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The Phase Boundary Potentials at the Interface between Two Immiscible Electrolyte Solutions

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The theoretical aspects of the calculation and measurement of the interphase [phase boundary] potential difference at the interface between two immiscible liquids are examined and the non-thermodynamic tetraphenylborate hypothesis, which makes it possible to determine the standard ion distribution potentials, is discussed. The electrochemical properties of charged interfaces are analysed and equations are presented for the interphase potential jumps in the presence of Donnan equilibrium, incomplete dissociation of the salt, two electrolytes with a common ion, complex formation in one of the phases, and an oxidation-reduction equilibrium. The experimental methods for the measurement of the interphase potential difference and for testing the thermodynamic theory of distribution potentials at reversible interfaces are examined
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I. INTRODUCTION

One of the fundamental problems in modern chemistry involves the elucidation of the mechanism of the distribution of charges at the interface between two immiscible liquids. The solution of this problem is essential for the development of phase-transfer and surface catalysis, electrochemistry and colloid chemistry, artificial photosynthesis and biochemistry, improvement of extraction processes, and the creation of ion-selective electrodes.

The electrochemistry of the interface between two immiscible electrolyte solutions developed significantly only in the last century. However, despite major advances, there are many obscure aspects and unsolved problems in this branch of physical chemistry. In the present review, an attempt is made to describe the main properties of charged interfaces between two immiscible electrolyte solutions.

As at any interface, a difference between electrical potentials arises at the interface between two immiscible liquids which in the case of equilibrium systems is called the boundary potential difference or briefly the boundary potential.[1]

The controversy concerning the nature of the potential jumps at the interface between two immiscible electrolyte solutions dates back to the beginning of the century.[2] Despite its apparent simplicity, this problem remains of current interest.[3-6] Some workers[7,8] have transferred, without adequate justification, the Donnan theory,[9] developed for the calculation of the potential differences between electrolyte solutions in two identical solvents α and α', differing only in the ionic composition, to the system of two arbitrary immiscible liquids α and β. The potential difference $\Delta_{\alpha}^{\alpha}\cdot\varphi$ between two identical phases α and α' is a thermodynamically measurable quantity. On the other hand, $\Delta_{\beta}^{\alpha}\varphi$ at an oil-water interface cannot be measured from the standpoint of thermodynamics but it can be estimated on the basis of model considerations.[3,4,10-14] The error associated with it, which was introduced in the above study,[7] led to the derivation of an incomplete formula for the Donnan potential, which is valid only in certain special cases for phases of identical nature. Unfortunately, this inaccuracy spread from the above study[7] to certain reviews[8] and has created the illusion that a purely thermodynamic determination of the Galvani potential difference is possible.

Finally, interphase oxidation-reduction potentials have been examined in the literature solely for certain special systems,[10,12,15] although it is undoubtedly important to give a general definition of this concept.

In the present reivew, an attempt is made to fill these gaps and to arrange systematically the definitions and formulae used to estimate interphase potentials.

II. INTERFACES

1. The Structure of Interfaces

If two pure liquids are placed in a vessel, then, depending on their physicochemical properties, there is a possibility of the formation of several types of structures. If the molecules of each liquid can interpenetrate one another, mixing in any proportions, such liquids can be called ideally miscible. Naturally, it is then impossible to obtain a potential difference between the two phases. An example of such a system is the well known water-ethanol pair. If the molecules of neither liquid can penetrate into the other, then such liquids can be referred to as ideally immiscible. Either a sharp boundary or a transitional layer, in which components from both phases are present, is established between them. An example of two ideally immiscible liquids is the mercury-water system. Sometimes the interface between two liquids is represented arbitrarily by a mathematical surface without thickness. This is an ideal boundary for which the term "interface" is used in the English language literature. However, in reality at the molecular level it is impossible to draw a sharp boundary between two phases. A transitional layer (interphase), whose properties differ from those of the phases in contact, is formed in this region. The thickness of the transitional

layer is $\sim 0.1-10$ nm. In this connection, it must be emphasised that the extremely convenient concept of the ideal boundary is a model one and is therefore outside the framework of thermodynamics.

This review is devoted to the electrochemistry of the interface between two immiscible liquids or more precisely two liquids with limited miscibility, an example of which may be an oil–water system: both phases are sparingly soluble in one another and there is an interface between them, constituting a transitional layer in which the properties of the medium vary from those of one phase to those of the other. The miscibility of the liquids in the most thoroughly investigated oil–water systems is low, being of the order of hundredths per cent (if nitrobenzene, dichloroethane, octane, or decane is used as the organic phase).

2. Polarisable and Non-polarisable Interfaces

The interfaces between two immiscible electrolyte solutions are characterised by polarisabilities of different types depending on the extent to which they are permeable to the charged species present in the system.[16-20] Since formulations which are not completely accurate are frequently encountered in the literature, we shall consider briefly this question.

If the charged species cannot pass through the interface, the latter is referred to as polarisable; otherwise the boundary is called non-polarisable or reversible. We shall begin the discussion with polarisable boundaries. Since any boundary is to some extent permeable to ions, in practice one has to speak only of a particular degree of approximation to the limiting version of polarisable boundaries. This limiting version is frequently referred to in modern literature as an ideally polarisable boundary. In the IUPAC recommendations,[16] a boundary between two phases is called polarisable if the phases contain no components in common or if the exchange of the components is difficult. As will be shown below, this definition is unsatisfactory, because, when the conditions indicated are fulfilled, there is a possibility of situations in which a direct current flows across the interface.

Next it is stated in the above recommendations that the interface can be divided into two components containing respectively charged species from the phases α and β only. This model idea, which constitutes a drastic simplification of the real situation, actually restricts the scope of the investigation of polarisable boundaries, reducing them to a single special case. Other versions, which can be realised in specific systems, escape the investigator's attention. Incidentally, the authors of the recommendations[16] agree that many of their definitions are based on specific models, stipulating this already in the first page of their report.

The use of specific models is not open to objection when this is necessary, but we believe that attempts to define a general thermodynamic property in terms of specific models is illegitimate because this deprives the property described of the necessary generality. However, as pointed out by Frumkin,[21,22] such simplification of the problem is not, in principle, necessary, because in this field a system of definitions not employing specific model concepts has existed for a long time. As early as 1891, Planck[17] introduced the rigorous thermodynamic concept of a completely polarisable boundary. He defined it as the "boundary whose state is fully defined by the charge passed through it starting from a certain instant".

In the first place, it follows from this formulation that the Planck definition fully excludes the possibility of the passage of a direct current through the boundary since otherwise the state of the boundary would no longer depend on the charge passed through it. The current may flow between the phases only in a transient regime. In this definition, nothing is said about the way in which the charged species which have arrived from different phases are distributed in the transitional layer. Their distribution may be of any kind and, in particular, they can overlap (Fig.1). Such a situation can arise on metallic electrodes when there is partial or complete electron transfer to adsorbed ions or from these ions to the metal. However, charge transfer between the bulk phases is impossible in the presence of a completely polarisable boundary.

A special case of a completely polarisable boundary is the ideally polarisable boundary whose underlying concepts have been formulated by Koenig.[18] Fig.1*b* illustrates the structure of Koenig's ideally polarisable boundary. There is a transitional layer between homogeneous phases α and β whose properties vary from those of the phase α to those of the phase β. In the transitional layer, the phases are arbitrarily divided by Koenig's surface which is impermeable to all charged species (both ions and electrons). This surface constitutes an infinitesimally narrow and infinitely high energy barrier for all charged species, which in fact constitutes the difference between ideally polarisable and completely polarisable boundaries. It is in principle unimportant in this case which charged species enter into the composition of each phase. Koenig's definition is outside the framework of thermodynamics, since a definite structure of the interfacial region is postulated in it and non-thermodynamic assumptions concerning the existence of an infinitely high energy barrier for all the charged species are used.

Although the concept of the ideally polarisable electrode was developed by Koenig in 1934, the term ideally polarisable boundary (or electrode) as such was introduced later[19] and Koenig himself[18] used Planck's term. The term "ideally polarisable boundary" has been used in modern literature in a somewhat loose sense starting from Grahame's review.[20] It frequently includes the concepts of both an ideally polarisable boundary and of a completely polarisable boundary. It is sufficient to say that such confusion occurs even in the "electrochemical nomenclature" recommended by IUPAC.[16] Since Grahame[20] did not differentiate the concepts of free and thermodynamic surface charges and did not consider the adsorption or local charge transfer at the interface, he assumed that there is no need to use Koenig's surface in order to introduce the concept of the ideally polarisable electrode. Many investigators repeat this error to the present day, although as early as two decades ago Frumkin and co-workers[21,22] analysed in detail the difference between ideally and completely polarisable electrodes. It was shown that a completely polarisable electrode can include, in contrast to an ideally polarisable electrode, systems with local or adsorption charge transfer. For example, at a platinum electrode, whose potential is more positive than the equilibrium hydrogen potential by up to 300 mV, hydrogen ions are adsorbed from solution, react with the electrons from the metal, and form adsorbed hydrogen atoms:

$$H_{ads} \rightleftarrows H^+ + e^-.$$

This reaction is rapid on platinum and, starting from a certain instant, can be regarded as reversible. Although local charge transfer occurs here and Koenig's surface cannot be introduced,

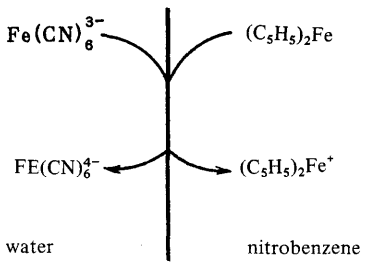
there is no charge transfer between the phases and the electrode is completely polarisable as defined by Planck but not ideally polarisable as defined by Koenig.

If the phases α and β contain even one common ion, which moves freely across the interface, then such an interface can be referred to as reversible or non-polarisable. Despite the fact that the latter term is generally accepted, it does not reflect quite accurately the state of the system. A reversible (non-polarisable) interface can be partly polarisable or completely non-polarisable. Large currents can flow in either direction across a completely non-polarisable interface between two phases containing at least one common ion without causing a deviation of the interphase potential difference from the equilibrium value. Ideally polarisable and completely non-polarisable interfaces do not exist in nature, although certain electrodes can have properties close to ideality under certain conditions.

A partially polarisable interface corresponds to the intermediate state between ideally (completely) polarisable and non-polarisable interfaces. This difference actually exists and is usually investigated in electrochemistry.

In conclusion, we shall show that the definition proposed by IUPAC,[16] namely that the boundary between phases should be regarded as ideally polarisable when the phases contain no common components or the exchange of the components is difficult and cannot be regarded as satisfactory.

Suppose that a lipophilic reductant and a hydrophilic oxidant have been added to a water–oil system where each phase contains electrolytes (but there are no common ions in the two phases), so that an electron exchange reaction takes place at the interface:



In this case the interface ceases to be ideally polarisable and becomes partly polarisable or non-polarisable depending on the reaction conditions, although the oil and water contain no common ions. One can foresee the objection that electrons can be regarded as a common component in the two phases although they are not present in them in a free form. However, this does not save the IUPAC definition[16] because it vitiates the significance of its first part: "...when the phases contain no common components".

