

Historical development of theories of the electrochemical double layer

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Abstract This review describes the evolution of important concepts related to potential drops at interfaces in electrochemical systems. The role of the thermodynamic theory of electrocapillarity of perfectly polarizable electrodes in the development of interfacial electrochemistry is emphasized. A critical analysis of the phenomenological models of the electrical double layer on ideally polarizable electrodes is given. Certain trends in studying solid electrodes with well-defined surfaces brought into contact with electrolyte solutions are summarized. Attention is drawn to several unsolved problems crucial for the future development of electrochemical surface science. Finally, some recent experimental data are analyzed for selected models.

Keywords Electrochemical interfaces · Volta problem · Electrocapillarity · Electrical double-layer models · Potential of zero charge

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Introduction

The end of the twentieth century and the beginning of the twenty-first century witnessed a burgeoning interest in the development of new materials and their high-technology applications. This trend has significantly affected modern electrochemistry, where attention has gradually shifted away from theoretical analysis toward materials characterization. Indeed, there is a risk today that electrochemistry may lose its status as a fundamental science and merely become a branch of materials science. From our point of view, however, at least two branches of electrochemistry will act as bulwarks against such a transformation. These are the detailed study of charged interfaces and the detailed study of charge transfer.

In this review, we attempt three things. Firstly, we summarize important historical trends in the study of charged interfaces. Secondly, we describe the current state of the art in this field. Finally, we attempt some prognoses of future developments.

The formation of interfaces is known to be accompanied by a spatial separation of charge, such that electric potential differences appear and the activities of various components are locally perturbed. Conventionally speaking, the electric double layer (EDL) is formed at such an interface. Below, we shall adopt this term; however, it will soon become clear that the term is not unconditional and sometimes does not reflect the real structure of the interface.

Interest in the structure and properties of charged interfaces increased steadily throughout the past century and stimulated vigorous discussions at many international conferences, as well as the publication of numerous special issues of leading electrochemical journals. In addition, many reviews, monographs, reference works, and encyclopedias were also published. Unfortunately, it is physically impossible for this abundance of material to be adequately summarized within the purview of one review, so in what

follows we shall cite only those articles that are most pertinent to our immediate goals.

Evolution of concepts related to the Volta problem in electrochemistry

A central problem of fundamental electrochemistry that manifested very early in the history of this new science was the “Volta problem”, i.e., understanding the relationship between the electromotive force (emf) of a galvanic cell and the potential drops inside it, particularly the contact potential differences at the metal boundaries.

The first ideas regarding the appearance of an emf were put forward by Volta [1]. He assumed (1) that the potential difference at the terminals of a correctly opened electrochemical circuit was localized at the boundary of the two different metals involved in the circuit and (2) that it was equal to the external contact potential difference (now called the Volta potential) $\Delta_{M1}^{M2}\psi$ at the boundary of the two metals M1 and M2. However, based on such ideas, it soon became clear that galvanic cells would have to be perpetual motion machines of the first kind, and of course they are not.

After the laws of conservation of matter, charge, and energy were established in the mid-nineteenth century, the theory of Volta was abandoned for a chemical theory conceived in its final form by Nernst [2]. According to Nernst, it was the *physicochemical processes* occurring at the electrode/solution boundary which were responsible for the conversion of chemical energy into electrical energy and which gave rise to the formation of the potential drops $\Delta\varphi_{\text{ion}}^{M1}$ and $\Delta\varphi_{\text{ion}}^{M2}$. These were assumed to be located in ionic double layers at the electrode–solution boundaries. According to Nernst, the algebraic sum of these ionic potential drops determined the emf, whereas $\Delta_{M1}^{M2}\psi = 0$. The widely known Nernst formula for the dependence of $\Delta\varphi_{\text{ion}}^M$ on concentration (activity) of potential-determining ions was triumphantly confirmed experimentally. On the other hand, non-zero values of $\Delta_{M1}^{M2}\psi$ were also observed experimentally and explained by Ostwald [3] as due to the presence of moisture on the surfaces of the two connected metals. However, this explanation was soon dispelled by Langmuir [4] who confirmed the existence of contact potential differences using vacuum technology to eliminate water from the junctions. Hence, it emerged that both the Volta theory and the Nernst theory contradicted experimental data, and the problem of the relationship between the emf and $\Delta_{M1}^{M2}\psi$ (the “Volta problem”) remained unsolved.

The first consistent—albeit approximate—solution of the Volta problem was proposed by Frumkin and Gorodetskaja [5]. They based their explanation on the concept of a potential of zero charge (PZC). By combining the concepts of Volta and Nernst [5–7] and focusing on solutions

containing no surface-active species, Frumkin was able to derive the difference of PZC between two metals as:

$$E_{\sigma=0}^{M2} - E_{\sigma=0}^{M1} = \Delta_{M1}^{M2}E_{\sigma=0} \approx \Delta_{M2}^{M1}\psi = [W^{M2} - W^{M1}]/e_0, \quad (1)$$

where $E_{\sigma=0}^M$ is the PZC of the metal M, W^M is the work function corresponding to the electron transfer from metal to vacuum, σ is the charge density on the electrode, and e_0 is the elementary charge. If the potentials of two electrodes differ from the PZC, then,

$$E_{\sigma}^{M2} - E_{\sigma}^{M1} = \Delta_{M1}^{M2}E_{\sigma} \approx \Delta_{M2}^{M1}\psi + [\Delta\varphi_{\text{ion}}^{(M2)} - \Delta\varphi_{\text{ion}}^{(M1)}]. \quad (2)$$

Evidently, the two terms on the right side of this equation correspond exactly to the Volta and Nernst theories. Later, some authors assumed that Eq. 1 was rigorous, which implied that it could be used to determine either the PZC (based on known work functions) or the work function (based on known PZC).

For certain metals placed in aqueous solutions, or molten salts, Eq. 1 was indeed confirmed by experimental data [6, 7]. However, for high-purity-grade mercury and gallium in aqueous solutions, the following substantial deviation was revealed [8]: $\Delta_{\text{Ga}}^{\text{Hg}}E_{\sigma=0} = 0.5\text{V}$, while $\Delta_{\text{Ga}}^{\text{Hg}}W/e_0 = 0.2\text{V}$. This was explained by different hydrophilicities of mercury and gallium. Mercury can be considered as virtually hydrophobic at its PZC, whereas on uncharged gallium, water dipoles are oriented with their negative poles pointing toward the metal. As a result, the PZC difference contains the negative contribution of the chemisorbed dipoles. On the other hand, if we shift the charge of the Ga electrode to high negative values ($\sigma_1 \ll 0$), no chemisorbed water dipoles are left on its surface and the quantity $\Delta_{\text{Ga}}^{\text{Hg}}E_{\sigma_1} = 0.17\text{V}$ turns out to be much closer to the difference of their work functions as compared with $\Delta_{\text{Ga}}^{\text{Hg}}E_{\sigma=0}$.

This result was used by Trasatti [9, 10] for calculating the so-called electrochemical work function of electrons from metals:

$$(W^M)_{\text{elch}}/e_0 = W^{\text{Hg}}/e_0 - \Delta_{\text{M}}^{\text{Hg}}E_{\sigma_1}. \quad (3)$$

The quantities $(W^M)_{\text{elch}}$ calculated from formula 3 could have been preferred over the experimental work functions because the accuracy of determination of the latter was lower (3). However, this approach is not flawless because the double-layer capacitances at high negative electrode potentials are different on different metals [11–13]; hence, σ vs. E curves in this region are not parallel to one another. In other words, the values of $\Delta_{\text{Ga}}^{\text{Hg}}E_{\sigma_1}$ at different $\sigma_1 \ll 0$ (e.g., at -12 and $-15 \mu\text{C cm}^{-2}$) are not the same, although the errors of their determination are not too high and can be eliminated by the introduction of a correcting term proportional to the electrode charge.

A modern approach to the Volta problem has been considered for specially selected model systems in a series of studies of one of the authors of the present review. The full list can be found in a review [14] (and in references [8–46] therein).

First of all, note that the exact relationship between the difference between the PZCs of two metals and the difference of their work functions should be written as the algebraic sum of *three* Volta potentials,

$$\Delta_{M1}^{M2} E_{\sigma=0} = \Delta_{M1}^{M2} W/e_0 + (\Delta_S^{M2} \psi)_{\sigma=0} - (\Delta_S^{M1} \psi)_{\sigma=0}. \quad (4)$$

Volta potentials at the interface between solution S and uncharged metals M1 and M2 are non-zero and, in the general case, do not compensate each other [15, 16]. Each potential can be expressed as the algebraic sum of surface potentials of solution χ_S and metal χ_M and also of the Galvani potential $(\Delta_S^M \varphi)_{\sigma=0} = \chi_M^{(S)} - \chi_S^{(M)}$. Here, the term $\chi_M^{(S)}$ corresponds to the surface potential of uncharged metal which changes upon contact with solution, and the term $\chi_S^{(M)}$ corresponds to the surface potential of solution which changes due to its contact with the uncharged metal. We express these changes in surface potential as $\delta\chi_M = \chi_M^{(S)} - \chi_M$ and $\delta\chi_S = \chi_S^{(M)} - \chi_S$. Then, taking into account that the terms χ_S cancel each other, Eq. 4 can be represented as follows:

$$\Delta_{M1}^{M2} E_{\sigma=0} = \Delta_{M1}^{M2} W/e_0 + \left[\Delta_{M1}^{M2} (\delta\chi_M)_{\text{phys}} \right]_{\sigma=0} + \left[\Delta_{M1}^{M2} (\delta\chi_M + \delta\chi_S)_{\text{chem}} \right]_{\sigma=0}. \quad (5)$$

Here, $\left[\Delta_{M1}^{M2} (\delta\chi_M)_{\text{phys}} \right]_{\sigma=0}$ is the difference of electron density perturbations for metals M1 and M2 under the condition that their contact with the solvent was not accompanied by chemisorption (donor–acceptor) interactions of the metal–solvent type. The third term on the right side of Eq. 5 that can be shortened as $(\Delta_{M1}^{M2} E_{\text{chem}})_{\sigma=0}$ expresses the changes in the surface potentials of the metal and the solvent upon the transition from metal M1 to metal M2, caused by different chemisorption interactions of these metals with the solvent.

