Sn	+0.24	+0.19^a	+0.30	+0.15
	+0.26^a	—	—	+0.23
	+0.28	—	—	—
Bi	+0.17	+0.35	+0.21	+0.35
	+0.24^a	—	+0.25^d	+0.23
	+0.28	—	—	—
Hg	+0.37	—	—	—
Sb	—	—	+0.61	+0.38
			+0.62	+0.37

^{a} 500°C.
^{b} 1050°C.
^{c} 400°C.
^{d} NaCl, KCl, RbCl, CsCl, 700–900°C.

Unfortunately, so far the determination of the differential capacity minimum has been the only method suggested for determination of the pzc of solid metals in melts. Ukshe and co-workers carried out some determinations of $E_{\min}$ for solid electrodes (Ag, Pt, Mo, C).(157) Ukshe and Bukun consider the obtained values of $E_{\min}$ to be close to the pzc. Delimarsky determined the pzc from the value of $E_{\min}$ for a large number of solid electrodes.(161)

Almost from the beginning of the investigation of the electrocapillary phenomena in melts, particular attention was given to the problem of the relationship between the differences of the pzc in melts and in solutions. Its correct interpretation is complicated by the fact that in addition to the change in the nature of the solvent, there is also a significant change of temperature.

Denoting by index L the quantities pertaining to the metal–electrolyte melt interface and following Ukshe and Bukun,⁽¹⁵⁷⁾ one can write

$$
\begin{aligned}
&(E_{\sigma=0}{}^{\mathrm{Me}_1} - E_{\sigma=0}{}^{\mathrm{Me}_2})_{\mathrm{H_2O}} - (E_{\sigma=0}{}^{\mathrm{Me}_1} - E_{\sigma=0}{}^{\mathrm{Me}_2})_{\mathrm{L}} \\
&\quad = \Delta T \frac{\partial \Delta W_{\mathrm{e}}}{\partial T} + (\Delta W_{\mathrm{m}}{}^{\mathrm{Me}_1} - \Delta W_{\mathrm{m}}{}^{\mathrm{Me}_2}) \\
&\qquad + [(\Delta_{\mathrm{Me}_1}{}^{\mathrm{H_2O}}\psi)_{\sigma=0} - (\Delta_{\mathrm{Me}_2}{}^{\mathrm{H_2O}}\psi)_{\sigma=0} + (\Delta_{\mathrm{Me}_2}{}^{\mathrm{L}}\psi)_{\sigma=0} - (\Delta_{\mathrm{Me}_1}{}^{\mathrm{L}}\psi)_{\sigma=0}]
\end{aligned}
\tag{6.19}
$$

Thus a distinction between the differences of $E_{\sigma=0}$ in aqueous medium and in a melt are the result of the difference in the temperature dependences of the work functions of the two metals, the change in the difference of the work functions due to melting of the metals $\Delta W_{\mathrm{m}}{}^{\mathrm{Me}_1} - \Delta W_{\mathrm{m}}{}^{\mathrm{Me}_2}$, if this occurs in the temperature range considered, and finally the change in the difference of Volta potentials at the uncharged metal–electrolyte interface when passing from water to the melt. The possibility of a change in the work function upon melting is defined by the difference in the work functions for different single-crystal faces. Therefore, it would be expedient to compare the data for aqueous solutions and melts without changing the state of aggregation of metals and, if this condition cannot be satisfied, to use for solid metals the data for polycrystalline specimens, for which the pzc values of individual faces are averaged, so that a minimum change would be expected upon melting.

The published data on the temperature coefficient of the work function are not reliable enough to make meaningful conclusions. Both the theoretical analysis and the experimental data show that this coefficient should be within 10^{-5}–10^{-4} eV/°K. Hence, it follows that when temperature changes by 400–700 K, the contribution of the temperature dependence of the work function to the shift of the pzc should exceed 0.05–0.10 V. Thus as a first approximation the temperature dependence of the difference of the pzc can be neglected, and the values of the differences of the pzc obtained in melts can be used for comparison with those obtained in aqueous solutions. In comparing the differences of the pzc in solutions and melts, the quantity in square brackets in Eq. (6.19) should be considered to be of greatest importance.