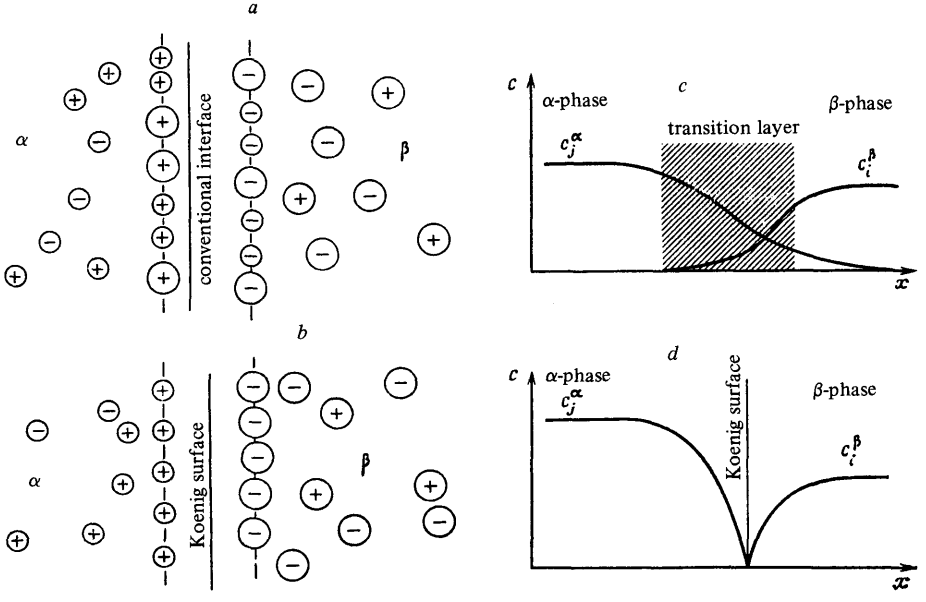


Figure 1. Schematic illustration of the distribution of ions and of the structure of the completely (*a*, *b*, *c*, and *d*) and ideally (*b* and *d*) polarisable interfaces.

III. INTERPHASE POTENTIALS

1. Boundary Potentials

As at any interface, an electrical potential difference is established at equilibrium at the interface between two immiscible liquids, which is referred to as the boundary potential difference or, briefly, the boundary potential. A classification of interphase potential jumps was introduced in 1930.[23] Fig.2 illustrates schematically the interphase potential jumps at the boundary between two immiscible phases, α and β, and also between these phases and the vacuum. The potential Ψ^{α}, measured *in vacuo* in the immediate vicinity of the above surface, is referred to as the Volta potential or the external potential. The potential φ^{α}, in the bulk of the phase, reckoned relative to a point in a vacuum at an infinite distance, is referred to as the Galvani potential or the internal potential. These two potentials differ by the surface potential jump χ^{α}.

In a study of the contact between the phases α and β, the Galvani potential difference

$$\Delta_{\beta}^{\alpha}\varphi = \varphi^{\alpha} - \varphi^{\beta},$$

which is determined by the specific distribution of the charged and polarised dipolar species in the vicinity of the interface, is of principal interest. The dipolar component of the interfacial potential difference $\Delta_{\beta}^{\alpha}\varphi_h$ is sometimes separated from the overall difference between the Galvani potentials; one can then obtain the quantity

$$\Delta_{\beta}^{\alpha}\varphi - \Delta_{\beta}^{\alpha}\varphi_h,$$

which is determined by the distribution of ions. Such separation is of practical value in those cases where the dipolar contribution to the potential jump is independent of the overall interphase potential difference (or depends only slightly on the latter), i.e. is ultimately independent of the ionic potentials and one can assume that all the changes in the interphase potential difference are described solely by the ionic contribution (the measurement and calculation of this contribution constitutes to a large extent the subject of the modern science of the interface between liquid electrolyte solutions). However, there is usually no certainty that the separation of the interphase potential difference into two independent components, due to the ionic and dipolar contributions, is valid and treatment of the results in such terms involves a certain degree of approximation.

One should also bear in mind that, contrary to the claim frequently encountered in the literature,[24] the dipolar potential jump $\Delta_{\beta}^{\alpha}\varphi_h$ at the interface between two immiscible electrolyte solutions is generally speaking not equal to the potential difference at the boundaries of these phases with a vacuum even in the case of specific adsorption:

$$\Delta_{\beta}^{\alpha}\varphi_h \neq \Delta_{\beta}^{\alpha}\chi = \chi^{\alpha} - \chi^{\beta}.$$

The reason is the mutual influence of the phases on the orientation of the dipolar molecules in the boundary layers of the liquid. Table 1 illustrates the thermodynamic feasibility of the experimental measurement of boundary potentials.

The equilibrium potentials at a reversible or non-polarisable interface are divided into three types depending on which species pass from phase to phase:

1. Potentials which arise in an equilibrium system where all the ions are capable of passing from one phase to the other are referred to as *distribution potentials.*

2. If the phases in contact contain ions some of which are capable of crossing the boundary while others are not, *Donnan potentials* or membrane potentials are generated. The transfer of ions may be prevented by either mechanical (as in semipermeable membranes) or chemical (as in ion exchangers) causes. If ions of only one kind can cross the interface, then the membrane potential difference is called the *Nernst potential.*

3. If two immiscible electrolyte solutions exchange electrons and are in equilibrium with respect to electrons, then an *oxidation-reduction potential* is established at the interface.

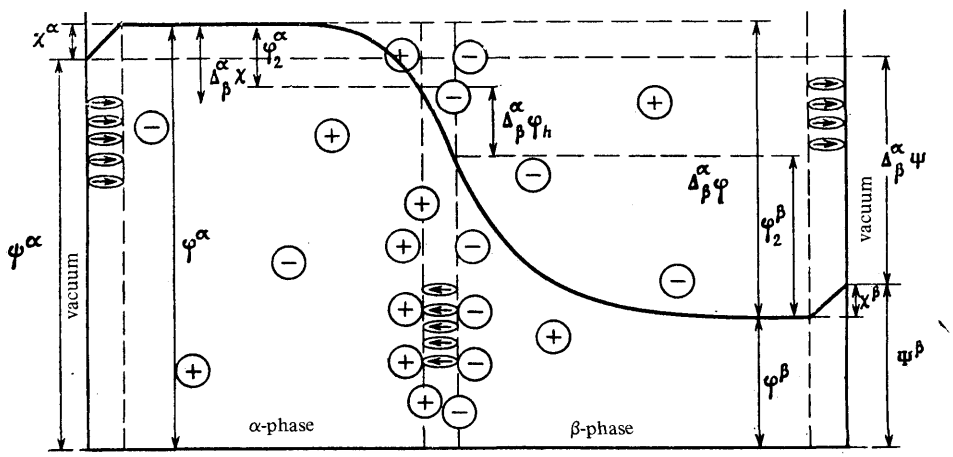


Figure 2. Boundary potentials in an oil–water system: $\psi^{\alpha}(\psi^{\beta})$—external potential or Volta potential; $\varphi^{\alpha}(\varphi^{\beta})$—internal potential of the phase α(β); $\chi^{\alpha}(\chi^{\beta})$—surface potential jump equal to the difference between φ^{α} and ψ^{α} (φ^{β} and ψ^{β}); $\Delta_{\beta}^{\alpha}\varphi$—Galvani potential difference; $\Delta_{\beta}^{\alpha}\psi$—Volta potential difference; $\Delta_{\beta}^{\alpha}\varphi_h$—the dipolar component of the interphase Galvani potential difference; φ_2^{α} and φ_2^{β}—potential jumps in diffuse layers.

Interphase potentials on completely (and ideally) polarisable boundaries can be due to the adsorption of charged or dipolar species at the interface or by the charging of the latter from an external source.

Table 1. Thermodynamic feasibility of the experimental measurement of the boundary potentials in immiscible liquid phases α and β.

Boundary potentials	Feasibility of measurement
External potential of one phase Ψ	Measured
Volta potential $\Delta_\beta^\alpha\Psi$	Measured
Surface potential χ	Not measured
Difference between surface potentials $\Delta_\beta^\alpha\chi$	Not measured, but can be determined when an additional non-thermodynamic hypothesis is used
Internal potential φ	Not measured
Difference between Galvani potentials $\Delta_\beta^\alpha\varphi$	Not measured, but if both phases have the same composition, measurement is possible
Change in $\Delta_\beta^\alpha\varphi$ during any process (adsorption, change in temperature, concentration, etc.)	Measured
Potential difference in the cell between phases of the same composition $E = \Sigma\Delta_\beta^\alpha\varphi$	Measured
Distribution potential of the salt or individual ion—$\Delta_\beta^\alpha\varphi$ or $\Delta_\beta^\alpha\varphi_i^0$	Not measured, but can be determined when an additional non-thermodynamic hypothesis is used
Change in $\Delta_\beta^\alpha\chi$ during any process (adsorption of dipoles, change in temperature, etc.)	Measured

Thermodynamics makes it possible to determine the interfacial potential only at a reversible interface. In the case of an ideally polarisable boundary, the potential is an additional independent variable characterising the state of the boundary and is specified by an external potential source. An electrostatic rather than an electrochemical equilibrium is maintained on an ideally polarisable boundary. It is analogous to the state of a charged condenser.

2. Standard Potentials and Standard Free Energies

Suppose that the phases α and β in contact contain ions I_i with a charge number z_i and an activity a_i. It follows from the condition for electrochemical equilibrium that

$$\Delta_\beta^\alpha\varphi = -\frac{\mu_i^{0,\alpha} - \mu_i^{0,\beta}}{z_iF} + \frac{RT}{z_iF}\ln\frac{a_i^\beta}{a_i^\alpha}, \quad (1)$$

where μ is the chemical potential and F the Faraday. The difference between the standard chemical potentials of the ion i in the two phases

$$\mu_i^{0,\alpha} - \mu_i^{0,\beta} \equiv \Delta_\beta^\alpha G_i^0(i) \quad (2)$$

represents the energy of transolvation or the standard Gibbs free energy $\Delta_\alpha^\beta G_i^0(i)$ of the transfer of the ion i from the phase α to the phase β. We introduce two further definitions: the distribution coefficient of the ions:

$$P_i^{\alpha/\beta} = \exp(-\Delta_\beta^\alpha G_i^0(i)/RT) \quad (3)$$

and the standard potential of the distribution of ions of the given kind:

$$\Delta_\beta^\alpha\varphi_i^0 = -\frac{\Delta_\beta^\alpha G_i^0(i)}{z_iF} \equiv \frac{RT}{z_iF}\ln P_i^{\alpha/\beta}. \quad (4)$$

According to Eqn.(3), it is evident that $P_i^{\alpha/\beta} = 1/P_i^{\beta/\alpha}$.