It is convenient to take a mercury electrode as the reference electrode in finding the potential drops that characterize the metal–solvent chemisorption interactions for a series of metals. In this case, the first two terms on the right side of Eq. 5 determine the corrected electrochemical work function so that Eq. 5 assumes the more compact form

$$\Delta_M^{\text{Hg}} E_{\sigma=0} = \left(\Delta_M^{\text{Hg}} W/e_0 \right)_{\text{elch}} + \left(\Delta_M^{\text{Hg}} E_{\text{chem}} \right)_{\sigma=0}. \quad (6)$$

In the aforementioned series of studies, high-precision measurements of the PZC and differential capacitance curves were performed on renewable liquid electrodes of mercury and gallium and also of In-Ga, Tl-Ga, Sn-Ga, Bi-Ga, Pb-Ga, and Cd-Ga alloys in surface-inactive electrolyte

solutions in the following solvents: water, methanol (MeOH), ethanol (EtOH), acetonitrile (AN), formamide (FA), *N*-methylformamide (NMF), dimethylformamide (DMF), dimethylsulfoxide (DMSO), propylene carbonate, ethylenediamine (EDA), and hexamethylphosphortriamide (HMPTA). In total, there were 41 different interfaces. Particularly, these studies demonstrated that In, Tl, Sn, Bi, Pb, Cd, and Hg in their alloys with Ga are surface-active components which are exposed to the interface and have double-layer characteristics close to those of pure metals dissolved in gallium. The following table shows the terms involved in Eq. 6 for the mentioned interfaces (Table 1).

Values shown in parentheses could not be obtained directly and were derived using Eq. 6. In the other cases, the tabulated data were obtained by independent methods and confirm the validity of the latter equation.

The tabulated data show that for a wide range of systems, no general dependence is observed between the PZC and the electron work function from metal to vacuum. This is associated with the fact that terms $\Delta_M^{\text{Hg}} E_{\sigma=0}$ and $(\Delta_M^{\text{Hg}} E_{\text{chem}})_{\sigma=0}$ depend not only on W^M but also on the distance, d_{ms} , of closest approach of the solvent dipoles to the ionic frame of the metal in the absence of metal–solvent chemisorption interaction [17, 18]. Note that the quantity d_{ms} can be assessed from the difference of reciprocal double-layer capacitances in the negative charge range where the chemisorption interaction of solvent dipoles with the electrode surface is no longer observed.

To understand the effect of one of these factors on $\Delta_M^{\text{Hg}} E_{\sigma=0}$ and $(\Delta_M^{\text{Hg}} E_{\text{chem}})_{\sigma=0}$, the other factor must be fixed. By focusing on systems $\sigma=0$ that have similar values of electrochemical work function (such as Ga, Bi–Ga, and Sn–Ga electrodes, and also Pb–Ga, In–Ga, and Cd–Ga electrodes), it can be shown that the donor–acceptor interaction between metal and solvent is stronger at smaller distances, d_{ms} . This is associated with the greater overlap of the electronic levels of the metal and solvent. The metal–solvent interaction is also strengthened by increasing the donor number of the solvent.¹

On the other hand, for metals with close d_{ms} , such as Tl–Ga, In–Ga, and Ga in all solvents, the metal–solvent chemisorption interaction characterized by the term $(\Delta_M^{\text{Hg}} E_{\text{chem}})_{\sigma=0}$ was observed to increase with an increase in the electron work function in the following series: Tl–Ga < In–Ga < Ga. This effect was strengthened with the increase in the donor number of solvent. As a result, the slope of the $\Delta_M^{\text{Hg}} E_{\sigma=0}$ vs. $(\Delta_M^{\text{Hg}} W/e_0)_{\text{elch}}$ dependence in solvents with the low donor numbers (DN) was positive, whereas in

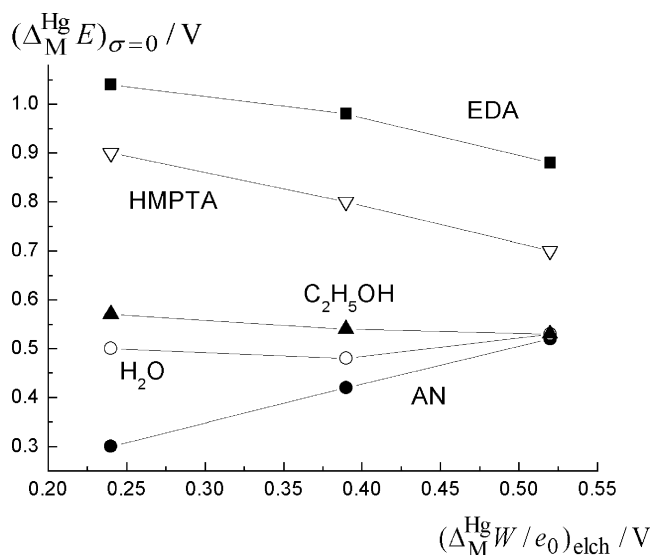
¹ For solvents under study, the donor numbers are as follows: AN, 14.1; PC, 15.1; water, 18.0; MeOH, 19.0; EtOH, 19.6; FA, 24.0; DMF, 26.6; DMSO, 29.8; HMPTA, 38.8; EDA, 55 [19].

Table 1 Relationship between PZC and electrochemical work function (in volts)

Metal	Solvent	$\Delta_M^{\text{Hg}} E_{\sigma=0}$	$(\Delta_M^{\text{Hg}} W/e_0)_{\text{elch}}$	$(\Delta_M^{\text{Hg}} E_{\text{chem}})_{\sigma=0}$
Ga	AN	0.30	0.25	0.05
	PC	0.30	0.24	0.06
	Water	0.50	0.24	0.26
	MeOH	0.56	0.25	0.31
	EtOH	0.57	0.25	0.32
	NMF	0.59	0.24	0.35
	DMF	0.64	(0.24)	0.40
	DMSO	0.72	(0.25)	0.47
	HMPTA	0.90	(0.24)	0.66
	EDA	1.04	(0.24)	0.80
In-Ga	AN	0.42	0.39	0.03
	PC	0.43	0.40	0.03
	Water	0.48	0.39	0.09
	MeOH	0.53	0.39	0.14
	EtOH	0.54	0.39	0.15
	NMF	0.55	0.39	0.16
	DMF	0.59	(0.39)	0.20
	DMSO	0.63	(0.39)	0.24
	HMPTA	0.80	(0.39)	0.41
	EDA	0.98	(0.40)	0.58
Tl-Ga	AN	0.52	0.52	0
	PC	0.53	0.53	0
	Water	0.52	0.52	0
	MeOH	0.53	0.53	0
	EtOH	0.53	0.52	0
	NMF	0.56	0.53	0.03
	DMF	0.58	(0.53)	0.05
	DMSO	0.59	(0.52)	0.07
	HMPTA	0.70	(0.53)	0.17
	Cd-Ga	PC	0.51	0.47
Water		0.56	0.45	0.11
MeOH		0.65	0.47	0.18
HMPTA		0.92	(0.46)	0.46
EDA		1.08	(0.48)	0.60
Bi-Ga	AN	0.185	0.18	0
	Water	(0.19)	0.19	0
Sn-Ga	AN	0.17	0.17	0
	Water	(0.20)	0.17	0.03
Pb-Ga	PC	0.42	0.42	0
	Water	0.42	0.42	0
	FA	0.42	0.42	0

solvents with high donor numbers (HMPTA, EDA), the slope became negative (see Fig. 1).

The described relationships were obtained for the so-called mercury-like metals (also called *s,p*-metals). But for many other metals, and particularly for the widely used *d*-metals which exhibit a pronounced anisotropy of both the

**Fig. 1** Relationship between PZC and electrochemical work function

PZC and the work function on different single-crystal faces, a rigorous analysis of the relationship between the PZC and the work function is still missing. Likewise, the analysis of the solvophobic–solvophilic characteristics and the derivation of the corresponding solvophilicity series have not been completed.

Finally, we note that the relationships mentioned above are still to be substantiated by quantum mechanical and quantum chemical approaches and the modern electronic theory of metals.

Development of the thermodynamics of surfaces

The basis of the thermodynamics of interfacial phenomena was laid by Lippmann [20] who put forward the famous equation named after him

$$\sigma = -(\partial\gamma/\partial\varphi)_{\mu_i}. \quad (7)$$

In this equation, γ is the reversible work of surface formation (for a liquid electrode, surface tension) and μ_i is the chemical potential of the *i*th solution component. The physical meaning of quantity σ will be discussed in detail below.