In Table 8, the values of $E_{\sigma=0}{}^{\mathrm{Me}} - E_{\sigma=0}{}^{\mathrm{Pb}}$ are compared in aqueous solutions and in molten media.⁽⁸⁾ Wherever possible, the values of the shift of the pzc corrected for the water orientation, i.e., the values of $E_{\sigma=q}{}^{\mathrm{Me}} - E_{\sigma=q}{}^{\mathrm{Pb}}$ at negative $\sigma = q$, are given. The second and third columns list the values of $E_{\sigma=0}{}^{\mathrm{Me}} - E_{\sigma=0}{}^{\mathrm{Pb}}$ determined from the position of the maximum of the electrocapillary curve in halide melts. The last column gives the values of $\Delta W_{\mathrm{e}} = W_{\mathrm{e}}{}^{\mathrm{Me}} - W_{\mathrm{e}}{}^{\mathrm{Pb}}$ taken from a table by Trasatti⁽¹⁵⁰⁾; the value for Te is taken from Fomenko.⁽¹⁶²⁾

On the whole the agreement between the values of $\Delta E_{\sigma=0}$ in aqueous solutions, of $\Delta E_{\sigma=0}$ in halide melts, and the values of ΔW_{e} can be considered

Table 8

Differences of Potentials of Zero Charge of Various Metals with Respect to That for Lead

Me	$\Delta E_{\sigma=0}$ (V) Aqueous solutions	$\Delta E_{\sigma=0}$ (V) LiCl + KCl 450°C	$\Delta E_{\sigma=0}$ (V) LiCl(NaCl + KCl) 700°C	ΔW (eV)
Te	1.16(?)	1.05	0.83	0.73
Hg	0.37(0.36)	0.44	—	0.49
Sb	0.41	—	0.56	0.55
Sn	0.18(0.26)	0.27	0.30	0.34
Bi	0.17(0.19)	0.27	0.30	0.28
Pb	0.00(0.00)	0.00	0.00	0.00
In	−0.09(0.02)	−0.05	−0.07	0.07
Ga	−0.13(0.18)	0.09	0.06	0.24
Tl	−0.15	−0.11	−0.11	−0.17
Cd	−0.19(0.01)	−0.15	—	0.04

satisfactory. After correction for the effect of the water dipoles orientation, for Ga the values of $\Delta E_{\sigma=0}$ in aqueous medium and in melts have the same sign.

At the present state of the measuring technique in melts, only the data obtained by one and the same investigator can be considered to be completely comparable. The most reliable results of the comparison of the values of $\Delta E_{\sigma=0}$ in chloride melts and ΔW_e were obtained by Kuznetsov and co-workers.(163) The value of ΔW_e was determined directly from the shift of the diode characteristic when passing from a streaming electrode from metal Me_1 to the alloy $Me_1 + Me_2$, and not from the difference of the work functions measured in independent experiments. To reduce the risk of contaminating one metal by the vapors of the other, a metal with a higher vapor tension was chosen as Me_1. The results of these measurements are listed in Table 9. The accuracy of the measurement of ΔW_e was estimated by the above authors to be ±0.05 V.

In these experiments the greatest approach between the difference of the pzc in halide melts and the difference in the work functions was achieved (the

Table 9

Differences of Work Functions and Potentials of Zero Charge among Various Metals

Me_1	Me_2 (at %)	$\Delta E_{\sigma=0}$ (V)	ΔW_e (eV)
Sn	Sn + 0.15% Te	−0.18	−0.15
Sn	Sn + 23.8% Tl	0.24	0.17
Sn	Sn + 53% Cd	0.27	0.25
Bi	Bi + 3.6% Te	−0.25	−0.30
Bi	Bi + 9% Te	−0.33	−0.35
Tl	Tl + 50% Te	−0.67	−0.65

root-mean-square deviation only 0.04 V). It is not clear, however, whether these conclusions could be extended to a wider range of systems.

6.4. Metal|Solid Electrolyte Interface

Recently, a method has been developed for the determination of the pzc of molten metal at the interface with the solid electrolyte (ZrO_2) from the dependence of the contact angle on polarization.(164) The results of the pzc determination at this interface are not numerous as yet and do not warrant any theoretical generalization.

7. Potentials of Zero Charge and Electrochemical Kinetics

Electrochemical reactions occur within the limits of the electric double layer, and their rate depends on its structure. At a given electrode potential and ionic strength of solution, the structure of the electric double layer is determined primarily by the pzc value. Thus, the connection between the rate of electrochemical reactions and the pzc is established. In a general case the position of the pzc influences the kinetics of electrochemical processes through the ψ_1 correction and through the influence of the double-layer charge on the adsorption and orientation of solvent molecules and other solution components. Different aspects of the relationship between the pzc and the characteristics of electrode reactions have been considered in detail.(8) Here, the discussion shall be restricted to the possibility of determining the pzc from the kinetic data and the use of these data for confirmation of the correctness of the pzc determination by other methods.