The interphase potential difference can be represented in the form

$$\Delta_\beta^\alpha\varphi = \Delta_\beta^\alpha\varphi_i^0 + \frac{RT}{z_iF}\ln\frac{a_i^\beta}{a_i^\alpha} \equiv \frac{RT}{z_iF}\ln\left(P_i^{\alpha/\beta}\frac{a_i^\beta}{a_i^\alpha}\right). \quad (5)$$

The equilibrium ratios of the activities of the ions i in two phases is described by the expression

$$\frac{a_i^\alpha}{a_i^\beta} = \frac{\gamma_i^\alpha c_i^\alpha}{\gamma_i^\beta c_i^\beta} = \exp\left[-\frac{z_iF}{RT}(\Delta_\beta^\alpha\varphi - \Delta_\beta^\alpha\varphi_i^0)\right] = P_i^{\alpha/\beta}\exp\left(-\frac{z_iF}{RT}\Delta_\gamma^\alpha\varphi\right), \quad (6)$$

where γ is the activity coefficient and c the concentration.

Hence the physical significance of the concepts introduced becomes clear. The standard distribution potential of the given ion represents the interfacial potential difference which would be established at the interface if the equilibrium activities of this ion in the two phases were identical. The partition coefficient of the ions $P_i^{\alpha/\beta}$ corresponds to the equilibrium ratio of the activities of the ions i in the two phases in the absence of an interphase potential difference.

It follows from the electroneutrality condition for the phases that

$$\sum_i z_ic_i^\alpha = 0; \quad \sum_i z_ic_i^\beta = 0. \quad (7)$$

The relation between the interphase potential $\Delta_\beta^\alpha\varphi$ and the concentration of ions in solutions is described by Eqns.(6) and (7). If there are n types of ions in the system, then the number of equations is $n + 2$ and the number of variables is $2n + 1$, i.e. the number of independent variables in the system is $n - 1$. In other words, it is possible to specify the concentrations of ions of all kinds in a single phase except one. The concentration of the ions of the remaining kind in this phase, the concentrations of all the ions in the other phase, and the interphase potential are then determined by solving a system of equations.

Apart from the activities of individual ions, it is convenient to use the concept of the mean activity of a 1:1 electrolyte BA:

$$a_{BA}^{\pm} = (a_Ba_A)^{1/2}. \quad (8)$$

The mean activity coefficient of the electrolyte is then given by

$$\gamma_{BA} = (\gamma_B\gamma_A)^{1/2}. \quad (9)$$

The partition coefficient of a 1:1 electrolyte can be introduced analogously:

$$P_{BA}^{\alpha/\beta} = (P_B^{\alpha/\beta}P_A^{\alpha/\beta})^{1/2}. \quad (10)$$

It is readily seen that $P_{BA}^{\alpha/\beta}$ is simply equal to the ratio of the mean activities of this electrolyte within the bulk of the phases α and β:

$$P_{BA}^{\alpha/\beta} = a_{BA}^{\pm\alpha}/a_{BA}^{\pm\beta}. \quad (11)$$

It is of interest that this ratio, in contrast ot the analogous ratio for

the individual ions [Eqn.6)], is independent of the interfacial potential. It is also independent of the presence of other ions in the solutions.

3. Distribution Potentials

(a) Fully Dissociated Electrolyte

We shall consider the simplest case where the boundary is non-polarisable and the phases α and β contain a binary 1:1 electrolyte B^+A^-:

$$\alpha,\ B^+A^-|B^+A^-,\ \beta. \tag{12}$$

The interfacial potential can be readily found from Eqn.(5) and the electroneutrality condition:

$$\Delta_\beta^\alpha\varphi = \frac{\Delta_\beta^\alpha\varphi_B^0 + \Delta_\beta^\alpha\varphi_A^0}{2} + \frac{RT}{2F}\ln\frac{\gamma_B^\beta\gamma_A^\alpha}{\gamma_A^\beta\gamma_B^\alpha}. \tag{13}$$

The first term reflects the individual characteristics of the ions in two media in the standard state, while the second depends on the activity coefficients, i.e. reflects the concentration effects. However, in practice the activity coefficients of the cation and anion can be regarded as approximately identical: $\gamma_A^\alpha \simeq \gamma_B^\alpha$ and $\gamma_A^\beta \simeq \gamma_B^\beta$. The expression for the interphase potential difference then assumes the simple form

$$\Delta_\beta^\alpha\varphi = \frac{\Delta_\beta^\alpha\varphi_B^0 + \Delta_\beta^\alpha\varphi_A^0}{2} \equiv \frac{RT}{2F}\ln\frac{P_B^{\alpha/\beta}}{P_A^{\alpha/\beta}}. \tag{14}$$

Thus the interphase potential difference is equal to the arithmetical mean of the standard distribution potentials of the individual ions. This potential difference between the two phases in the presence of a binary electrolyte has been called the distribution potential.[2,25] In this approximation, the distribution potential is independent of the concentration of the electrolyte BA. It is also independent of the structure of the interface, because it is determined solely by the thermodynamic properties of the bulk phases. This rule has been confirmed by experimental studies (see Section 5), although under certain conditions deviations from it occur. At low concentrations of the salt BA, the interphase potential difference depends also on the presence of other ions into which the solvent molecules dissociate and also of HCO_3^- ions if the measurements are performed in air and not in an inert gas.

When the number of ions in the system is greater than two, the distribution potential is known to depend on the concentrations of the ionic component of the system. The structure of the interface between two immiscible electrolyte solutions is also determined by the volume properties of the phases in contact. If a monolayer of a surfactant almost insoluble in both phases is adsorbed at the interface, then formally this should not alter the value of $\Delta_\beta^\alpha\varphi$ determined from Eqn.(13). However, the blocking of the surface by the surfactant molecules may disturb the thermodynamic equilibrium, as a result of which the measured potential difference ceases to correspond to the equilibrium value and differs from the distribution potential. The interphase potentials at an interface between two immiscible electrolyte soslutons have been calculated in different specific situations.[11,22,26]

One may consider the general case of an asymmetric electrolyte:

$$\alpha,\ B_p^{k+}A_t^{l-}|B_p^{k+}A_t^{l-},\ \beta. \tag{15}$$

In this case, the interphase potential, determined by the distribution of electrolytes between two phases, is described by the expression

$$\Delta_\beta^\alpha\varphi = \frac{z_B\Delta_\beta^\alpha\varphi_B^0 - z_A\Delta_\beta^\alpha\varphi_A^0}{z_B - z_A} + \frac{RT}{(z_B - z_A)F}\ln\frac{\gamma_B^\beta\gamma_A^\alpha}{\gamma_B^\alpha\gamma_A^\beta}. \tag{16}$$

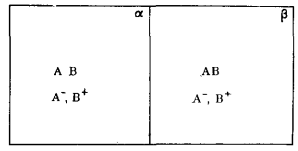
For an asymmetric electrolyte, the partition potential depends on the salt concentration. The second term on the right-hand side of Eqn.(16) is given by the following expression according to the Debye–Hückel theory:

$$\frac{RT}{(z_B - z_A)F}\ln\frac{\gamma_B^\beta\gamma_A^\alpha}{\gamma_B^\alpha\gamma_A^\beta} \simeq (z_B + z_A)\frac{e_0^3\sqrt{125}N_A^3}{2\pi F\varepsilon_0^{3/2}\sqrt{RT}}(I_\alpha^{1/2}\varepsilon_\alpha^{-3/2} - I_\beta^{1/2}\varepsilon_\beta^{-3/2}),$$

where I_α is the ionic strength of the solution in the phase α, N_α the Avogadro number, ε_0 the electrical constant, and ε_α the dielectric constant of the phase α. In terms of the Debye approximation, the distribution potential is independent of concentration only for a symmetrical electrolyte, where $z_A = -z_B$.

4. Incomplete Dissociation of the Salt

With the aid of the scheme



we shall consider the question of how the incomplete dissociation of the electrolyte can be reflected in the interphase distributions.

Suppose that the reaction

$$B^+ + A^- \overset{K_{BA}^\alpha}{\rightleftarrows} BA, \tag{17}$$

where K_{BA}^α is the dissociation constant of the BA molecule, takes place in the phase α. This means that the equality

$$a_B^\alpha a_A^\alpha = K_{BA}^\alpha a_{BA}^\alpha. \tag{18}$$

holds at equilibrium. The dissociation constant K_{BA}^α is related to the chemical potentials μ of the corresponding species by the equation

$$RT\ln K_{BA}^\alpha = \mu_{BA}^{0,\alpha} - \mu_{B^+}^{0,\alpha} - \mu_{A^-}^{0,\alpha}, \tag{19}$$

where μ^0 is the standard chemical potential. The same equations can be written for the dissociation in the β-phase.

The undissociated BA molecules can be distributed between the phases and the partition coefficient $P_{BA}^{\alpha/\beta}$ is defined by the equation

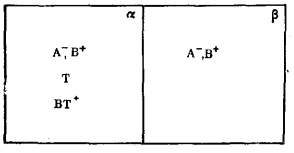
$$RT\ln P_{BA}^{\alpha/\beta} = \mu_{BA}^{0,\beta} - \mu_{BA}^{0,\alpha}. \tag{20}$$

The incomplete dissociation of the molecules does not affect the interphase potential. A distribution potential, defined by Eqn.(5), is established at the boundary. The standard distribution potentials of individual ions [Eqn.(4)] also do not change. However, owing to the presence of the dissociation equilibrium and the distribution of the undissociated molecules between the phases, a relation arises between the constants of these processes and the difference between the standard Gibbs free energies of the ions (and hence also the standard potentials):[26]

$$RT\ln\frac{K_{BA}^{\beta}}{K_{BA}^{\alpha}P_{BA}^{\alpha/\beta}}=\Delta_{\beta}^{\alpha}G_{B+}^{0}+\Delta_{\beta}^{\alpha}G_{A-}^{0}=F\Delta_{\beta}^{\alpha}\varphi_{A-}^{0}-F\Delta_{\beta}^{\alpha}\varphi_{B+}^{0}. \qquad (21)$$

5. Complex Formation in One of the Phases

Suppose that the binary electrolyte BA is distributed between the phases α and β and that the phase α contains in addition a neutral complexone T which can combine with the cation B^+ to form the charged complex BT^+:



The reaction

$$B^+(\alpha)+T(\alpha)\overset{K_{BT}^{\alpha}}{\rightleftarrows}BT^+(\alpha). \qquad (22)$$

takes place in the phase α and the dissociation constant K_{BT}^{α} is defined by the equation

$$RT\ln K_{BT}^{\alpha}=\mu_{BT+}^{0,\alpha}-\mu_{B+}^{0,\alpha}-\mu_{T}^{0,\alpha}. \qquad (23)$$

Apart from the homogeneous dissociation constant K_{BT}^{α} of the ocmplex BT^+, it is also possible to introduce the constant of the heterogeneous or surface dissociation $K_{BT}^{\alpha/\beta}$ referring to a process in which the complexone T and the complex BT^+ are in the phase α while the ion B^+ is in the phase β. This constant is defined by the equation

$$RT\ln K_{BT}^{\alpha/\beta}=\mu_{BT+}^{0,\alpha}-\mu_{T}^{0,\alpha}-\mu_{B+}^{0,\beta}. \qquad (24)$$

There is a simple relation between the two dissociation constants introduced and the partition coefficient of the ion B^+:

$$K_{BT}^{\alpha/\beta}=K_{BT+}^{\alpha}/P_{B+}^{\alpha\beta}. \qquad (25)$$

The equation for the heterogeneous dissociation equilibrium is

$$c_{T}^{\alpha}c_{B}^{\beta}=K_{BT+}^{\alpha/\beta}c_{BT}^{\alpha}\exp(F\Delta_{\beta}^{\alpha}\varphi/RT). \qquad (26)$$

The case where the complex BT^+ is very stable (i.e. its homogeneous dissociation constant K_{BT}^{α} is small) while the ion B^+ is only slightly soluble in the α-phase (the partition coefficient $P_{B+}^{\alpha/\beta}$ is small) is of special interest. One can then assume that, apart from the charged complex BT^+, the α-phase contains only one charged species—the counterion A^-. Using the usual procedures, it is possible to find the interphase potential difference for this case:[26]

$$\Delta_{\beta}^{\alpha}\varphi=\frac{RT}{F}\ln\left[\left\{\left(\frac{c_{B+}^{\beta}}{2K_{B+}^{\alpha/\beta}}\right)^{2}+\frac{c_{KOM}^{\alpha}}{P_{A-}^{\alpha/\beta}K_{BT+}^{\alpha/\beta}}\right\}^{1/2}-\frac{c_{B+}^{\beta}}{2K_{BT+}^{\alpha/\beta}}\right]. \qquad (27)$$

where c_{com}^{α} denotes the overall concentration of the complexone in the free and bound forms in the phase α and the activity coefficients are assumed to be unity for the sake of simplicity.