The thermodynamic theory was further advanced by Gibbs [21, 22] and Planck [23]. Gibbs not only put forward a general adsorption equation to describe surface phenomena but also emphasized the difference between the work of surface formation and the surface tension for solid surfaces. Initially, Lippmann called the quantity σ the electrical capacitance of a unit surface at a constant potential difference. According to Gibbs, the left side of this equation corresponds to the surface density of an adsorbed electro-

chemically active substance expressed in electric units. Planck derived Eq. 7 for the so-called perfectly (or completely) polarizable electrode (“vollkommen polarisierbare Elektrode”), i.e., an electrode the state of which is completely determined by the amount of electricity passed through it. Planck stressed that this does not establish any relationship between this value and the free charges on both sides of the electrode surface. The Planck concept could be fully applied only in the 1960s–1970s [7], which led to the formulation of the modern concept of electrode charge and the derivation and testing of thermodynamic relationships for perfectly polarizable electrodes, as is shown below.

Since 1934, studies of electrocapillarity and the electrical double layer have operated with the concept of Koenig [24] of the “ideally polarizable” electrode, i.e., an electrode whose surface cannot be crossed by charged species. In this case, the Lippmann quantity σ becomes identical with the density of free charge on the EDL and, at fixed temperature and pressure, the system should obey Gibbs’ equation of electrocapillarity in the form [25]:

$$d\gamma = -\sigma d\varphi - \sum_i \Gamma_i d\mu_i. \tag{8}$$

Here, Γ_i is the surface excess² of the i th component. Experimental procedures make it possible to determine only relative surface excesses $\Gamma_i^{(S)}$ corresponding to $\Gamma_S = 0$, where S is the solvent.

From Eq. 8, the Lippmann Eq. 7 and the formula for specific differential capacitance of the electrode can be derived

$$C = (\partial\sigma/\partial\varphi)_{\mu_i} = -(\partial^2\gamma/\partial\varphi^2)_{\mu_i}. \tag{9}$$

When determining the surface excesses $\Gamma_i^{(S)}$ for different concentrations c_i and different potentials based on experimental data and using Eq. 8, we, however, do not know how the concentration profile of component i changes with the distance x from the electrode surface, how it changes with the electrode potential, and what is the surface concentration of this components (i.e., how many species i are in direct contact with the electrode surface unit). To answer these questions, an adsorption model of the near-electrode layer should be developed, i.e., an EDL model.

If the solution contains a redox system and the following equilibrium is established on the electrode



so that the potential is determined by the Nernst equation

$$dE = d\mu_{\text{Ox}} - d\mu_{\text{Red}} \tag{11}$$

where μ_{Ox} and μ_{Red} are chemical potentials of Ox and Red, then the Gibbs adsorption equation can be written as follows [7, 26]:

$$d\gamma = -\Gamma_{\text{Ox}}d\mu_{\text{Ox}} - \Gamma_{\text{Red}}d\mu_{\text{Red}} - \sum_i \Gamma_i d\mu_i \tag{12}$$

where Γ_{Ox} and Γ_{Red} are the Gibbs adsorption values of Ox and Red expressed in electric units. Hence, the following electrocapillarity equations apply for a reversible electrode:

for $\mu_{\text{Ox}} = \text{const}$

$$d\gamma = \Gamma_{\text{Red}}dE - \sum_i \Gamma_i d\mu_i \tag{13}$$

For $\mu_{\text{Red}} = \text{const}$

$$d\gamma = -\Gamma_{\text{Ox}}dE - \sum_i \Gamma_i d\mu_i \tag{14}$$

and also equations

$$(\partial\gamma/\partial E)_{\mu_{\text{Ox}}, \mu_i} = \Gamma_{\text{Red}} = -Q' \tag{15}$$

$$(\partial\gamma/\partial E)_{\mu_{\text{Red}}, \mu_i} = -\Gamma_{\text{Ox}} = -Q''. \tag{16}$$

The latter two relationships can be considered as the Lippmann equations for a reversible electrode. In the general case, the number of characteristic electrocapillarity equations and Lippmann equations is apparently determined by the number of independent variables in the Nernst equation that expresses the equilibrium conditions for the system.

The quantities Q' and Q'' are referred to as the surface total charges (STC) at a constant chemical potential of Ox (STC of the first kind) and Red (STC of the second kind), respectively. Indeed, they are equal to the quantities of electricity that can be produced by the complete electrode reduction of Q'' or (with opposite sign) the complete oxidation of Q' assuming that these redox processes occur in a surface unit and no charge is exchanged between the electrode surface and the solution volume. Correspondingly, this involves the introduction of the following terms: electrocapillary curves of the first and second kinds, charging curves of the first and second kinds, and EDL differential capacitance curves of the first and second kinds.

To reveal the relationship between Q' and Q'' , on the one hand, and the surface free charge σ , on the other hand, one must go beyond thermodynamic considerations and use a model for the nature of the solution components in their adsorbed state. Thus, after assuming the absence of all other charge transfer routes except the process determined by Eq. 10, and after designating the amount of Ox and Red per surface unit as A_{Ox} and A_{Red} , respectively, we obtain the relationships

$$\Gamma_{\text{Red}} = -Q' = -\sigma + A_{\text{Red}} \tag{17}$$

$$\Gamma_{\text{Ox}} = Q'' = \sigma + A_{\text{Ox}}. \tag{18}$$

² This is the amount of a given component that should be introduced into the solution so that the increase in the interface by a surface unit would not change the volume phase composition.

The thermodynamic theory of electrocapillarity of reversible electrodes has been subjected to thorough experimental testing, particularly by means of disperse metals of the platinum group (see [7, 27–31] and references therein). For the platinum–hydrogen electrode, in place of Eqs. 17 and 18, we obtain

$$\Gamma_{\text{H}} = -Q' = -\sigma + A_{\text{H}} \quad (19)$$

$$\Gamma_{\text{H}^+} = Q'' = \sigma + A_{\text{H}^+}. \quad (20)$$

In determining the free charge, it was assumed that in the surface layer, a sharp distinction existed between hydrogen atoms and hydrogen ions, and it was also assumed that no partial charge transfer occurred during the adsorption of solution ions.

The validity of the thermodynamic theory of perfectly polarizable electrodes has been confirmed by many experiments in the hydrogen and double-layer potential regions of platinum, and also in the region of low surface coverages with adsorbed oxygen. For electrocapillary, charging, and differential capacitance curves of the first and second kinds of platinum electrodes, see publications [7, 27–31].

Within the framework of the thermodynamic approach, the problem of partial charge transfer during the adsorption of solution components on the interface has also been discussed. The concept of partial charge transfer was put forward by Lorenz [32] and further developed in a large series of his studies, but was also subject to some criticism [33, 34]. However, the very possibility of such transfer in the presence of a covalent bond formed between an ion located in the dense part of the EDL and the metal is indisputable. If a redox process (Eq. 10) occurs via an intermediate adsorption state Ad



then the quantities n_1 and n_2 , which are called the formal charge transfer coefficients, can be found from the following equations [35]

$$n_1 = -(\partial Q' / \partial \Gamma_{\Sigma})_E = (\partial \Gamma_{\text{Red}} / \partial \Gamma_{\Sigma})_E \quad (23)$$

$$n_2 = (\partial Q'' / \partial \Gamma_{\Sigma})_E = (\partial \Gamma_{\text{Ox}} / \partial \Gamma_{\Sigma})_E \quad (24)$$

where $\Gamma_{\Sigma} = \Gamma_{\text{Ox}} + \Gamma_{\text{Red}}$, $n_1 + n_2 = 1$.

In essence, the quantities n_1 and n_2 provide information on neither the adsorbed state of the substance nor even on which solution components are involved in the formation of the state. Thus, they are not identical to true charge transfer

coefficients. Hence, it is beyond reason to call these values “electrosorption valences,” as was done in [36, 37]. The formal nature of n_1 and n_2 and their difference from true charge transfer coefficients follow from the results of calculations of n_1 and n_2 for the Hg, Tl, Tl^+ , H_2O system [38]. It was shown that upon reaching a certain potential value, the dependence of n_2 on the potential has a discontinuity, i.e., $n_2 \rightarrow \pm\infty$.

Attempts to derive true coefficients from formal coefficients, such as those based on model considerations undertaken by Schultze and coworkers [39, 40], failed. In order to be successful, the method requires the use of an independent physical technique (such as in situ spectroscopy) together with the appropriate theory.

The thermodynamic theory of electrocapillarity still remains topical and is actively being developed. This is evident from various publications [41, 42] and from a number of studies in which the thermodynamic approach is used for analyzing surface phenomena on well-defined surfaces of platinum group metals (see, e.g., [43–47]). These studies consider different constituents of the surface layer in deriving the thermodynamic relationships as compared with the earlier studies on disperse platinum metals. Moreover, the solution compositions chosen for the measurements do not always coincide with those used earlier [27–31]. For this reason, the recent measurements cannot be compared directly with those made earlier. Undoubtedly, such a comparison is desirable.

For acidic solutions, it can be assumed with a sufficiently high degree of approximation that in the presence of an excess of foreign electrolyte, hydrogen ions are for the most part displaced from the surface layer of platinum. Hence, it is possible to distinguish between hydrogen ions and atoms. In alkaline solutions, the situation requires further consideration. The possibility of making a distinction between adsorbed OH^- ions and some forms of adsorbed oxygen is still to be confirmed. Note that in the literature, one can often find the assumption of a very high specific adsorbability of hydroxyl ions on *d*-metals. The problem is complicated by the fact that oxygen chemisorption turns out to be irreversible, which makes the rigorous description of oxygen-adsorbing systems impossible within the framework of equilibrium thermodynamics. Moreover, other important problems have emerged. For example, surface phenomena on electrochemically intercalated materials (such as lithium cathodes and metal–hydride systems) are in great need of precise study.