Frumkin was the first to show that if the rate of the establishment of equilibrium between the surface layer and the solution bulk is large as compared to that of the electrode process, then, in the absence of concentration polarization, the current density i is

$$i = k_0 n F c_i^0 \exp\left\{\frac{F}{RT}[-\alpha n_a E + (\alpha n_a - z_i)\psi_1]\right\} \tag{7.1}$$

where k_0 is a constant, n is the total number of electrons participating in the electrochemical process, α is the transfer coefficient, n_a is the algebraic number of electrons transferred from the electrode to a reacting particle in an elementary act of the process, and z_i is the charge of the reacting particle.

It is easily found from Eq. (7.1) that the hydrogen overvoltage should decrease with a decrease in the absolute value of ψ_1, i.e., with decreasing diffuseness of the double layer if $\psi_1 > 0$, and should increase if $\psi_1 < 0$. In surface-inactive electrolyte solutions at the pzc, $\psi_1 = 0$, and therefore, in these solutions the reaction rate should not depend on the supporting electrolyte concentration. In principle this conclusion can be used as a basis in the pzc determination. A tendency of the η–log i curves of hydrogen evolution to draw closer as the pzc is

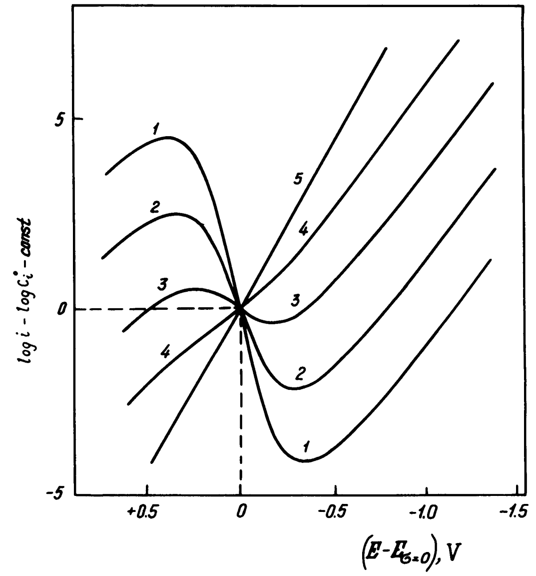

Figure 36. Polarization curves calculated by means of Eq. (7.1) at $z_i = -2$, $\alpha = 0.5$ for the ψ_1 potentials corresponding to the potential of the outer Helmholtz plane of a mercury electrode in solutions: 1, 0.001 *M* NaF; 2, 0.01 *M* NaF; 3, 0.1 *M* NaF; 4, 0.9 *M* NaF; 5, $\psi_1 = 0$.(111)

approached in solutions of different concentrations was pointed out for bismuth by Palm and Tenno.(165)

The pronounced ψ_1 effects leading to a change in the shape of the *i–E* curves were studied in detail for anion electroreduction reactions. Figure 36 shows the polarization curves of a double-charged anion electroreduction in the presence of different concentrations of a specifically nonadsorbable 1,1-valent electrolyte, calculated by means of Eq. (7.1).(111) $E_{\sigma=0}$ is the abscissa of the common point of intersection of the curves at different supporting electrolyte concentrations. So far, such intersection was observed only in the case of $S_2O_8^{2-}$ anion reduction at a dropping mercury electrode from solutions in dimethylsulfoxide (Figure 37). It was stated that the intersection of the curves actually lies at the

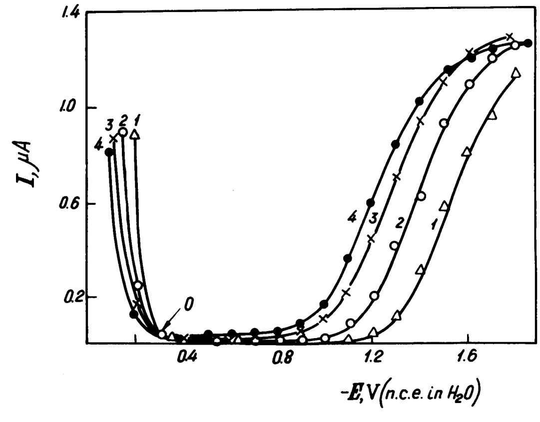

Figure 37. Polarograms of $S_2O_8^{2-}$ anion electroreduction on a dropping mercury electrode from the solutions 5×10^{-4} *M* $Na_2S_2O_8$ in dimethylsulfoxide in the presence of $NaClO_4$ in concentrations: 1, 10^{-2} *M*; 2, 2.5×10^{-2} *M*; 3, 5.0×10^{-2} *M*; 4, 1.0×10^{-1} *M*. 0— the intersection point of the curves roughly corresponding to $E_{\sigma=0}$.(166)