We shall consider two limiting cases arising from Eqn.(27). Supposing that the concentration of the A^-B^+ electrolyte is low. Then, by expanding Eqn.(27) as a series, we obtain

$$\Delta_{\beta}^{\alpha}\varphi\simeq\frac{RT}{2F}\ln\frac{c_{com}^{\alpha}}{P_{A-}^{\alpha/\beta}K_{BT+}^{\alpha/\beta}}. \qquad (28)$$

Eqn.(28) can be given a more usual form by introducing the interphase partition coefficient of the ion B^+ taking into account complex formation:

$$\tilde{P}_{B+}^{\alpha/\beta}=c_{com}^{\alpha}/K_{BT+}^{\alpha/\beta}. \qquad (29)$$

The expression for the interfacial potential is then

$$\Delta_{\beta}^{\alpha}\varphi=\frac{RT}{2F}\ln\frac{\tilde{P}_{B+}^{\alpha/\beta}}{P_{A-}^{\alpha/\beta}}. \qquad (30)$$

This is a typical expression for the distribution potential which does not include directly the complexone concentration and the form of the relation is determined by the valences of the electrolyte. Eqn.(30) is valid for a 1:1 electrolyte. For arbitrary valences, it assumes the following form:

$$\frac{F}{RT}\Delta_{\beta}^{\alpha}\varphi=\frac{1}{z_{B}-z_{A}}\ln\frac{c_{com}^{\alpha}}{P_{A}^{\alpha/\beta}K_{BT}^{\alpha/\beta}}. \qquad (31)$$

The dependence of $F\Delta_{\beta}^{\alpha}\varphi/RT$ on $\ln c_{com}^{\alpha}$ is described by a straight line whose slope is 1/2 for a 1:1 electrolyte, 1/3 for a 1:2 electrolyte, and 1/4 for a 2:2 electrolyte.[26]

We shall now proceed to another limiting case. Suppose that the electrolyte concentration is high so that the concentration of the complexone in the phase α is close to saturation. We then obtain for Eqn.(29)

$$\Delta_{\beta}^{\alpha}\varphi=\frac{RT}{F}\ln\frac{c_{com}^{\alpha}}{P_{A-}^{\alpha/\beta}c_{A-}^{\beta}}. \qquad (32)$$

Fig.3 illustrates the dependence of $F\Delta_{\alpha}^{\beta}\varphi/RT$ on $\ln c_{A-}^{\beta}$, which consists of two linear sections. The slope of the second section is −1 for a univalent anion A^- or $1/z_{A-}$ in the arbitrary case. The point of intersection M (Fig.3) of the two sections yields $0.5\ln(c_{com}^{\alpha}K_{BT+}^{\alpha/\beta}/P_{A-}^{\alpha/\beta})$, which makes it possible to determine the heterogeneous dissociation constant of the complex BT^+.

6. The Donnan Potential

The Donnan potential is the name given to the interphase potential difference when some of the ions cannot cross the interface between two immiscible electrolyte solutions while the remaining ions are free to move reversibly from one phase to the other. Suppose, for example, that an ion R with a charge number z_R has

such a high partition coefficient $P_R^{\alpha/\beta}$ that it is almost totally concentrated in the phase α. Apart from the ions R, the system contains a binary electrolyte B^+A^- whose concentration in the β-phase is c_{BA}^{β}

$$\alpha, R^{z_R}, B^+A^- \mid B^+A^-, \beta. \tag{33}$$

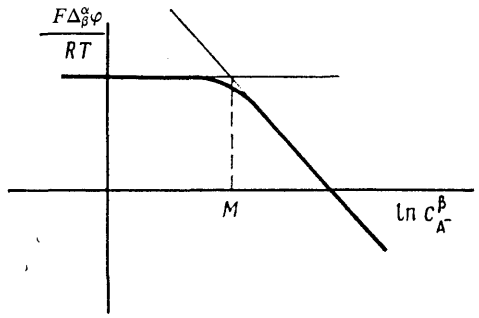


Figure 3. Dependence of the distribution potential on the electrolyte concentration in the phase β during the complex formation reaction in the phase α.

This type of equilibrium was first considered by Donnan[9] for two ideal aqueous ($\alpha \equiv \beta$) electrolyte solutions separated by a semipermeable membrane. The Donnan equilibrium was then investigated also by other workers, but the modifications which they introduced reduced in essence to the replacement in the Donnan equation of the concentrations of ions by their activities, which made it possible to change over from ideal to real solutions. Almost all investigators considered the Donnan equilibrium between two aqueous solutions. However, in the general case the phases α and β can be different and the above equilibrium can be achieved also in the absence of a semipermeable membrane.

The Donnan equilibrium at the interface between two immiscible liquids was first considered in a monograph[1] and then in another study for two ideal electrolyte solutions. Since there are inaccuracies in the study of Joos et al.,[7] we shall present the correct derivation of the Donnan equations for ideal and real immiscible electrolyte solutions in accordance with the study of Markin and Volkov.[26]

By definition, the partition coefficient of the salt is given by

$$P_{AB}^{\alpha/\beta} = a_{AB}^{\alpha}/a_{AB}^{\beta}. \tag{34}$$

Hence follows the equation relating the activities of the ion B^+ and A^- in both phases:

$$a_{B^+}^{\alpha}a_{A^-}^{\alpha} = (P_{AB}^{\alpha/\beta})^2\, a_{A^-}^{\beta}a_{B^+}^{\beta}. \tag{35}$$

From this equation and the two phase electroneutrality conditions

$$z_R c_R^{\alpha} + c_{B^+}^{\alpha} - c_{A^-}^{\alpha} = 0, \tag{36}$$

$$c_B^{\beta} - c_A^{\beta} = 0, \tag{37}$$

it is easy to find the Donnan potential:

$$\Delta_\beta^\alpha\varphi = \frac{RT}{2F}\ln\left(\frac{P_{B^+}^{\alpha/\beta}}{P_{A^-}^{\alpha/\beta}} \times \frac{\gamma_{B^+}^{\beta}\gamma_{A^-}^{\alpha}}{\gamma_{A^-}^{\beta}\gamma_{B^+}^{\alpha}}\right) + \frac{RT}{2F}\ln\left(1 + \frac{z_R^{\alpha}c_R^{\alpha}}{c_{B^+}^{\alpha}}\right). \tag{38}$$

Eqn.(38) resembles Eqn.(14) obtained by Grundwald et al.[28] but differs from it by the distribution potential of the salt defined by the first term on the right-hand side of Eqn.(38).

The Donnan potential can also be formulated as a function of the concentration of the dissolved electrolyte AB:

$$\Delta_\beta^\alpha\varphi = \frac{RT}{2F}\ln\left(\frac{P_{B^+}^{\alpha/\beta}}{P_{A^-}^{\alpha/\beta}}\frac{\gamma_{B^+}^{\beta}\gamma_{A^-}^{\alpha}}{\gamma_{A^-}^{\beta}\gamma_{B^+}^{\alpha}}\right) + \\ + \frac{RT}{F}\ln\left\{\left[1 + \left(\frac{z_R c_R^{\alpha}\gamma_{BA}^{\alpha}}{2P_{BA}^{\alpha/\beta}a_{BA}^{\beta}}\right)^2\right]^{1/2} + \frac{z_R c_R^{\alpha}\gamma_{BA}^{\alpha}}{2P_{BA}^{\alpha/\beta}a_{BA}^{\beta}}\right\}. \tag{39}$$

As can be seen from Eqns.(38) and (39), the Donnan potential is represented by a sum which includes the distribution potential and a term depending on the concentration of the ion R which does not permeate into the electrolyte. If the concentration of the ion R is low, then the second term can be assumed equal to zero and Eqns.(38) and (39) become identical with the expression for the distribution potential. The distribution of ions between phases is then determined by known expressions.

At a high concentration of the ion R, a different expression is obtained for the potential. If we put $z_R > 0$ to make the treatment concrete, we obtain

$$\Delta_\beta^\alpha\varphi = \frac{RT}{F}\ln\frac{z_R c_R^{\alpha}\gamma_{A^-}^{\alpha}}{P_{A^-}^{\alpha/\beta}a_{A^-}^{\beta}}. \tag{40}$$

In this case, the concentration of the counterions A^- in the phase α ceases to depend on the distribution coefficient and the interphase potential and approaches the limiting value

$$c_A^{\alpha} \simeq z_R c_R^{\alpha}. \tag{41}$$

The coions B^+ are then almost fully displaced from the phase α:

$$c_{B^+}^{\alpha} = \frac{1}{z_R c_R^{\alpha}}\left(\frac{P_{BA}^{\alpha/\beta}a_{BA}^{\beta}}{\gamma_{BA}^{\alpha}}\right)^2. \tag{42}$$

7. The Nernst Potential

We shall consider the especially important special case of the Donnan potential when ions of only one type can cross the boundary. Suppose that these are the B^{z_B} ions. The type and number of other ions do not play a significant role. The interphase potential difference arising in such a system is referred to as the Nernst potential:

$$\Delta_\beta^\alpha\varphi = \Delta_\beta^\alpha\varphi_B^0 + (RT/z_BF)\ln(a_B^{\beta}/a_B^{\alpha}). \tag{43}$$

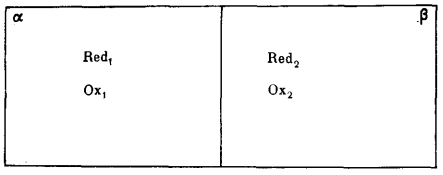
If the phases α and β are identical but are separated by a membrane permeable to the ions B^+, then $\Delta_\beta^\alpha\varphi_B^0 = 0$ and the potential difference is given by

$$\Delta_\beta^\alpha\varphi = (RT/z_BF)\ln(a_B^{\beta}/a_B^{\alpha}). \tag{44}$$

Sometimes the potential difference determined from Eqn.(43) is also referred to as the Nernst–Donnan potential, because, although historically a formula of this type was first obtained by Nernst,[27] it corresponds to a special case of the Donnan equilibrium.