The current importance of the thermodynamic theory of electrocapillarity is illustrated by the fact that recent discussions [48–54] actually considered the problem of a relationship between the surface tension and the reversible surface work for the solid electrode/solution interfaces. Attention to this problem was initiated by the appearance of

new possibilities for measuring surface tension of solid electrodes (probe methods) and the further development of laser interferometry [48, 55]. Note that a comparison of the surface tension and the reversible work of surface formation on the level of their derivatives based on the concept of total charge of a perfectly polarizable electrode was carried out by Gokhshtein [56] by the “estance method” which he developed (estance is the derivative of the surface tension of a conducting solid with respect to an electrical variable). The estance technique was later supplemented by the data from the newly developed methods of electrocapillary expansion and surface dilution [57].

Phenomenological models of EDL

Since the middle of the nineteenth century, different phenomenological models of EDL have been developed. The experimental data which laid the basis of these models were largely obtained by the following two electrochemical methods: electrocapillary curves and EDL differential capacitance curves. The former method was initiated by Lippmann [20] and the latter was proposed by Varley [58]. However, correct differential capacitance values for the mercury electrode were obtained by this method only in 1935 by Proskurnin and Frumkin [59] who for the first time carried out experiments under conditions that ruled out the appearance of impurities in solution and their adsorption on the electrode surface. The very concept of the electric double-layer formation on an interface and its first model were formulated by Helmholtz [60, 61].

EDL phenomenological models in the absence of specific adsorption

In the simplest case, where no neutral species other than solvent dipoles are present and the adsorption of ions from electrolyte solution is totally due to their electrostatic interactions with the charged electrode, the interface structure can be illustrated by Fig. 2. As shown in this figure, the potential difference at the interface, i.e., the Galvani potential $\Delta_S^M \varphi$, reckoned from a point in the solution bulk is as follows:

$$\Delta_S^M \varphi = \Delta\varphi_{ion} + \Delta\varphi_{dip} + \Delta\varphi_{met} \tag{25}$$

where $\Delta\varphi_{ion}$ is the potential difference associated with the presence of the free electrode charge and the surface excesses of ions Γ_i (ionic potential difference) that compensate the latter; $\Delta\varphi_{dip}$ is the potential difference associated with a certain preferential orientation of solvent dipoles on the surface; $\Delta\varphi_{met}$ is the potential difference due

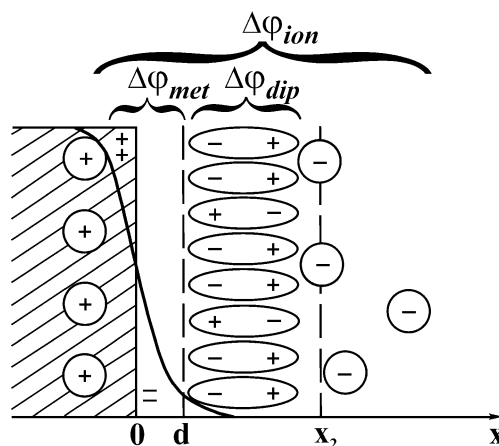


Fig. 2 Illustration of the electrical double-layer structure at the interface of metal with a solution of a surface-inactive electrolyte at a positive electrode charge

to the so-called “electron tails” that go beyond the ionic frame of the metal. The ionic potential difference is divided into two terms that pertain to the dense layer $\Delta\varphi_H$ and the diffuse layer $\Delta\varphi_d$. If the potential is reckoned from the zero free charge potential $E_{\sigma=0}$, then Eq. 25 can be written as follows:

$$\varphi = E - E_{\sigma=0} = \Delta\varphi_H + [\Delta\varphi_{met} - (\Delta\varphi_{met})_{\sigma=0}] + [\Delta\varphi_{dip} - (\Delta\varphi_{dip})_{\sigma=0}] + \Delta\varphi_d. \tag{26}$$

Differentiation of Eq. 26 leads to the following relationship:

$$1/C = 1/C_H + 1/C_{dip} + 1/C_{met} + 1/C_d \tag{27}$$

where C is the differential capacitance of EDL, C_H is the Helmholtz layer capacitance, C_{dip} is the capacitance caused by solvent dipoles, C_{met} is the capacitance due to EDL metal plate, and C_d is the diffuse layer capacitance.

The Helmholtz theory took into account only the first term in the right-hand part of this equation, whereas the Gouy–Chapman theory [62, 63]³ considered only the last term. The Stern model [64] that combined the above two theories considered both the first and the last terms. The Stern model does not contradict Eqs. 26 and 27. Its use means that potential drops caused by the presence of solvent dipoles and metal’s electron plasma are independent of the electrode charge. Tests of this model [65] show that it does not adequately describe the differential capacitance curves of the mercury electrode.

³ Chapman [63] derived quantitative relationships of the diffuse layer theory 3 years later than Gouy [62], albeit quite independently. As was noted in [7] (chapter 5), the name “Gouy–Chapman theory” seems to be historically incorrect.

Grahame [66] assumed that the EDL capacitance could be represented as

$$1/C = 1/C_{02} + 1/C_d \quad (28)$$

where C_{02} was a certain “effective dense layer capacitance” independent of the surface-inactive electrolyte concentration. This assumption for not-too-high electrolyte concentrations was justified by non-local electrostatics [67]. By using the equation of the Gouy–Chapman theory in calculating C_d , it proved possible to find the dependence of C_{02} on the charge. The result was then used to compare the predictions of different model theories. The fact that the $1/C_{02}$ value calculated from experimental data contained contributions from the dipolar and metallic EDL components was evident even without elucidating the latter in explicit form.

In discussing the nature of the so-called hump observed in EDL differential capacitance curves of mercury electrodes in aqueous solutions, Grahame [68] was convinced of the necessity of taking into account the contribution of water dipoles into the dependence of double-layer properties on surface charge. The term $1/C_{\text{dip}}$ had been explicitly considered in the analysis of EDL properties since the studies of Watts-Tobin [69] and Macdonald [70]. The former author [68] considered a model of two states of water dipoles oriented with either plus or minus to the surface and also interacting laterally with one another. Later studies discussed the possibility of the formation of associates of two or more solvent molecules [71, 72], the presence of dipoles oriented in parallel to the surface [73], the existence of non-electrostatic interactions between solvent molecules within the surface-adjacent layer and with the molecules of the next monolayer [74], and several other effects. For the critical review of these studies, see [75]. Overall, it is now considered that the Grahame model supplemented with the Gouy–Chapman equation provides a quantitative description of the EDL in solutions of surface-inactive electrolytes at interfaces formed by various *s,p*-metals not only with water but also with many non-aqueous solvents [14].

On the other hand, thermodynamic tests [76, 77] of the diffuse layer theory and its implications for electrode kinetics have shown that Eq. 7 is valid only under the condition that the classical formulas for C_d [66] include the activities of ions rather than their concentrations. For 1,1-valent electrolytes with $c < 0.1$ M, the differences between concentrations and activities of ions are compensated by the dense layer capacitance C_{02}^0 found empirically from the data in solutions with the higher concentration so that Eq. 28 turns out to be well consistent with numerous experimental data. At the same time, if the approximate expression $\ln f_i \approx \ln f_{\pm} z_i^2 / |z_+ z_-|$ is used for estimating the activity

coefficients of individual ions f_i , then Eq. 28 appears to be applicable for describing the differential capacitance curves on different electrodes even in solutions which are by no means ideal, such as $\text{La}_2(\text{SO}_4)_3$ [78].

The contribution of the metal component to the EDL capacitance was considered by O. Rice back in 1928 [79]. However, this study was far ahead of its time, and the role of the metal electrons in the EDL structure has been widely discussed only since the 1980s (it should be stressed that the considerations of the term $1/C_{\text{dip}}$ often ignore the presence of the term $1/C_{\text{met}}$ in the overall $1/C_{02}$ value). Interest in this problem was greatly stimulated by an International Symposium held at Logan in 1982 that dealt with non-traditional approaches for studying the metal/solution interface. A critical survey of the first studies considering the role of metal electronic structure in the EDL structure can be found in [17, 18, 80–84].

The question of how far the “electronic tails” extend into the solution also deserves mention. This depends on the sign and magnitude of the surface charge. The latter determines the gap d_{ms} between the metal core and the solvent molecules closest to the metal (see Fig. 2). The tails repel dipoles from the metal and the effect strengthens with an increase in the negative charge of the metal. Simultaneously, the EDL contracts due to the electrostatic interaction between the electrode charge and the solvated cations in solution. As a result, the dependence of the gap on the negative charge may pass through a maximum [81].

Attempts have also been made to distinguish the dipolar and the metallic components from the overall C_{02} values [82–85]. However, unambiguous estimation of the contribution of individual components is very complicated and still remains a task for the future. An additional complication is associated with the fact that C_H depends, in fact, not on the dense layer thickness x_2 but on the correlation length Δ that characterizes the region of the most pronounced dependence of permittivity of the medium on the distance x [86]. The ratio between x_2 and Δ also determines the degree of approximation that should be borne in mind when using equations of the classical diffuse layer theory in calculating C_d and the potential drop in the diffuse layer.

