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Structure of the Electrical Double Layer in Non-aqueous Solvents

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Systematic quantitative studies of the structure of the electrical double layer in non-aqueous solvents published during the past 10 years are reviewed. Methods for studying quantitatively the adsorption of ions at the electrode-solution (non-aqueous) interface are described, and the main experimental results on the specific adsorption of ions from non-aqueous media are summarised and compared with theoretical adsorption isotherms. The factors which determine the energy of adsorption and its dependence on the nature of the solvent, on the charge on the electrode, and on the number of pre-adsorbed particles are discussed. Existing models of the ionic double layer are tested for their ability to describe the specific adsorption of ions from non-aqueous solutions. Theoretical models of the fixed part of the electrical double layer are considered (in the absence of specific adsorption of ions), and used to interpret differential capacity curves in various solvents. 105 references.

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I. INTRODUCTION

Important new developments, associated with the use of non-aqueous solvents, have occurred in the last few years in both experimental and theoretical electrochemistry. In applied electrochemistry the practical aim of this work is to develop new cells in which the electrolyte consists of a non-aqueous solution. The electro-synthesis of organic compounds can also be carried out conveniently in non-aqueous solvents, since both organic and inorganic compounds are readily soluble in many non-aqueous solvents. Non-aqueous solutions are used in new electrochemical information-processing devices. The technical application of various solvents invariably leads to corrosion problems, and special studies of the corrosion of metals in contact with non-aqueous solvents have been reported. This work in applied electrochemistry underlines the importance of theoretical advances in our understanding of the kinetics and mechanisms of electrochemical reactions in non-aqueous media. Studies of the structure and properties of the electrical double layer and of adsorption phenomena at the electrode-non-aqueous solvent interface are an essential part of this type of work.

The first studies of the structure of the electrical double layer in non-aqueous solutions, based on measurements of electrocapillarity, were reported by Gouy[1] and by Frumkin[2,3]. Gouy measured the surface tension maxima of mercury in a series of non-aqueous solvents, and Frumkin plotted the full electrocapillary curves of the mercury electrode in methanol and ethanol, in pyridine, and in acetone. From these results Frumkin calculated the average double layer capacity for a negatively charged electrode, and he concluded that the effective dielectric constant within the electrical double layer bears little relation to the dielectric constant in the bulk of the solution[2,3]. Renewed interest in non-aqueous solvents in the early 1950's resulted in a series of publications on the electrochemistry of non-aqueous solutions and in particular on the structure of the electrical double layer. However most of this work is qualitative or, at best, semi-quantitative.

The first stage in the collection of qualitative data on the structure of the electrical double layer at the electrode-non-aqueous solvent interface was essentially completed in 1970. The results were fully reviewed by Payne[4,5]. The main conclusions can be summarised as follows.

1. There is a qualitative analogy between the mercury-water and the mercury-non-aqueous solvent interface. This analogy is most evident in the relative position of the electrocapillary and the differential capacitance curves for solutions of a series of surface-active anions[2-5].

2. The Gouy-Chapman-Grahame theory[6] of the diffuse part of the double layer is also applicable to non-aqueous solutions of surface-inactive electrolytes. In dilute solutions of these electrolytes a minimum appears in the differential capacitance curve near the zero charge potential, and the capacitance at the minimum varies with electrolyte concentration as predicted by the theory of the diffuse part of the electrical double layer[6]. This was first demonstrated by Grahame for NaF solutions in methanol[7], and later confirmed for other solvents[4,5,8,9].

3. General thermodynamic relationships (including those derived from the basic electrocapillarity equation) are applicable to the structure of the electrode-non-aqueous solvent interface. In particular, comparison of experimental electrocapillary curves with those calculated by double integration of the differential capacitance curves confirms the validity of the expression

$$C = -\partial^2\sigma/\partial E^2, \qquad (1)$$

where C is the double-layer capacitance, σ is the interfacial tension, and E is the potential[8-11].

4. The double-layer capacitance can be correlated with the thickness of the electrical double layer, determined by the size and shape of the solvent molecules[4,5,12], but it cannot be correlated with the bulk dielectric constant of the solvent.

Since Payne's review deals mainly with the boundary between a mercury electrode and the solution we shall discuss the above conclusions by considering the bismuth electrode, on which extensive experimental data have been

obtained in recent years by Pal'm and his colleagues of the Tartu State University (reviewed in Refs. 13 and 14).

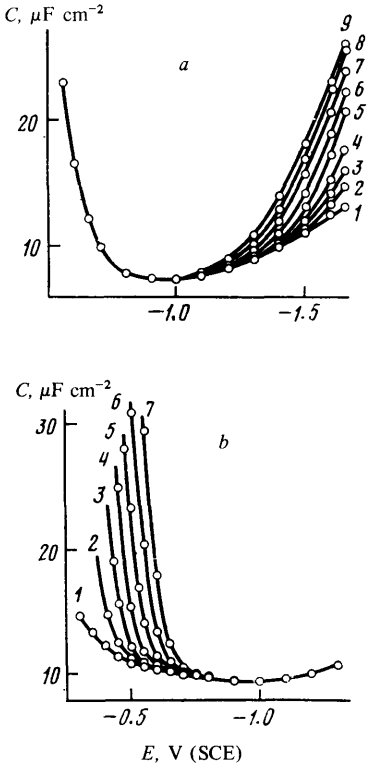


Figure 1. Differential capacitance curves for the Bi/C_2H_5OH interface in the following systems: (*a*) mc KSCN + $(1-m)c$ LiSCN for $c = 0.1M$ and the following values of m[*1*) 0, *2*) 0.005, *3*) 0.01, *4*) 0.02, *5*) 0.05, *6*) 0.1, *7*) 0.2, *8*) 0.5, *9*) 1.0]; (*b*) mc KCN + $(1-m)c$ KF for $c = 0.1M$ and the following values of m[*1*) 0, *2*) 0.003, *3*) 0.01, *4*) 0.03, *5*) 0.1, *6*) 0.3, *7*) 1.0] (from Ref. 14).