8. The Oxidation-Reduction Interphase Potential

Suppose that each of the two phases, α and β, contains its own oxidation-reduction couple Red/Ox:



As a result of the exchange of n electrons across the interface, an oxidation-reduction reaction takes place:

$$\nu_1 \mathrm{Red}_1 + \nu_2 \mathrm{Ox}_2 \rightleftarrows \nu_3 \mathrm{Red}_2 + \nu_4 \mathrm{Ox}_1. \tag{45}$$

At equilibrium, the followig equality holds:

$$\nu_1 \bar{\mu}^{\alpha}_{\mathrm{Red}_1} + \nu_2 \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \nu_3 \bar{\mu}^{\beta}_{\mathrm{Red}_2} + \nu_4 \bar{\mu}^{2}_{\mathrm{Ox}_1}. \tag{46}$$

Hence we find the interphase oxidation-reduction potential:

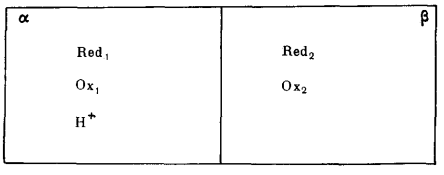
$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} + \frac{RT}{nF} \ln \frac{(a^{\alpha}_{\mathrm{Red}_1})^{\nu_1} (a^{\beta}_{\mathrm{Ox}_2})^{\nu_2}}{(a^{\alpha}_{\mathrm{Ox}_1})^{\nu_4} (a^{\beta}_{\mathrm{Red}_2})^{\nu_3}}. \tag{47}$$

In this case $\Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}}$ denotes the standard interphase oxidation-reduction potential of reaction (45):

$$\Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} = (\nu_1 \mu^{0,\alpha}_{\mathrm{Red}_1} + \nu_2 \mu^{0,\beta}_{\mathrm{Ox}_2} - \nu_3 \mu^{0,\alpha}_{\mathrm{Ox}_1} - \nu_4 \mu^{0,\beta}_{\mathrm{Red}_2})/nF, \tag{48}$$

where n is the number of electrons transferred from Red_1 to Ox_2. In terms of its physical significance, Eqn.(48) represents the interphase potential for equal activities of the ions of the oxidised and reduced forms in each solvent. We may note that the interphase oxidation-reduction potential is defined by Eqns.(47)–(48) when reaction (45) occurs even when the oxidant or reductant in any of the redox pairs is a neutral species.

If reaction (45) is accompanied by a change in the pH in one of the phases, i.e.



and the reaction

$$\nu_1 \mathrm{Red}_1 + \nu_2 \mathrm{Ox}_2 \rightleftarrows \nu_3 \mathrm{Red}_2 + \nu_4 \mathrm{Ox}_1 + m\mathrm{H}^{+}_{\alpha}, \tag{49}$$

takes place, then from the condition for equilibrium

$$\nu_1 \bar{\mu}^{\alpha}_{\mathrm{Red}_1} + \nu_2 \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \nu_3 \bar{\mu}^{\beta}_{\mathrm{Red}_2} + \nu_4 \bar{\mu}^{\alpha}_{\mathrm{Ox}_1} + m\bar{\mu}^{\alpha}_{\mathrm{H}^+} \tag{50}$$

it is possible to find the interphase redox potential

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} + \frac{RT}{nF} \ln \frac{(a^{\alpha}_{\mathrm{Red}_1})^{\nu_1} (a^{\beta}_{\mathrm{Ox}_2})^{\nu_2}}{(a^{\alpha}_{\mathrm{Ox}_1})^{\nu_4} (a^{\beta}_{\mathrm{Red}_2})^{\nu_3} (a^{\alpha}_{\mathrm{H}^+})^{m}}, \tag{51}$$

where

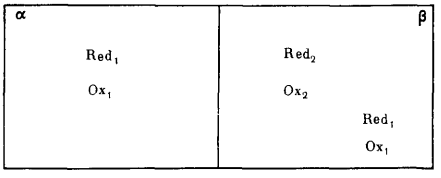
$$\Delta^{\alpha}_{\beta}\varphi = (\nu_1 \mu^{0,\alpha}_{\mathrm{Red}_1} + \nu_2 \mu^{0,\beta}_{\mathrm{Ox}_2} - \nu_3 \mu^{0,\alpha}_{\mathrm{Ox}_1} - \nu_4 \mu^{0,\beta}_{\mathrm{Red}_2} - m\mu^{0,\alpha}_{\mathrm{H}^+})/nF. \tag{52}$$

Analysis of the influence of the interface between two liquids on the standard redox potential of an electron-exchange reaction[11-14] has shown that, by selecting the phases α and β, it is possible to displace the standard chemical potential of the oxidants and reductants in the required direction and to achieve at the interface reactions which do not occur at a sufficiently high rate in each phase.

9. The Mixed Potential

If the two immiscible liquids each contain, apart from their own redox couple also common ions or compound redox couples, then a mixed potential is established at the interface to which both the interphase oxidation-reduction potential and the distribution of the ions between the phases contribute.

There is a possibility of various combinations of electron-exchange reactions in the two-phase system. Suppose, for example, that each of the phases α and β has its own redox couple but one of the couples is soluble in both phases:



In this case electron-exchange reactions are possible both at the interface, i.e.

$$\mathrm{Red}^{\alpha}_1 + \mathrm{Ox}^{\beta}_2 \rightleftarrows \mathrm{Ox}^{\alpha}_1 + \mathrm{Red}^{\beta}_2, \tag{53}$$

and in the bulk of the phase β:

$$\mathrm{Red}^{\beta}_1 + \mathrm{Ox}^{\beta}_2 \rightleftarrows \mathrm{Ox}^{\beta}_1 + \mathrm{Red}^{\beta}_2. \tag{54}$$

It follows from the condition for equilibrium that

$$\bar{\mu}^{\beta}_{\mathrm{Red}_1} - \mu^{\alpha}_{\mathrm{Red}_1} = 0, \tag{55}$$

$$\bar{\mu}^{\beta}_{\mathrm{Ox}_1} - \bar{\mu}^{\alpha}_{\mathrm{Ox}_1} = 0, \tag{56}$$

whence

$$\Delta^{\alpha}_{\beta}\varphi = \frac{RT}{nF} \ln \frac{P^{\alpha/\beta}_{\mathrm{Ox}_1}}{P^{\alpha/\beta}_{\mathrm{Red}_1}} + \frac{RT}{nF} \ln \frac{a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1}}{a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1}}. \tag{57}$$

The standard potential for reaction (53) is defined by the expression

$$\Delta^{\alpha}_{\beta}\varphi^{0}_{\mathrm{R/O}} = (RT/nF) \ln (P^{\alpha/\beta}_{\mathrm{Ox}_1}/P^{\alpha/\beta}_{\mathrm{Red}_1}). \tag{58}$$

Eqn.(57) is identical with Eqn.(14) for the partition potential only in the case of a two-electron reaction subject to the condition that $z_{\mathrm{Red}_1} = -1$, $z_{\mathrm{Ox}_1} = +1$, and $a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1} / a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1} = 1$. The last requirement, concerning the ratio of the concentrations of the redox couple, is artificial in character and may hold only at one point for definite fixed activites of all the ingredients. It does not follow from the phase electroneutrality condition because, apart from the redox couples, there are also other ions in both phases.

Eqn.(57) does not include the second redox couple $\mathrm{Red}_2/\mathrm{Ox}_2$ but the latter does enter implicitly into the second term on the right-hand side of this equation. The second redox couple is forced to become automatically adjusted with respect to the first because, apart from Eqns.(55) and (56), a further two equations, determined by the equilibrium in the system, also hold:

$$\bar{\mu}^{\alpha}_{\mathrm{Red}_1} + \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \bar{\mu}^{\alpha}_{\mathrm{Ox}_1} + \bar{\mu}^{\alpha}_{\mathrm{Red}_2}, \tag{59}$$

$$\bar{\mu}^{\beta}_{\mathrm{Red}_1} + \bar{\mu}^{\beta}_{\mathrm{Ox}_2} = \bar{\mu}^{\beta}_{\mathrm{Ox}_1} + \bar{\mu}^{\beta}_{\mathrm{Red}_2}. \tag{60}$$

The introduction of a common electrolyte $B_p A_t$ into both phases is not reflected in the form of Eqn.(57) but, by virtue of the electroneutrality of both phases, i.e.

$$\sum_i z_i^{\alpha} c_i^{\alpha} = 0, \quad \sum_j z_j^{\beta} c_j^{\beta} = 0$$

the distribution of the concentrations of the redox components in each phase changes, which makes a considerable contribution to the second term on the right-hand side of Eqn. (57).

The majority of the redox reactions occurring on the liquid water–oil and water–biomembrane interfaces are accompanied by changes in pH, for example:

$$\mathrm{NADH} \rightleftarrows \mathrm{NAD}^+ + 2e^- + \mathrm{H}^+. \tag{61}$$

We shall consider a system of two immiscible liquids α and β:

α	β
Red_1	Red_2
Ox_1	Ox_2
	H^+
	Red_1
	Ox_1

Suppose that each phase has its own redox couple and that one of them is common to both phases:

$$\mathrm{Red}_1^{\alpha} + \mathrm{Ox}_2^{\beta} \rightleftarrows \mathrm{Ox}_1^{\alpha} + \mathrm{Red}_2^{\beta} + m\mathrm{H}_{\beta}^+,$$

$$\mathrm{Red}_1^{\beta} + \mathrm{Ox}_2^{\beta} \rightleftarrows \mathrm{Ox}_1^{\alpha} + \mathrm{Red}_2^{\beta} + m\mathrm{H}_{\beta}^+, \tag{62}$$

If n electrons are transferred from Red_1 to Ox_2 in the course of the reactions then, when $m \neq n$, we obtain from the equilibrium condition an expression for the mixed potential:

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} - \frac{RT}{(n-m)F} \ln \frac{a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1}}{a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1}}, \tag{63}$$

in which the standard potential is defined by the formula

$$\Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} = \frac{RT}{(n-m)F} \ln \frac{P^{\alpha/\beta}_{\mathrm{Ox}_1}}{P^{\alpha/\beta}_{\mathrm{Red}_1}}. \tag{64}$$

From the condition for thermodynamic equilibrium and the electroneutrality of phases for reaction (61), one can write $4+2=6$ equations for the two redox couples, which exceeds the number of independent variables in the system. If a proton equilibrium is established during reaction (61) between the phases α and β, then the mixed potential can be formulated as follows:[26]

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} - \frac{RT}{nF} \ln \frac{a^{\beta}_{\mathrm{Red}_1} a^{\alpha}_{\mathrm{Ox}_1}}{a^{\alpha}_{\mathrm{Red}_1} a^{\beta}_{\mathrm{Ox}_1}} + \frac{2{,}3RT}{nF} \Delta^{\alpha}_{\beta}\mathrm{pH}, \tag{65}$$

where

$$\Delta^{\alpha}_{\beta}\varphi^0_{\mathrm{R/O}} = -\frac{RT}{nF} \ln \frac{P^{\alpha/\beta}_{\mathrm{Red}_1}}{P^{\alpha/\beta}_{\mathrm{Ox}_1} P^{\alpha/\beta}_{\mathrm{H}^+}}. \tag{66}$$

IV. MEASUREMENTS OF INTERPHASE POTENTIAL JUMPS

1. The Tetraphenylborate Hypothesis

It is known from thermodynamics that the absolute difference between electrical potentials can be measured only in conductors of identical composition. For this reason, the difference between the Galvani potentials between a point in an aqueous phase and a point in the bulk of an organic solvent is not susceptible to experimental measurement.