EDL models in the presence of specific adsorption of ions

The EDL structure is greatly complicated in the presence of specific adsorption of solution components on the electrode surface. A large body of experimental data has been obtained for the adsorption of ions on ideally polarizable electrodes at a constant ionic strength of $mc_{\text{CA}^*} + (1-m)c_{\text{CA}}$ and $mc_{\text{C}^*\text{A}} + (1-m)c_{\text{CA}}$ (system (A)), where c is the overall electrolyte concentration and m is the molar fraction of a salt containing specifically adsorbed anions A^*

or cations C^* . For such systems, the charge of specifically adsorbed ions σ_1 can be calculated using the formula [87, 88]

$$\sigma_1 = \mp(F/RT)(\partial\Delta\gamma/\partial\ln m)_E \tag{29}$$

where $\Delta\gamma$ is the two-dimensional pressure caused by specifically adsorbed ions at $E=\text{const}$. The $\Delta\gamma$ values were found either directly from electrocapillary curves or from the EDL differential capacitance curves obtained by twofold integration.

For many systems, the observed dependences of σ_1 on the electrode charge are well described by the phenomenological model of Grahame–Parsons (GP model) [89, 90]. According to this model, specifically adsorbed ions are partly desolvated and enter the dense part of the EDL with their centers localized in the so-called inner Helmholtz plane at a distance $x=x_1 < x_2$. The discrete nature of these charges determines the non-equipotential character of the inner Helmholtz plane, while the outer Helmholtz plane ($x=x_2$) is considered an equipotential surface.

For $\sigma=\text{const}$, the GP model postulates the linear summation of potential differences associated with the charge of the electrode, the charge of specifically adsorbed ions in the dense part of the EDL, and the charges of ions in the diffuse part of the EDL. Physically, this implies that the transfer of ions from the outer Helmholtz plane to the inner Helmholtz plane obeys the isotherm with virial coefficients, where the constant of adsorption equilibrium (the first virial coefficient) is a function of electrode charge.

In the GP model, the potential of the outer Helmholtz plane with respect to the bulk of solution, which is equal to the potential difference across the diffuse layer $\Delta\varphi_d$, is calculated from the Gouy–Chapman theory. Within the framework of this model, the potential drop in the dense layer is determined by a formula

$$\psi = \varphi - \Delta\varphi_d = \sigma/K_{02} + \sigma_1/K_{12} \tag{30}$$

where K_{02} and K_{12} are the integral capacitances of the total dense layer and the gap between the outer and inner Helmholtz planes. A significant assumption of the GP model is the independence of K_{02} from σ , which actually fails for large anions (ClO_4^- and NO_3^- [91–93] and also for organic anions [94, 95]). In these cases, phenomenological models in which the EDL dense part is represented as two plate capacitors connected in parallel demonstrate certain advantages. For example, assuming that the capacitances are proportional to the surface fractions of free $(1 - \theta)$ and occupied (θ) with adsorbate, then

$$K_{02} = K_{02}^0(1 - \theta) - K_{02}^1\theta. \tag{31}$$

This latter model can readily be extended to include the double-layer capacitance C_d connected in series and evaluated in terms of the Gouy–Chapman theory

$$C_d = (F/RT)\sqrt{4A^2c + (\sigma + \sigma_1)^2} \tag{32}$$

where $A = \sqrt{2\varepsilon\varepsilon_0RT}$, $\varepsilon_0 = 8.854 \times 10^{-12} \text{ F m}^{-1}$. This model was proposed by Alekseev, Popov, and Kolotyrlin (APK model) [96] and later supplemented [97, 98] by the Frumkin adsorption isotherm (or a system of two mixed Frumkin isotherms [99]). In this case, the adsorption equilibrium constant is a function of the potential drop in the dense part of the EDL. In particular, it was shown that the GP and APK models are not mutually exclusive but are consistent with one another under the condition that $K_{02}/K_{12}=\text{const}$. A similar approach was developed by Nikitas (for references, see his reviews [100, 101]).

For ionic adsorption, the use of the APK model allows several limitations of the GP model to be eliminated, particularly when describing the adsorption of ions leading to a decrease in the true EDL capacitance at the $\text{Hg}/\text{H}_2\text{O}$ boundary. For example, the dependence of the adsorption energy on charge in systems of the type $\text{Hg}/[\text{H}_2\text{O} + mc\text{KNO}_3 + (1 - m)c\text{KF}]$ (system (B)) deviates a long way from the straight line predicted by the GP model. At the same time, within the framework of the APK model, if the adsorption of any component leads to a decrease in the EDL capacitance, the dependence of the adsorption energy on ψ (and, hence, on the electrode charge) becomes quadratic, in full agreement with experimental data. Furthermore, the use of the GP model for describing the specific adsorption of ions gives rise to a situation where the calculated dependence of the electrode potential on its positive charge passes through a maximum. At this maximum, the differential capacitance demonstrates a $\pm\infty$ discontinuity and becomes negative at still more positive potentials [102]. In the APK model, no anomalous situations of this kind appear.

The APK model is not perfect, however. It fails to explain the transition of the quadratic dependence of the adsorption energy on the electrode charge in system (B) to the linear dependence for $m=1$, i.e., when going from a mixed solution with the constant ionic strength to a binary solution. To eliminate this drawback, it has been proposed [103] that the dense layer capacitance (corresponding to the absence of NO_3^- ions in the dense layer) be expressed in the form:

$$C_{02(\theta=0)}^{(m)} = mC_{02(\theta=0)}^{(m=1)} + (1 - m)C_{02(\theta=0)}^{(m=0)}. \tag{33}$$

Here, $C_{02(\theta=0)}^{(m=0)}$ is the dense layer capacitance in a pure KF solution, easily estimated from Eq. 28 based on the Grahame model [66], and $C_{02(\theta=0)}^{(m=1)}$ is the dense layer capacitance in a KNO_3 solution under the hypothetical condition that the total

excess of NO_3^- ions is localized in the diffuse part of the EDL. The capacitance $C_{02(\theta=0)}^{(m=1)}$ can also be found from experimental data and expressed by a polynomial as a function of the potential drop in the dense layer (see [103]). It has been demonstrated [102] that this approach correctly describes the transformation of the adsorption energy vs. ψ dependence (from quadratic to linear with the increase in m) and also adequately describes the differential capacitance curves in systems of the (B) type.

In the GP and APK models, the outer Helmholtz plane is considered to be an equipotential surface. An attempt to take into account the nonequipotential nature of the outer Helmholtz plane at specific adsorption of ions was undertaken by Vorotyntsev based on concepts of non-local electrostatics. The basics of this approach were formulated in [104] and its detailed description can be found in [105]. In the Vorotyntsev model, it is assumed that the overall electrode charge consists of the following two parts: the charge uniformly “spread” over the metal surface and the sum of electronic counter charges localized near specifically adsorbed ions. The non-uniform distribution is analogous to that of the diffuse layer of ionic plasma. In principle, the Vorotyntsev approach makes it possible to take into account the penetration of the electric field into the metal, the spatial structure of solvent. Other factors that can be accounted for include the protrusion of the metal’ electron density into the solvent surface layer, the finite sizes of specifically adsorbed ions, the possible partial charge transfer of these ions into the metal, and the screening of the electric field of adsorbed ions by the diffuse layer. At the same time, the model cannot be used in systems for which the adsorption of ions can substantially change the dielectric properties of the surface layer, as observed, for example, during the adsorption of organic ions.

For a long time, experimental corroboration of phenomenological models of the electrical double layer for the case of specific adsorption was performed by comparing the theoretically calculated σ_1 vs. σ dependences at different $mc=\text{const}$ (or σ_1 vs. $\ln(mc)$ dependences at different $\sigma=\text{const}$) with the corresponding experimental dependences found using Eq. 29. However, this approach is not very sensitive and the resulting data can often be fitted by different models within experimental error. A better approach is to compare experimental and calculated differential capacitance curves [106, 107]. Figure 3 shows that different models produce significantly different differential capacitance values and their deviations exceed possible experimental errors. However, despite this possibility, the problem of developing an adequate phenomenological EDL model for the adsorption of ions can hardly be considered as solved. It also deserves emphasizing that all the models developed so far employ experimental data in their calculations, i.e., they are semi-empirical in character.

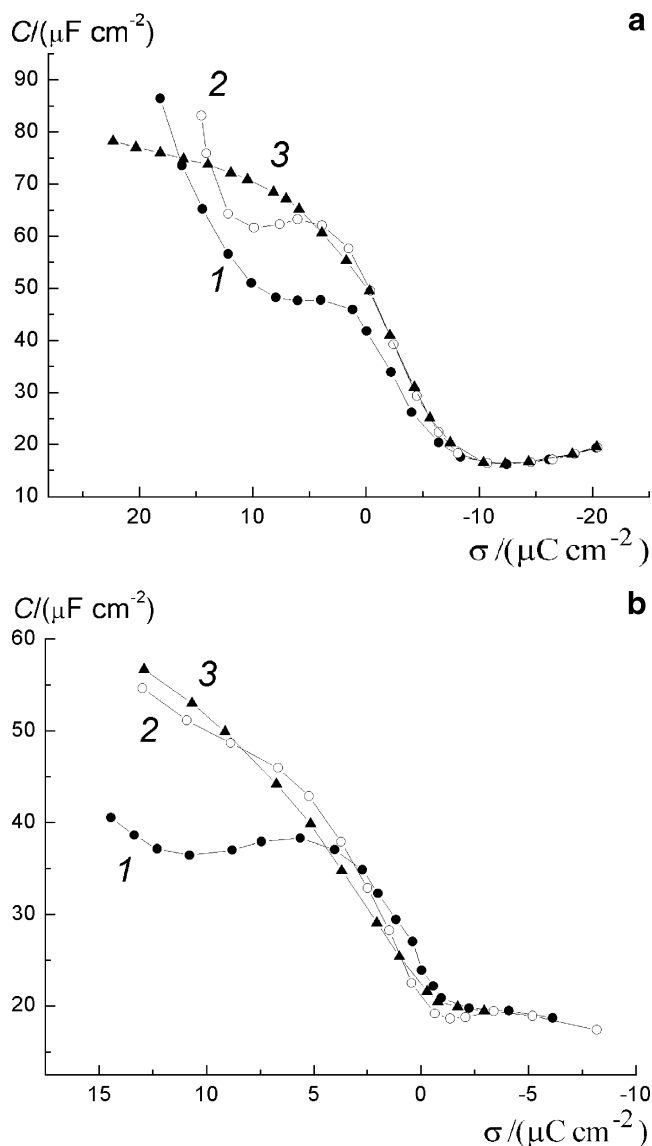


Fig. 3 Differential capacitance curves of a mercury electrode in aqueous 0.1 M KBr (a) and 0.03 M NaCl (b) solutions: 1 experimental curves, 2 calculations according to the GP model, 3(a) calculations according to the APK model, 3(b) calculation according to the Vorotyntsev model