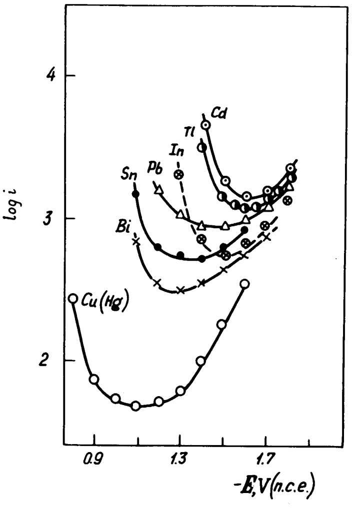

Figure 38. Dependence of the reduction rate of the $S_2O_8^{2-}$ anion in 5 × 10^{-4} *M* $Na_2S_2O_8$ + 9 × 10^{-3} *M* NaF on potential at rotating disk electrodes from Cu(Hg), Bi, Sn, Pb, In, Tl, Cd.(167)

pzc.(166) The intersection could be observed because of a low rate constant of electroreduction of $S_2O_8^{2-}$ from this solvent. The use of this method for the pzc determination in other systems is not easy since it involves elimination of the diffusion difficulties. For such systems it is possible to assess the correctness of the calculation of the ψ_1–E dependences, and hence the correctness of the choice of the pzc value for the cathode material by comparing the experimental i–E curves with Eq. (7.1). It is especially convenient to use for this purpose the dependence of $\log i + (z_iF/2.3RT)\psi_1$ on $-(E - \psi_1)$, which became known as the corrected Tafel plot(115) (CTP). As follows from Eq. (7.1), in the absence of specific adsorption of the reacting particle and the reaction product, the CTP should be be invariant under a change of the supporting electrolyte concentration.

Figures 38 and 39 give the results of the comparison of the polarization curves and CTP for different metals in the electroreduction reaction of S_2O_8.(167) Though the polarization curves differ strongly for different metals, the CTP show

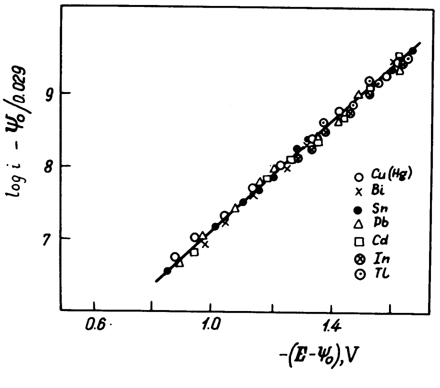

Figure 39. Corrected Tafel plots of the $S_2O_8^{2-}$ anion electroreduction in the same solutions and at the same metals as in Figure 38.(167)

fairly good coincidence. This coincidence confirms the correctness of the pzc values used in calculations. However, the solution of the inverse problem, viz., the finding of an accurate pzc value from the experimental log i–E curve, presents difficulties, since when the nature of the electrode changes, it is not only the pzc value which changes, but also the character of the σ–E dependence and hence the shape of the ψ_1–E curve; this is associated with the influence of water chemisorption on the capacity of the double layer.

The coincidence of the CTP proves conclusively that the work function into a vacuum does not figure directly in the equations of electrochemical kinetics.

8. Conclusion

Considerable progress has been made in the development of the methods of the pzc determination both for ideally polarizable and reversible electrodes. For some metals reliable pzc values have been obtained by these methods. Various factors influencing the pzc have been defined; and the relationship between the pzc and other characteristics of metals, as well as the role of the pzc in electrochemical kinetics, has been established.

At the same time there are many electrochemical systems for which reliable pzc values have not been obtained. In further studies the crystallographic inhomogeneity of polycrystalline electrodes can gravely complicate the conventional interpretation of experimental data. In particular the minimum on the differential capacity curve in dilute solutions of a symmetrical surface-inactive electrolyte may not coincide with the pzc. In this case it is necessary to change from polycrystalline to single-crystal electrodes, at any rate in investigating metals for which the pzc of individual faces differ by some tenths of a volt. Such a change is also necessary for better elucidation of the role of the pzc in the kinetics of electrode processes.

The increasing use of nonaqueous solvents in electrochemistry requires further systematic determinations of the pzc in nonaqueous media.

Finally, it might be well to point out the importance of obtaining more reliable data on the work functions, which will permit a more accurate determination of the quantitative relationship between the work function and the pzc.

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