For the determination of the difference between Galvani potentials and surface potential jumps, it is necessary to resort to additional non-thermodynamic hypotheses. It is comparatively easy to measure the relative change in the phase boundary potential difference when the type of dissolved salt is altered, for example, when one of the ions in the salt is changed. One can then measure the partition coefficient of each salt $P^{\alpha/\beta}_{\mathrm{salt}}$. With the aid of Eqn.(5), the phase boundary potential can be expressed in the form

$$\Delta^{\alpha}_{\beta}\varphi = \Delta^{\alpha}_{\beta}\varphi_i - \frac{RT}{z_i F} \ln P^{\alpha/\beta}_{\mathrm{salt}} \tag{67}$$

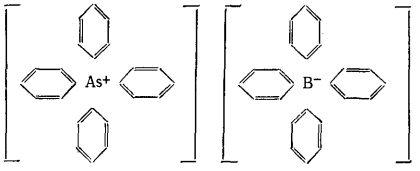
Thus it is possible to set up a scale of the changes in the potentials when one of the ions is altered, but this scale will include the unknown constant term $\Delta^{\alpha}_{\beta}\varphi^0_i$—the standard partition coefficient of the unchanged ion. The problem reduces to the correct selection of the zero on this scale.

The zero cannot be chosen by thermodynamic methods and requires the invocation of additional hypotheses. The most popular tetraphenylborate hypothesis was formulated in 1960 [28] and then developed in other studies.[29–42] The history of its development has been described in a review.[43]

The essential feature of the tetraphenylborate hypothesis is as follows. If one selects a cation and an anion with identical standard energies of transfer between two solvents, then the interphase distribution potential for such a salt is found to be zero. In this case the partition coefficients of the ions are equal to the partition coefficient of a salt, which can be readily determined experimentally. Having determined it, we find the standard free energy of the transfer and the standard distribution potentials of the individual ions. As can be readily seen, these potentials are identical in absolute magnitude and opposite in sign:

$$\Delta^{\alpha}_{\beta}\varphi^0_{+} = -\Delta^{\alpha}_{\beta}\varphi^0_{-}. \tag{68}$$

It now remains only to select the suitable ions. Preference has been given to different ions in different investigations. For example, Koczorowski[3] used tetraethylammonium picrate $(Et)_4NPi$. In other studies[28–43], preference was given to tetraphenylarsonium tetraphenylborate (TPATPB). The constituent ions of this salt TPB^- and TPA^+, i.e.



are similar, firstly, because they are symmetrical species whose shapes approach those of spheres having identical and fairly large radii, which permits the assumption that the hydrophobic effect is the same for both and, secondly, their charges are equal in absolute magnitude and are located in centres of ionic spheres and are shielded from the solvent, so that the electrostatic contribution to the free energy of transolvation of these ions should be the same. The ions have a comparatively low polarisability and a low surface charge density and hardly enter into specific interactions with the solvent molecules. All these factors permit the hope that the standard energies of the transfer of such ions will be the same for any pair of solvents.

With the aid of the tetraphenylborate hypothesis, it is possible to determine the standard distribution potentials by methods such as cyclic voltammetry, chronopotentiometry, polarography at a dropping electrolyte electrode, chronoammetry, and also solubility and extraction data.[31,35,37,38,40–42,44,45]

Fig.4 illustrates a typical cyclic voltammogram obtained at a scanning rate of 25 mV s^{-1} in the water–nitrobenzene (NB) system containing 10 mM TPATPB in the non-aqueous phase and 10 mM Li_2SO_4 in water.[53] The range of applied potential differences is limited in the negative region by the potential of the transfer of TPA^+ from nitrobenzene to water and in the positive region by the potential of the transfer of TPB^-. Since

$$\Delta^{H_2O}_{NB}\varphi^0_{TPB^-} = -\Delta^{H_2O}_{NB}\varphi^0_{TPA^+},$$

it is possible to select the starting point for the readings on the potential scale and to change over, as in Fig.4, from the applied potential difference scale to the Galvani potential scale or the distribution potential scale.

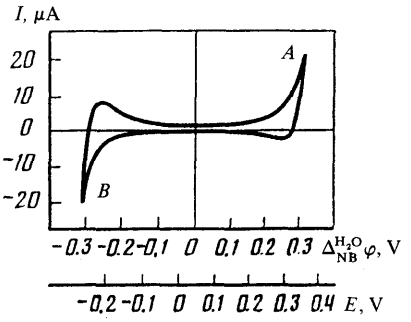


Figure 4. Cyclic voltammetric curve for the water–nitrobenzene system in the presence of TPATPB in nitrobenzene and of Li_2SO_4 in water. Peaks *A* and *B* are due to the transfer of TPA^+ and TPB^- from nitrobenzene to water respectively. The experimental curve has been taken from Hundhammer and Solomon.[31]

The block diagram of the apparatus, on which it is possible to determine the distribution potentials of ions and to investigate the electrochemical properties of the interface between two immiscible

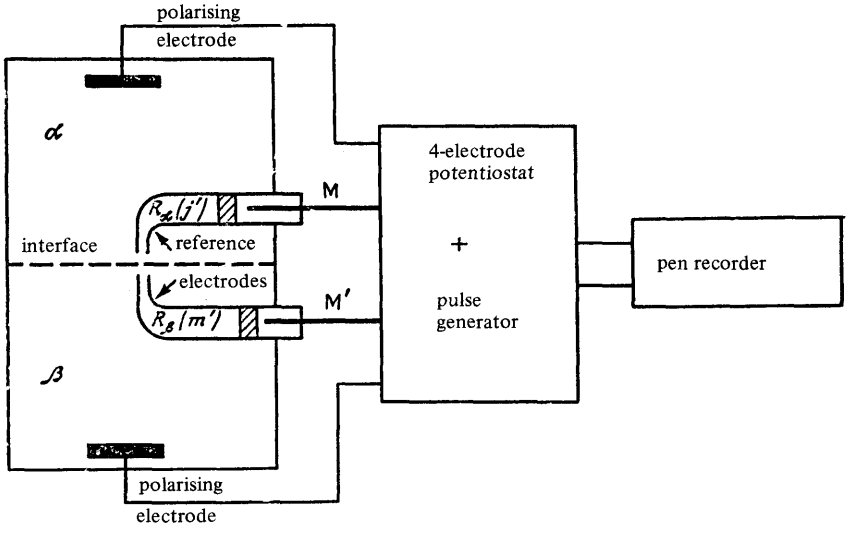


Figure 5. Diagram of the four-electrode apparatus for the measurement of the electrochemical characteristics of the interface between two immiscible electrolyte solutions.

liquids, is illustrated in Fig.5 and the cell and the electrical circuit are presented in Fig.6. The standard distribution potential of an ion depends both on the nature of the solvent (primarily on the optical and static dielectric constant) and on the ionic radius.

Fig.7 presents the dependence of the distribution potentials of ions on their radii for the water–nitrobenzene, water–1,2-dichloroethane, and water–dichloromethane systems plotted on the basis of a series of data[35,37,38,40–42,44–54] and published in a review.[56] The radii of inorganic ions were taken from Gourary and Adrian[57] and those of tetra-alkylammonium salts were taken from Robinson and Stokes.[58]

Figs.7 and 8 show that the distribution potential of an ion decreases sharply with increase in the size of the ion and in the dielectric constant of the non-aqueous solvent. The continuous line in Figs.7*a* and 7*b* represents the theoretical calculation with the aid of non-local electrostatic theory.[13,14] For ions with radii less than 0.3 nm, the main contribution to $\Delta_{\beta}^{\alpha}\varphi_i^0$ comes from the electrostatic component of the free energy of transolvation, while for ions with a radius greater than 0.3 nm the contribution of the solvophobic effect is greatest.[13,14]

2. Methods for the Measurement of the Interphase Potential Difference

The difference between the Volta potentials and the change in the surface or Galvanic potential in a system of two immiscible electrolyte solutions can be measured by the dynamic condenser, radioactive probe, and streaming electrode methods and also with the aid of concentration cells.

The dynamic condenser method, proposed by Kelvin, was subsequently developed in detail in other studies.[59,60] All the experimental methods for the measurement of Volta potentials between the phases α and β are based on the compensation method, which involves the application of a potential difference equal in absolute magnitude but opposite in sign to the Volta potential between the phases α and β.[59–86]

Two types of sensors are normally employed for the periodic measurement of the capacitance of the condenser formed by the surface of the electrode and the interface investigated, namely vibrating and rotating electrodes. The vibrating electrode is less complex than the rotating electrode but its stability is lower.

The block diagram of the apparatus for the measurement of the Volta potential by the dynamic condenser method is presented in Fig.9.[61] The generator of mechanical vibrations causes the vibration of a gold electrode placed at a distance of 0.2–1.0 mm from the surface of the liquid phase investigated. The aqueous solution is connected via a salt bridge filled with a saturated KCl solution (to eliminate the diffusion potential) to a reversible reference electrode. The displacement current arising in the vibration of the gold electrode is compensated by applying to the vibrating electrode a potential equal in magnitude but opposite in sign to the measured Volta potential. The equivalent electrical circuit for the method[62] is presented in Fig.10.