Phenomenological models of the reversible adsorption of organic compounds

The first phenomenological model describing the reversible adsorption of organic substances on the mercury/water interface was proposed by Frumkin in 1926 (the model of two parallel capacitors or 2PC model) [108]. His model operated with the following isotherm [109]:

$$\beta c = \frac{\theta}{1 - \theta} \exp(-2a\theta) \quad (34)$$

which differed from the Langmuir isotherm by the presence of the constant a that takes into account the lateral

interaction between adsorbed molecules. In the latter equation, β represents the adsorption equilibrium constant. The electrode potential φ was chosen as the independent variable. Today, this isotherm 34 is named after Frumkin.

If the total surface excess of organic molecules is localized in a monolayer and the mole fraction of adsorbate $N_i \ll 1$, then for a fixed concentration of the surface-inactive supporting electrolyte, the following relationship follows from Eq. 8 in the first approximation:

$$d\gamma = -\sigma d\varphi - RT\Gamma_m \theta d \ln c \tag{35}$$

where Γ_m is the limiting surface concentration of the organic substance corresponding to $\theta=1$. Combining Eqs. 34 and 35 produced the following relationship for $\varphi=\text{const}$:

$$\sigma = \sigma_{\theta=1}\theta + \sigma_{\theta=0}(1 - \theta) \tag{36}$$

which corresponds to the 2PC model.

As was shown in [110–115], the Frumkin theory quantitatively describes the adsorption of numerous simple aliphatic compounds on *s,p*-metals, although the linear a vs. φ dependence and certain other minor peculiarities must be taken into account. On the other hand, a self-contradiction does appear if the limiting surface concentration of the organic substance (for $\theta = 1$) depends on the electrode potential. This self-contradiction can be eliminated [116] if the following more general equation is used in place of isotherm 34:

$$\beta N/(1 - N) = \frac{\theta}{1 - \theta} \exp[-2a(\theta - N)] \tag{37}$$

from which the Frumkin isotherm follows as a special case when the mole fraction of organic substance in bulk solution $N \ll 1$.

Studies carried out within the framework of phenomenological models in the system $\text{Hg}/[\text{H}_2\text{O} + x\text{M}(\text{NaF}) + y\text{M}(n - \text{C}_4\text{H}_9\text{OH})]$ (system (C)) led to the following unexpected conclusions: First, the Grahame model [66] turns out to be quantitatively applicable to this system. Thus, the curves of the dense layer capacitance (C_{02} vs. ψ) are virtually independent of the NaF concentration in the presence of a given butanol concentration. Second, it would seem obvious that according to the simple physical meaning, these C_{02} vs. ψ curves should be better described by the 2PC model as compared with experimental C vs. φ curves. However, regression analysis actually shows that the standard deviation between the data calculated using the 2PC model and experimental curves was approx. 2.5 times higher for C_{02} vs. ψ curves as compared with C vs. φ curves [117]. Third, a series of intricate differential capacitance curves has been described with high accuracy on the basis of two different model approaches, as illustrated in Fig. 4. The points in this figure correspond to C vs. φ curves derived from C_{02} vs. ψ curves calculated using the model of three parallel capaci-

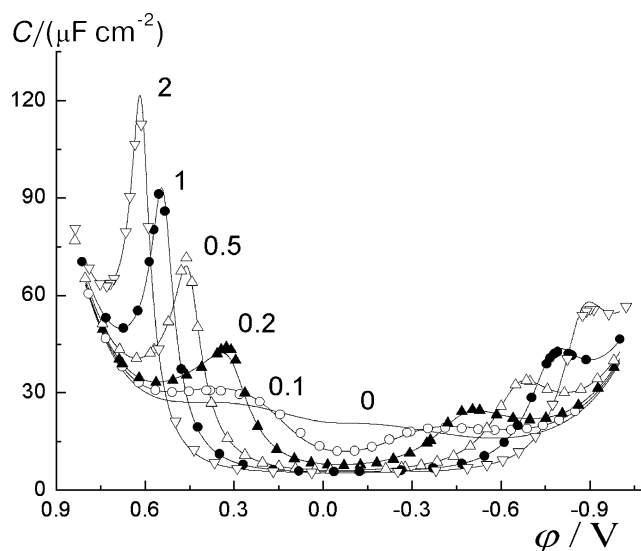


Fig. 4 Differential capacitance curves in system (C): 1 experiment, 2 calculation according to the model of three parallel capacitors, 3 calculations by the 2PC model

tors, followed by their recalculation to obtain C vs. φ curves in terms of the Grahame model [66]. The solid lines were calculated based on the 2PC model with a set of effective adsorption parameters obtained by performing the regression analysis of C vs. φ curves calculated by the former method. The standard deviation between these two series of C vs. φ curves is $\Delta \approx 3.3\%$. At the same time, the standard deviation between the experimental C vs. φ curves in system (C) and the calculations in terms of the 2PC model with the allowance made for the linear dependence of a_{ef} on φ was $\Delta \approx 6.45\%$ [118].

Based on the obtained results, it was concluded that the $n\text{-C}_4\text{H}_9\text{OH}$ molecules at the $\text{Hg}/\text{H}_2\text{O}$ interface were adsorbed in two different states differing in both the dipole orientation and the strength of the lateral interaction. With changes in electrode potential, the ratio between the two adsorbate states changed, which manifested as changes in the parameter a_{ef} . This interpretation was confirmed by an examination of system (C) [119]. It was shown that the experimentally determined dependence of effective adsorption parameters on the NaF concentration was in good agreement with the predictions following from calculations in terms of a model that described the dense layer as three parallel capacitors, which were connected with the diffuse layer capacitor as in the Grahame model [66].

At sufficiently large attractive interaction between adsorbed organic molecules, two-dimensional condensation can occur, which is characterized by discontinuities in C vs. φ curves, discontinuities in adsorption isotherms, and discontinuities in the entropy of surface layers [120–122]. The formation of condensed layers on mercury may also be the reason for the appearance of a new type of polaro-

graphic maximum (the so-called maximum of the third kind) [121]. Numerous studies in the field of two-dimensional condensation are summarized in reviews (e.g., see [123–125]), and various theoretical descriptions have also been developed [126–129].

Approaches to the description of electrochemical interfaces on a molecular level

The phenomenological and related models are still widely used for the initial analysis of experimental data. However, such models have been categorized as “primitive” [130]. Nevertheless, phenomenological models have also found some use as a basis for comparison with theoretical predictions. This is very important because the observed deviations between theory and experiment indicate areas of future research. Thus, the possibilities of the phenomenological models are by no means exhausted.

On the whole, the undeniable trend of the past few decades has been a transition from mean field theories toward molecular theories. This has been favored by the introduction of new theoretical models and the widespread availability of intensive computation. The successful development of the statistical theory of the diffuse layer has also made it possible to elucidate the conditions and the degrees of approximation that are associated with the application of the Gouy–Chapman theory to the calculation of C_d and $\Delta\varphi_d$. Today, it seems likely that the continuing development of the statistical approach within the continuum solvent model [131–133] will result in the modification of several phenomenological models.

At the end of the twentieth century, the rapid development of computational techniques allowed more complicated EDL models to be explored so that the intrinsic sizes of ions could be included, as well as at their mutual interactions. For example, theories based on the modified Poisson–Boltzmann equation were developed, which could take into account the finite sizes of ions [134–136]. Monte-Carlo (MC) and molecular dynamics techniques were also introduced [137, 138]. Furthermore, it was also shown that results close to those produced by the MC method could be obtained by solving a complex system of integral equations (the hypernetted chain approach) [139].

For various reasons—including the cumbersome nature of the calculations—these theories have rarely been used by experimental electrochemists. As was demonstrated in a series of studies by Fawcett (see studies cited in [140]), results close to those provided by the MC method and the hypernetted chain method can be obtained if in place of the charge and the concentration in equations of the classical diffuse layer theory we put certain Taylor series with coefficients that depend in a certain manner on σ , c , and

sizes and charge numbers of ions. Such an approach considerably simplifies calculations and may favor the wider uptake of the theory. However, it should be noted that as a rule, the creators of molecular models rarely test the consistency of their models with the laws of thermodynamics (Eq. 8). At the same time, in certain cases, deviations of the outer Helmholtz plane potential found using molecular models from $\Delta\varphi_d$ values found based on the classical diffuse layer theory were opposite in sign to those predicted by self-consistent theories [76, 77]. This clearly requires further analysis.