The Volta potential $\Delta\psi$ at the boundary between two immiscible equilibrated (mutually saturated) solutions of electrolytes B^+A^- can be determined experimentally as the compensation potential E_1 in the cell

$$\begin{matrix} M\,|\text{water},\, B^+A^-|\text{gas}|\text{Nitrobenzene},|M. \\ B^+A^- \end{matrix} \qquad (I)$$

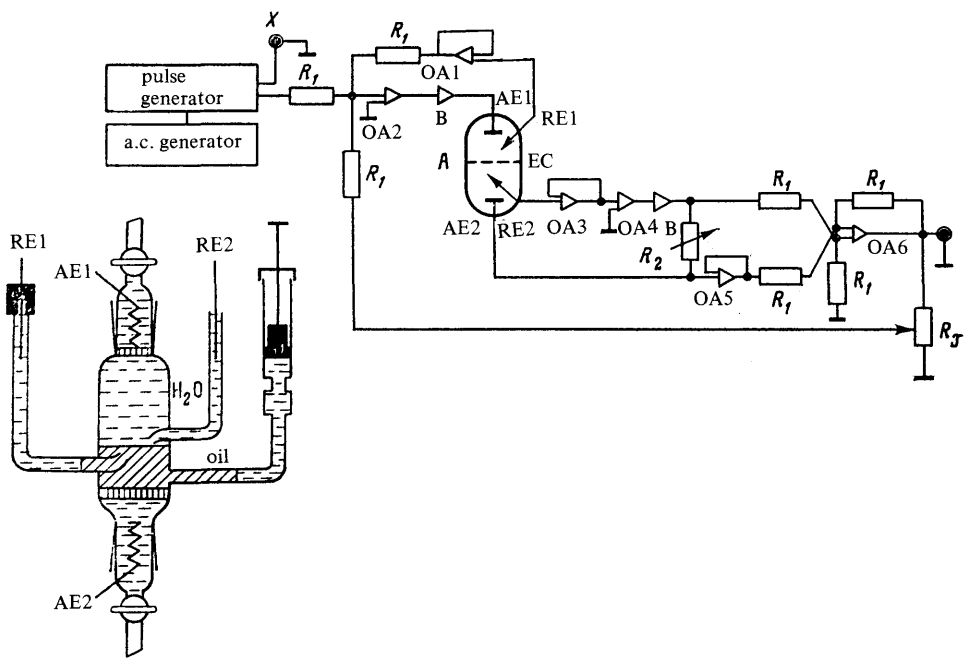


Figure 6. The cell and the electrical circuit of the apparatus for the measurement of the electrochemical properties of the interface between two immiscible electrolyte solutions; EC—electrochemical cell; OA—operational amplifier; AE—auxiliary electrode; RE—reference electrode; A—oil–water interface.[46]

The term gas implies a chemically inert gas phase, i.e. nitrogen, argon, or pure air, M is a metallic electrode, and B^+A^- is the electrolyte.

The Volta potential can be measured by the vibrating electrode method as the difference between the e.m.f.'s E_{II} and E_{III} of cells (II) and (III):

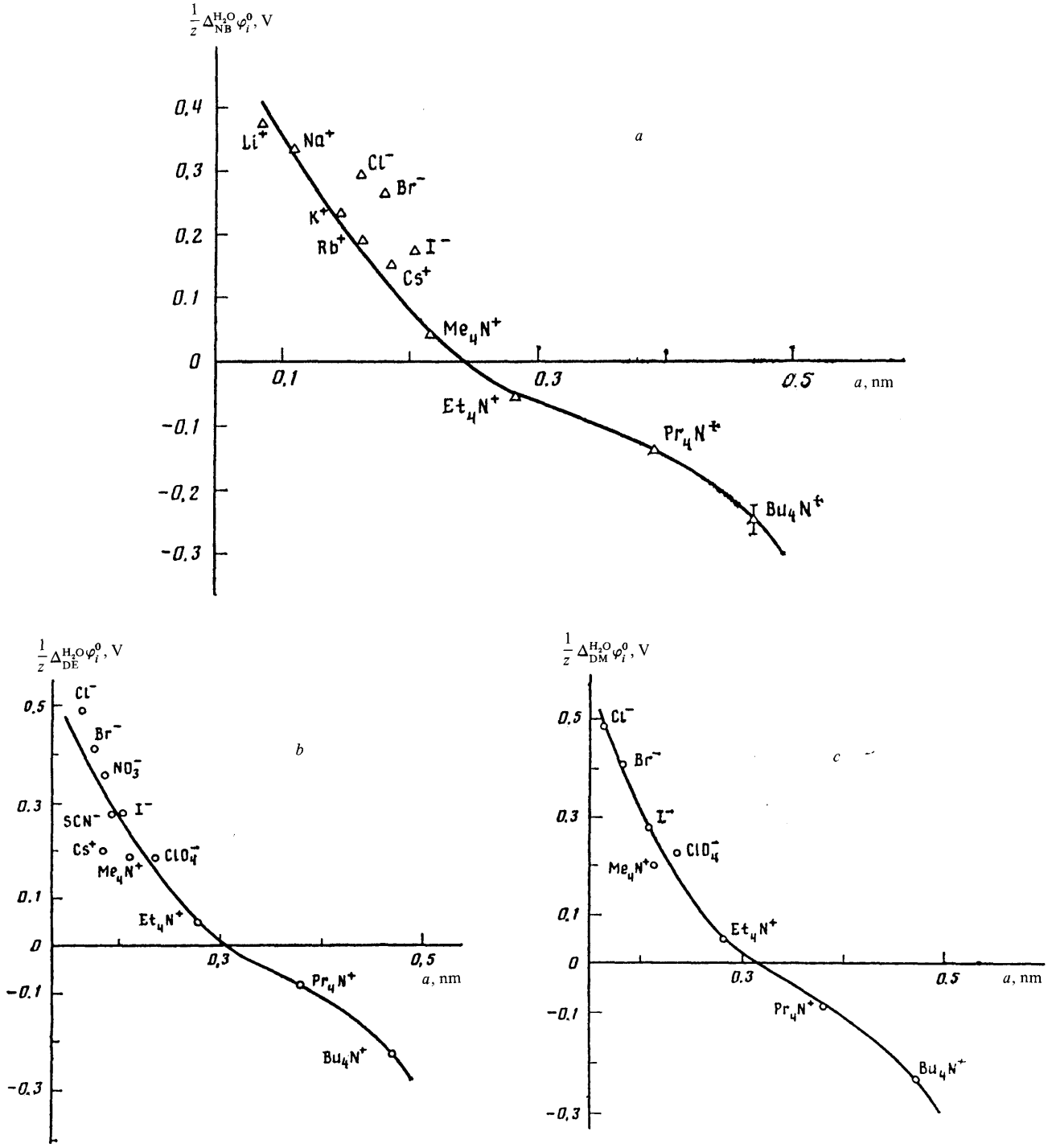


Figure 7. Dependence of the standard distribution potential of an ion on its radius in different systems: *a*) water–nitrobenzene; *b*) water–1,2-dichloroethane (DE); *c*) water–dichloromethane (DM). The experimental data have been taken from a review.[56]

$$\text{M}\,|\,\text{vibrating electrode}\,|\,\text{N}_2\,|\,\text{nitrobenzene } B^+A^-\,|\,\text{water, } B^+A^-\,|\,\text{saturated calomel electrode}\,|\,\text{M}, \quad \text{(II)}$$

$$\text{M}\,|\,\text{vibrating electrode}\,|\,\text{N}_2\,|\,\text{water, } B^+A^-\,|\,\text{saturated calomel electrode}\,|\,\text{M}. \quad \text{(III)}$$

In other words, the relation

$$\Delta^{H_2O}_{org}\psi(MX) = E_I = E_{II} - E_{III}, \quad (69)$$

holds, provided that the following conditions are fulfilled: (a) the constancy of the surface potential of the vibrating electrode: (b) the constancy of the surface potential of the water-saturated nitrobenzene phase; (c) the constancy of the surface potential of the nitrobenzene-saturated aqueous phase; (d) the stability of the calomel electrode and a constant and identical contribution of the diffusion potential between the aqueous phase and the solution in the calomel electrode.

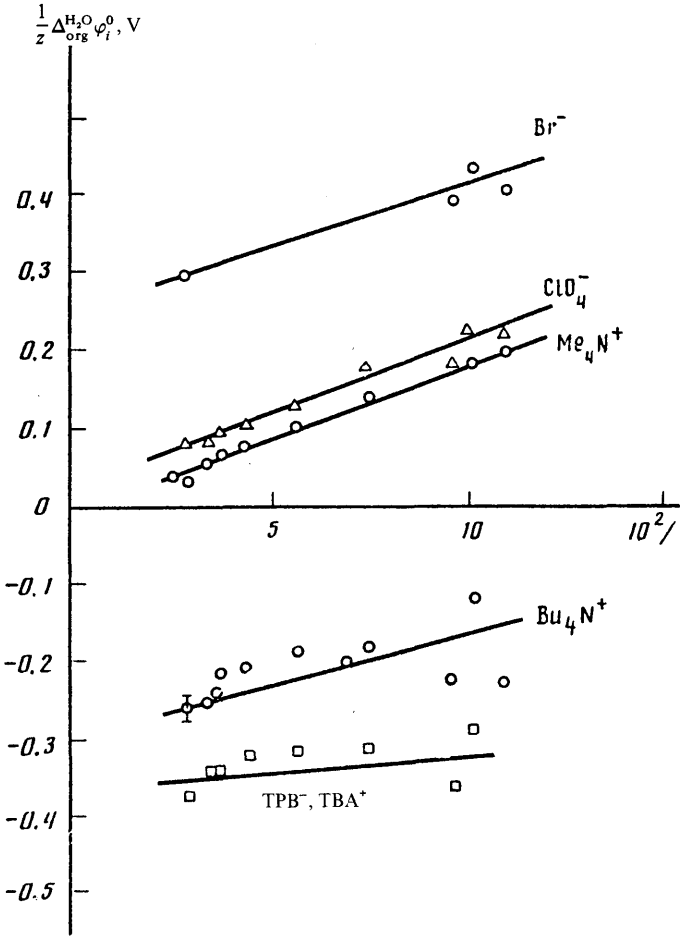


Figure 8. Dependence of the standard distribution potential of the ion on the static dielectric constant ε of the non-aqueous solvent. The experimental data were taken from a review.[56]

The design of the rotating electrode has been described by Dudko[64] and by Freyer and Ohlenbusch.[65] The equivalent circuit is presented in Fig.11. The rotating electrode is placed over a circular cell in such a way that the geometrical centre of the circle which it describes during its rotation coincides with the geometrical centre of the cell. The cell, divided by a partition into identical sections, is filled with the test liquids.

The essential feature of the radioactive probe method is the reduction of the resistance of the air gap between the electrode and the surface of the test liquid when it is bombarded with α-particles from a radioactive source.[66,67] As a result of ionisation, the gap becomes electrically conducting due to the appearance of charged particles. The ^{210}Po, ^{241}Am, and ^{239}Pu isotopes are normally employed.[68,72,73] The ^{241}Am isotope has an advantage over ^{210}Po because of its longer half-life (458 years instead of 138.4 hours); furthermore, ^{241}Am can be used in the form of a foil which has a large surface area and can readily be insulated.[73] The accuracy and reproducibility of the results in the radioactive probe method is lower than in the vibrating electrode method. The equivalent circuit of the method is presented in Fig.12.

An obligatory condition in the measurement of the Volta potential by the radioactive probe method is careful shielding of the measuring chamber and of the electrometer input. An unduly large gap between the electrode and the surface of the solution of the test electrolyte is frequently a source of errors in the measurement of the potential difference as a result of scattering of the radiation and parasitic leakages. If the gap is too small, incorrect values are also obtained owing to the interaction of α-particles with the molecules of the test liquid. The design of the apparatuses whose operation is based on the radioactive probe method and the experimental technique have been described in detail.[69]

In the streaming electrode method,[70,71] a stream of the test liquid flows downwards along the axis of a tube whose inner surface is coated with a down-flowing film of another liquid (Fig.13). The reversible reference electrodes placed in the solutions are connected to the measuring system consisting of a potentiometer and a null instrument with a very large internal resistance. At the instant of compensation, the external potential of this stream is equal to the external potential of the solution flowing along the inner walls of the cylinder. This method is rarely used to investigate the interface between two immiscible electrolyte solutions.[71,73]

All three methods yield identical results in the determination of the Volta potentials of electrolyte solutions.[74-76]

3. The Adsorption Potential

The term adsorption potential is given to the interphase difference between Galvani potentials due to the adsorption of ions or dipoles at the interface.

The problem of the appearance of the adsorption potential, despite its apparent simplicity, has been the subject of a prolonged controversy.[2,4,25,80-86] If two immiscible liquids, α and β, are in equilibrium, the interphase potential difference arises in a transition adsorption layer between them. Formally, it is possible to calculate the electrolyte distribution potential knowning only the solvation energies of the ions in each phase without paying attention to the properties of the interfacial adsorption layer. However, at equilibrium, the properties of the ions in the adsorption layer are unambiguously related to the properties of the ions in the bulk of each of the

phases in contact. The distribution potentials can therefore be calculated in two ways—from the bulk-phase properties of the solvents α and β and from the properties of the adsorption layer.[4]

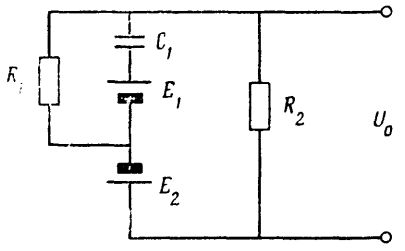


Figure 10. Equivalent electric circuit of the vibrating electrode: R_1—leakage resistance between the electrodes; C_1—capacitance of the vibrating electrode; E_1—potential difference between the vibrating electrode and the surface investigated; E_2—e.m.f. of the source of compensating potential; R_2—resistance in the compensation circuit.

At the beginning of this century, Beutner[87,88] showed that the formal thermodynamic theory of the distribution of ions is sufficient for the determination of the potential difference between two immiscible electrolyte solutions and that no additional hypotheses need be introduced into it.[87,88] However, these views have been criticised.[89,90] Some workers[89,91,92] regarded the adsorption potential as being superimposed on the partition potential jump, while others[2,4,93] assumed that the adsorption potential jump is part of the partition potential.

The partition potential is a purely thermodynamic concept. The calculation of the adsorption potential is outside the framework of thermodynamics. Definite structural ideas are used in it. Nevertheless, both approaches lead to identical results if the hypothesis concerning the structure of the adsorption layer corresponds accurately enough to the real picture. To some extent the adsorption approach appears to be more general: if ionic equilibrium at the interface has been disturbed as a result of the blocking of the interface by a surfactant or if the non-aqueous solvent is non-polar (octane, decane, and heptane), then the theory of distribution potentials cannot be applied to such systems, while adsorption analysis makes it possible to describe them with fair accuracy.[4,68,72,82]

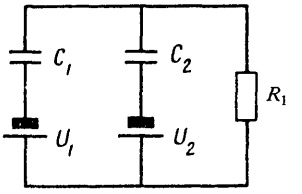


Figure 11. Equivalent electrical circuit of the rotating electrode: R_1—load resistance; C_i—capacitance between the half-cells and the rotating electrode; U_i—compensating potential.

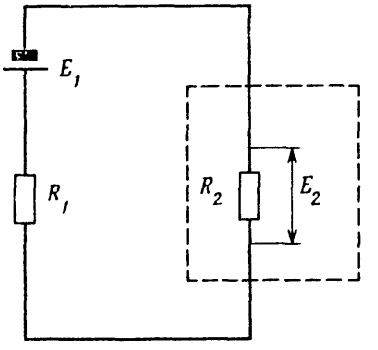


Figure 12. Equivalent circuit for the measurement of the potential jump by the radioactive probe method: E_1—measured potential difference; R_1—input resistance of the electrometer; R_2—resistance of the air gap; E_2—potential jump at the input to the electrometer.

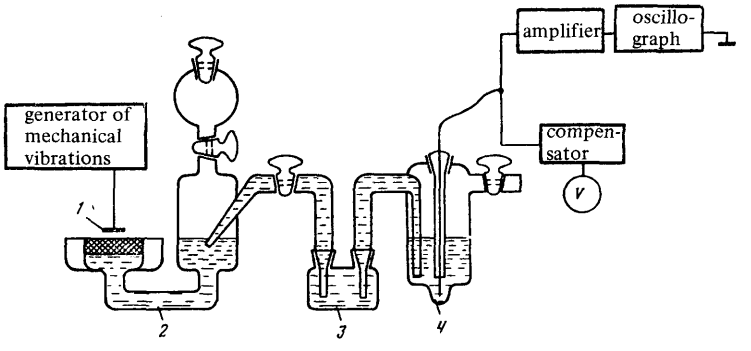


Figure 9. Block diagram of the apparatus for the measurement of the Volta potentials between two immiscible liquids: *1*) vibrating gold electrode; *2*) aqueous electrolyte solution; *3*) salt bridge for the elimination of the diffusion potential; *4*) reference electrode.[61]

V. TEST OF THE THERMODYNAMIC THEORY OF INTERPHASE POTENTIALS

The following cell has been proposed for the measurement of interfacial potentials:[25]

$$\begin{array}{l|l|l|l|l|l|l|l|l} \mathrm{Hg, Hg_2Cl_2} & \mathrm{H_2O,} & \mathrm{H_2O,} & \text{diisopropyl} & \text{diisopropyl} & \mathrm{H_2O,} & \mathrm{Hg_2Cl_2, Hg;} & \text{(IV)} \\ & \mathrm{KCl} & \mathrm{M^+X^-} & \text{ketone or} & \text{ketone,} & \mathrm{Et_4N^+,} & & \\ & & & \text{nitrobenzene,} & \mathrm{(Et)_4NPi} & \mathrm{Pi^-} & & \\ & & & \mathrm{M^+X^-} & & & & \end{array}$$

$$\Delta^{H_2O}_{RE_1}\varphi = \text{const}\ \Delta^{H_2O}_{H_2O}\varphi \simeq 0\ \Delta^{org}_{H_2O}\varphi_{M^+X^-}\ \Delta^{org}_{org}\varphi = \text{const}\ \Delta^{H_2O}_{org}\varphi_{Et_4NPi} = \text{const}\ \Delta^{RE_2}_{H_2O}\varphi = \text{const}$$

where M^+X^- is the salt investigated, distributed between the two solvents, the distribution corresponding to equilibrium, and RE is the reference electrode. If it is supposed that the diffusion potentials $\Delta^{H_2O}_{H_2O}\varphi$ and $\Delta^{org}_{org}\varphi$ are zero while the distribution potential $\Delta^{H_2O}_{org}\varphi_{Et_4NPi}$ = const., then, by replacing the M^+ or X^- ions by others, it is possible to determine the change in the distribution potential $\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX}$ on passing from one salt (M_1X) to the other (M_2X):

$$\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX} = \frac{RT}{F}\ln\frac{P^{org/H_2O}_{M_1X}}{P^{org/H_2O}_{M_2X}} = \frac{RT}{2F}\ln\frac{P^{org/H_2O}_{M_1}}{P^{org/H_2O}_{M_2}} \quad (70)$$

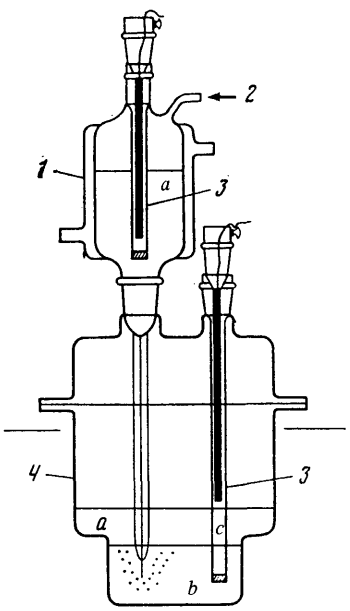


Figure 13. Diagram of apparatus for the measurement of the potential difference at the interface between two immiscible electrolyte solutions by the flow method: *a*) aqueous solution; *b*) oil; *c*) aqueous salt bridge; *1*) water reservoir; *2*) inlet for an inert gas; *3*) reference electrode; *4*) vessel for the streaming electrode.

Eqn.(70) has been tested experimentally for the water–isopropyl ketone,[25] water–acetonitrile, water–quinoline,[86] and water–nitrobenzene[68,81,85] systems.

It has also been suggested that $\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX}$ be measured in the cell[81]

$$\begin{array}{l|l|l|l|l|l|l|l} \text{Au, vibrating electrode} & \text{gas} & \text{nitrobenzene,} & \text{water,} & \text{water,} & \mathrm{Hg_2Cl_2, Hg;} & \text{(V)} \\ & & \mathrm{M^+X^-} & \mathrm{M^+X^-} & \text{sat.KCl} & & \end{array}$$

$$\Delta^{gas}_{Au}\varphi = \text{const}\ \ \Delta^{org}_{gas}\chi = \text{const}\ \ \Delta^{H_2O}_{org}\varphi\ \ \Delta^{H_2O}_{H_2O}\varphi_{dif} = 0\ \ \Delta^{RE}_{H_2O}\varphi = \text{const.}$$

The potential measured in cell (V) is the sum of the potential jumps at all the interfaces. When M_1X is replaced by M_2X in cell (V), it is possible to obtain $\Delta^{M_1}_{M_2}\Delta^{org}_{H_2O}\varphi_{MX}$ as the difference between the potentials of cell (V) in the presence of M_1X and M_2X. The methods of measurement and calculation have been described in detail elsewhere.[81]

Table 2. The distribution potential differences for two binary electrolytes M_1/M_2 with a common ion X in the water–nitrobenzene system at 298 K.

M_1/M_2	X	$\Delta^{M_1}_{M_2}\Delta^{NB}_{H_2O}\varphi$, mV			
		from Ref.81	from Ref.25	from Ref.68	calc. by Eqn.(70)
Na^+/K^+	Cl^-, Br^-, I^-	−52	−53	—	−50
Li^+/K^+	Br^-, I^-	−78	—	—	−73
Cl^-/I^-	K^+, Na^+, Et_4N^+, But_4N^+	+98	+102	+100. +92	+95
Br^+/I^-	Li^+, Na^+, K^+, But_4N^+	+79	—	+70. +75	+77
Cl^-/NO_3^-	K^+	+70	—	—	—
Cs^+/K^+	Cl^-	+40	—	—	—
K^+/NH_4^+	I^-	+30	—	—	—
Et_4N^+/K^+	I^-, Cl^-	+128	+126	+120	+124
Me_4N^+/K^+	—	—	—	+65	—

The results of the test of the thermodynamic theory of distribution potentials are presented in Table 2, where it is evident that the experimental changes in the distribution potential of the salt following the replacement of one of the ions agree satisfactorily with the result of the calculation from the partition coefficient of the salt by Eqn.(70).

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The interest in the processes occuring at the interface between two immiscible liquids is associated with the fact that we live in essence in a multiphase world. Almost all energy-transforming processes in living systems (respiration, photosynthesis) take place at the interface between two liquid phases.

It may be hoped that the role of the boundary potentials and of the spatial charge separation on the surfaces of biomembranes and their models in bioenergetic mechanisms of respiration, artificial and natural photosynthesis, and the coupling of biochemical reactions will be elucidated in the next few years.

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