In parallel with the EDL molecular models in which ions and solvent dipoles are represented as rigid spheres, there appeared models based on quantum chemical computations of interactions of different ions and molecules with metal clusters imitating the electrode surface [141–143]. The limited nature of these models is, however, due to the fact that quantum chemical calculations of the volume structure of electrolyte solutions ignored the very high electric field intensity near the electrode surface. For the cluster calculations, serious problems arise when we pass to macroscopic values. Finally, trends in the development of modern molecular models of the EDL can be found in reviews [144–147]. The EDL molecular models will undeniably be used in the future; however, studies in this direction are as yet only beginning.

Studying the interfaces of electrodes of Ag, Au, and the platinum group metals

Since the 1930s, the study of interfaces formed by noble metals, i.e., Ag, Au, platinum group metals, and their alloys with electrolyte solutions, has attracted progressively increasing attention. Initially, the objects of study were polycrystalline materials and highly dispersed materials (e.g., platinum black). However, polycrystalline materials can hardly be described as “well-defined surfaces” (the term “well-defined surfaces” came into prominence after a work by Hubbard [148]). Nevertheless, under certain standardized pretreatment conditions, these electrodes demonstrated reproducible responses that were stable in time. Keen attention was focused on the electrochemical treatment of platinum electrodes, especially potential cycling in electrolyte solutions, which resulted in the discovery of electrochemical faceting [149] and electrochemical microstructuring [150, 151]. Attempts are also undertaken to study the electroplating process more thoroughly than previously in order to develop another class of well-defined electrodes (e.g., see [152, 153]).

At the end of the twentieth century, studies on the faces of single-crystal electrodes and electrodes with highly ordered surfaces became very popular. The latter included

multicomponent electrodes, e.g., single-crystal faces modified with ordered layers of adatoms. This work was concomitant with the appearance of reliable methods of preparation and stabilization of clean surfaces of individual faces (such as the flame annealing technique, sometimes referred to as the Clavilier method [154]; see also [155]). It was found that in contrast to reactive metals (Bi, Cd, Pb, Sb, etc.) [156, 157], noble metals demonstrated remarkable differences in the behavior of different crystal faces. The development and the wide use of new highly sensitive methods for studying surfaces, including atomic-level techniques, played and still play a crucial role in these techniques. Their success has been achieved by the combined use of electrochemical, spectroscopic, and nanoscopic measurements.

The behavior of Ag and Au in certain potential ranges can be considered as typical of ideally polarizable electrodes [156, 157]. In these systems, the anisotropy of zero free charge potentials (PZFC) was observed depending on the structure and the packing of crystal faces, which stimulated the attempts to trace correlations between the nature of metal and the nature of face, on the one hand, and the PZFC, on the other hand, and also to simulate the behavior of polycrystalline electrodes within the framework of the phenomenological approach. Studies in this direction are far from complete and remain topical. It has been found that the structure of the crystal face has a strong effect on surface hydrophilicity. Potential cycling causes restructuring of crystal faces, the surface being characterized by a transition from one type of sub-lattice to another [158, 159]. Different restructuring mechanisms have been discussed in various studies (e.g., see [160]). This has involved the use of both electrochemical and nanoscopic methods. We note that a large body of new data on interface structure, which has been obtained by probe methods on Ag and Au single-crystal faces, has still not been fully analyzed. Attempts to determine the state of water at interfaces [161, 162] have also attracted recent attention. However, so far, the information gained from probe methods has turned out to be most informative for adsorbates in the dense layer.

The behavior of platinum group metals in electrolyte solutions has attracted and continues to attract the keenest attention. The first quantitative data on the dependence of the surface free charge on the potential on platinized platinum at a fixed solution pH (curves of the total charge of the first kind) were obtained in studies by Frumkin, Slygin, and Medwedowsky using the method of adsorption curves [163–165]. Later, experiments using radiotracer methods were conducted [166–168]. The radiotracer technique was modernized to allow measurements on smooth polycrystalline electrodes and single-crystal faces to be carried out [169].

Systematic studies on electroplates of platinum group metals were carried out within the framework of testing the

thermodynamic theory of electrocapillarity of perfectly polarizable electrodes [7, 27–31]. In the process, the following new methods were invented and developed: the methods of isoelectric [170] and adsorption [171] potential shifts and also the method of potentiometric titrations under isoelectric conditions [172]. The latter made it possible to obtain the dependence of the electrode total charge of the second kind on the electrode potential and also to find the differential capacitance curves and electrocapillary curves of the second kind for disperse platinum metals.

The first studies allowed the role of hydrogen and oxygen atoms in the interface region to be elucidated. The presence of these atoms, and the overlap of hydrogen and oxygen adsorption regions, explained the unusual dependence of the surface free charge of the first kind on the potential and solution pH (Fig. 5). The thermodynamic theory of electrocapillarity of perfectly polarizable electrodes allowed relationships for the dependences of potentials of zero total and zero free charges on the solution pH to be formulated. To explain these dependences, it was not necessary to assume a strong specific adsorption of OH^- ions. It was quite sufficient to note that the bonds formed by the adsorbed hydrogen and oxygen species were polar and that the introduction of these species into the surface layer decreased the EDL capacitance and shifted the PZFC.

An attempt at a phenomenological description of the dependence of the surface free charge on the potential of electrodes adsorbing hydrogen and/or oxygen was undertaken by Damaskin and Petrii [173]. A model of two limiting states was also proposed [174] for describing the EDL properties in the absence of specific adsorption of ions. As follows from Fig. 5, the equilibrium curves of differential capacitance of the first kind should demonstrate regions of negative capacitance values in the oxygen adsorption range and when approaching the reversible

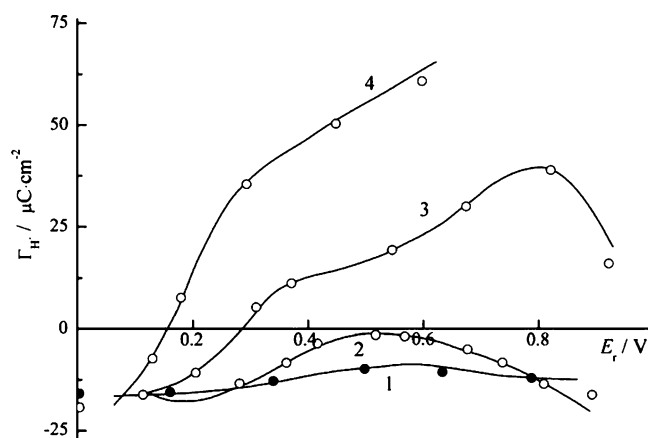


Fig. 5 Dependences of the surface free charge of the first kind for a platinized platinum electrode on the potential in the following solutions: 0.01 M KOH (1), 0.01 M KOH+1 M KCl (2), 0.01 M KOH+1 M KBr (3), 0.01 M KOH+1 M KI (4). E_r is potential vs RHE in the same solution

hydrogen potential. Such curves of the EDL differential capacitance of the first kind were actually obtained by the method of isoelectric potential shifts accompanying the changes in the solution pH (Fig. 6). However, no negative capacitance values were revealed by impedance measurements in the same systems [175]. This observation stimulated a more comprehensive analysis of the relationship between equilibrium measurements and those carried out by applying alternating currents of different frequencies. The dependences of the surface free charge of the second kind on the potential have a simpler form (Fig. 7) because under the conditions of constant hydrogen pressure in the system, the variations in the amount of adsorbed hydrogen accompanying the pH variations are small.

Measurements in solutions of different composition allowed the adsorption series of cations and anions on platinum metals to be determined in both acidic and alkaline media, including a series of perfluorinated anions [176, 177], alkali, and alkali-earth metal cations [178, 179]. Specific adsorption of ions is much more pronounced on platinum metals compared with *s,p*-metals, as demonstrated most clearly by measurements in mixed electrolytes [178]. However, the Esin–Markov effect failed to appear on platinum metals, probably due to the fact that the charge of specifically adsorbed ions is “spread” by the electron plasma of metal [28]. Note that according to Grahame, the Esin–Markov coefficient means the potential derivative at a fixed free charge with respect to the logarithm of adsorbate concentration. This is the meaning assigned to the Esin–Markov coefficient in [28]. Actually, in light of the electrocapillarity theory of reversible electrodes, two Esin–Markov coefficients can be obtained that correspond to fixed free or total electrodes charges, respectively. Due to

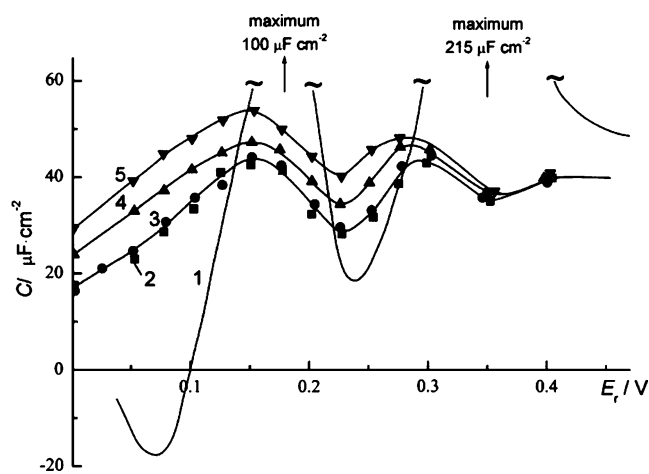


Fig. 6 Equilibrium differential capacitance curve of the first kind on the platinumized platinum in 0.005 M H₂SO₄+0.5 M Na₂SO₄ (1) and differential capacitance curves on the smooth polycrystalline platinum at 100 kHz in 0.005 M H₂SO₄ with 0.5 M Li₂SO₄ (2), Na₂SO₄ (3), K₂SO₄ (4), Cs₂SO₄ (5)

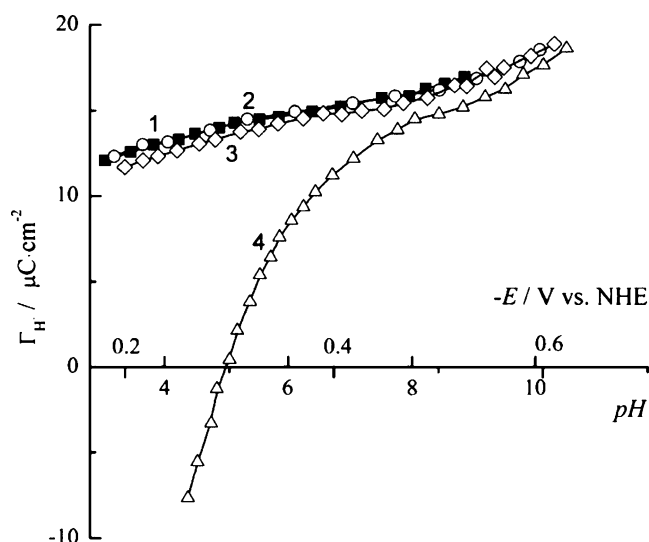


Fig. 7 Surface free charge of the second kind at the reversible hydrogen potential on a platinumized platinum electrode as a function of pH of the following solutions: 0.05 M Na₂SO₄ (1), 0.1 M NaCl (2), 0.1 M NaBr (3), 0.1 M NaI (4)

the pronounced charge transfer from adsorbed ions to the metal surface, the ions can pass into their adatom state, thus modifying the metal surface. The EDL structure radically depends on where one assigns the adatoms, i.e., to the metal surface or to the solution phase [180]. Interesting features were observed for the co-adsorption of anions and cations [181]. Finally, it was shown that the adsorption of organic compounds on smooth polycrystalline and disperse platinum metals is accompanied by different chemical transformations of adsorbed molecules (dehydrogenation, hydrogenation, self-hydrogenation, the break of C–C, C–O, and other bonds, etc.). As a result, the adsorbate composition may differ from that of solute molecules [110].

In studying single-crystal faces and other well-defined surfaces, voltammetry has played a special role due to its simplicity and sensitivity. Voltammetric responses can be considered as “fingerprints” of a surface. The keenest attention has been paid to voltammetric curves of Pt(111), which are called “butterfly curves.” This kind of response was first observed in [154] and later reproduced in many laboratories all over the world [182–184]; the results stimulated the steady development of crystallo-chemistry of electrode surfaces. The most interesting feature of Pt (111) voltammograms is the pronounced reversible current peaks apparently corresponding to the formation of ordered adlayers involving solution anions. Yet another interesting peculiarity is the virtually constant current in the hydrogen adsorption region throughout a wide potential range, which in fact is typical of uniformly heterogeneous surfaces with a high heterogeneity factor.

Thirty years of active studies have led to impressive progress in understanding the role of the crystal structure of

the platinum surface on its adsorption behavior. These achievements and prospects for further development have been surveyed by Feliu [185]. In particular, it has been demonstrated that the additive approach (according to which the properties of polycrystalline electrodes can be interpreted as the superposition of properties of individual faces) is far from correct in many cases. Imitating crystallographically heterogeneous surfaces in experiments with stepped single crystals faces appears to be more promising.

The phenomenon of underpotential deposition of ions has reached a new level of understanding. The trend for preferential adsorption of many adsorbates on steps having a particular crystallographic orientation (the step decoration effect) has been thoroughly demonstrated. Individual and mixed adlayers have been characterized as two-dimensional lattices and the degree of consistency between surface sublattices and the surface has been described as *commensurate* and *incommensurate*. The role of two-dimensional phase transitions in adlayers has also been stressed. Lateral interactions between adatoms have been widely observed and reversible redox transitions in irreversibly adsorbed layers of adatoms have been described. These peculiarities often disappear on perfect surfaces characterized by small terraces and are not observed on polycrystalline surfaces either.

The properties of metal adlayers can be described only by making allowance for the co-adsorption of solution anions, especially in attempts to characterize self-organization phenomena upon co-adsorption. Apparently, metal sub-monolayers allow the most thorough comparative analysis of modern calculation methods especially if the lateral interaction is quantitatively described. The effect of oxygen atom adsorption on crystal face restructuring has reached a high state of development. Interestingly, the destruction of organic molecules, and the stability of adsorbates, have both proved to be very structure-sensitive. Certain crystal faces have allowed the study of long-range order in organic adlayers, and the transition to reversible adsorption has also been observed. The specifics of adsorption on stepped surfaces have attracted attention, and the conditions for chiral electrosynthesis have also been explored. Finally, a detailed study of CO adsorption has led to the development of the “CO displacement technique” for PZTC determination.

A detailed picture of strong chemisorption has been obtained by comparing electrochemical measurements with those carried out on electrodes withdrawn from cells and placed into vacuum (emersed electrodes). By means of this technique, various physical measurements of surface structure have been obtained *ex situ* [148, 186–200]. One remarkable approach has been suggested in which the experimental behavior of the metal/solution interface might

be studied in a vacuum, while the hydration of adsorbed metal ions was followed after the introduction of water vapor [199]. However, this approach has not been developed. It should be noted that for specifically adsorbed ions at high surface coverage, comparative studies of the metal/solution and metal/vacuum interfaces can be carried out without removing the electrode from solution, but instead combining electrochemical measurements with *in situ* IR spectroscopy [200].

The practical importance of small particles (nanoparticles) in electrocatalysis continues to attract keen attention, especially their behavior with respect to the adsorption of various components of solution. Probably, the thermodynamics of strongly curved surfaces can be applied in this case. Some attempts have been made to compare the behavior of nanoparticles with individual faces of metal crystals. One approach to bridging the gap between nanoparticles and single crystal surfaces is based on the phenomenon of adsorbate-induced and potential-induced faceting of single-crystal faces under electrochemical conditions, as was recently demonstrated for Ir(210) [201], and analyzed based on the density functional theory (DFT) and the extended *ab initio* atomistic thermodynamic approach. DFT calculations have been proven useful for gaining atomistic insights into the voltammetric de-alloying (de-leaching) of Pt bimetallic nanoparticles [202]. It should also be mentioned that the small sizes of metal clusters allow high-level computations to be successfully carried out [203], an idea that will be of fundamental importance for future understanding of adsorption and electrocatalysis.

Concluding remarks

The phenomenon of EDL formation at interfaces has recently found an exciting new application in the form of electrochemical supercapacitors [204, 205]. The development and optimization of these devices has drawn widespread attention to the surface characterization of various disperse carbon materials, not to mention iridium and ruthenium dioxides and other materials. It should be stressed, however, that the energy storage and dissipation in such systems typically involves redox-active centers as well as the electrical double layer. For bulk carbon materials, the adsorption properties have been studied for more than a century [7], and the electrical double layer of porous carbon electrodes has likewise been studied for quite some time [206–208]. Certain approaches to analyzing and modeling the structure of interfaces on oxide and oxide-like materials may be found in [209, 210]. In particular, an attempt was undertaken [210] to use procedures developed earlier for platinum group metals in the studies of oxide materials.

Although attempts have been made to study the surfaces of the iron group metals (Fe, Co, Ni) in electrolyte solutions, the results have failed in both breadth and depth to match the great practical importance of these metals. Evidently, future progress in this field depends on whether new experimental approaches suitable for analyzing the iron group metals can be found. A new method of iron electrode pretreatment [211] has made it possible to observe a capacitance minimum (possibly corresponding to the PZFC potential in dilute solutions), but measurements on iron single-crystal faces would be far preferable. A method of surface renewal by cutting in electrolyte solutions has also been developed, and this shows some promise [212, 213]. The same technique has also been proven useful for studying Pt group metals in aprotic solvents [214].

Another area of great technological importance is that of chemically modified electrodes [215]. For these systems, approaches to the description of the interface structure must take into account the individual and structural peculiarities of each particular system, the thermodynamics of interface phenomena, and the presence of functional groups. In connection with this latter point, substantial progress has been achieved in EDL studies on thiol-modified surfaces [216].

Studies of the interface between electrodes and molten salts (including polymeric electrolytes) are still topical due to their numerous practical applications. Recent developments in the study of the electrode/ionic liquid interface [217–220] may shed light on the broader problem metal/melt interfaces. This relatively new class of electrolytes is potentially huge and is currently attracting great interest and attention.

Liquid–liquid interfaces are an example of the so-called soft interfaces, and they are also under active investigation. Various approaches to studying these interfaces have been reviewed in [221]. In the near future, investigation of the semiconductor/electrolyte interface is also expected to increase due to the growing interest in photo-electrochemical energy conversion. Undoubtedly, the structure of interfaces formed between electrolytes and membranes (especially biological membranes) will also continue to attract attention.

Overall, the appearance of new materials and new fields of application will continue to stimulate research into interfaces. This is especially true of electrochemical sensors and molecular electronics. Furthermore, the wide range of techniques accessible to electrochemical surface science, coupled with those accessible to ultrahigh vacuum science [222], suggests that electrochemistry will continue to play a leading role in surface science for a long time to come.

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