Fig. 1 shows the differential capacitance curves for the Bi/ethanol interface in mixtures of two salts at constant ionic strength[14]. The first of the two systems illustrates the replacement of the surface-inactive Li^+ cation by the surface-active K^+ cation, and the second illustrates the analogous replacement of the F^- by the CN^- anion. It can be seen from Fig. 1 that the capacity increases with the concentration of the surface-active component. A similar behaviour had been observed previously at a mercury electrode in aqueous solutions, for which the transition from an inactive to an active ion is accompanied by an increase in double-layer capacitance[15]. By using the reverse integration method[16] together with Eqn. (1) we can obtain two series of electrocapillary curves for the above systems to the precision of a single integration constant; in these curves an increase in the relative amount of surface-active ion is accompanied by a decrease in σ and a shift in the position of the electrocapillary maximum.

Fig. 2 shows the differential capacity curves of a bismuth electrode in ethanol solutions of the surface-inactive electrolyte $LiClO_4$.[17] In dilute solutions a characteristic minimum appears near the zero-charge potential (Fig. 2*a*). A plot of the reciprocal of the measured capacitance against the reciprocal of the calculated capacitance of the diffuse part of the double layer gives a straight line of unit slope, as expected from the theory of the electrical double layer (Fig. 2*b*).

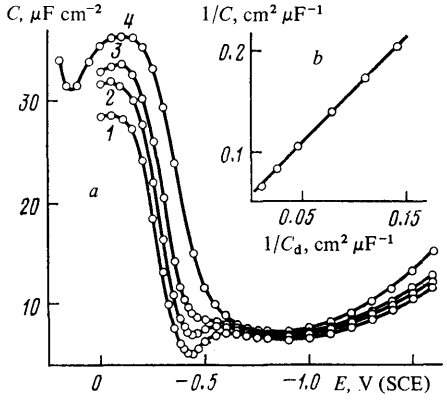


Figure 2. Differential capacitance of a bismuth electrode in standard solutions of $LiClO_4$: (*a*) capacitance against potential for various concentrations of $LiClO_4$ [*1*) 0.003, *2*) 0.01, *3*) 0.03, *4*) 0.5 *M*]; (*b*) reciprocal capacitance against reciprocal diffuse layer capacitance at zero surface charge (from Ref. 14).

The second stage in the study of the electrical double layer in non-aqueous solvents, with which the present review is mainly concerned, is characterised by quantitative studies of the adsorption of ions at the interface between the metal and the non-aqueous solvent. Quantitative data on the structure of the electrical double layer are needed to study the relationship between these results and the model structure of the double layer, to choose an isotherm which adequately describes the adsorption of ions, and to interpret the role of the non-aqueous solvent in determining the structure of the electrical double layer.

II. METHODS OF QUANTITATIVE STUDY OF THE ELECTRODE–NON-AQUEOUS SOLVENT INTERFACE

All the basic data on the structure of the electrical double layer at the boundary between *s,p* metals and aqueous solutions have been obtained by measurements of surface tension and differential capacity. However, the measurement of electrocapillary curves in non-aqueous solutions presents a number of difficulties. In experiments with the Gouy capillary electrometer[18,19] the non-aqueous solution often fails to wet the area between the mercury and the wall of the capillary (unlike aqueous solutions, which have a good wetting action). Thus the condition of full-wetting (which is essential in the capillary electrometer

method) is infringed, leading to unsatisfactory experimental results. In another method of measuring surface tension, based on squeezing a mercury drop from a U-shaped capillary[20], measurements in non-aqueous solutions are complicated by the need to achieve full wetting of the capillary tip whilst avoiding seepage of the solution into the capillary. In the case of aqueous solutions the combined requirements are met by making the capillary hydrophobic over its entire length before cutting off the capillary tip (which thus remains hydrophilic). In non-aqueous solvents this method is not applicable because the wetting powers of organic solvents towards hydrophobic and towards clean glass surfaces are almost identical. Thus, in spite of the large number of published studies of the double layer at the mercury/non-aqueous solution interface based on measurements of electrocapillary curves[8-11,21-27], the number of systems to which the method can legitimately be applied is limited by the above considerations. We should also note that the electrocapillary curve method cannot be used with solid electrodes. Therefore the most important method of studying the electrode/non-aqueous solution interface experimentally is the measurement of the differential capacitance of the electrical double layer.

Differential capacitance data can be used in two ways, which have been termed the binary electrolyte method[28-30] and the mixed electrolyte method[15,31]. In the case of a binary 1,1 electrolyte the surface excess of anions (Γ_-) for a given electrode charge q is calculated by the equation

$$\Gamma_- = (\Gamma_-)_{q=q^*} + (q-q^*)\left(\frac{\partial\Gamma_-}{\partial q}\right)_{q=q^*} - \frac{1}{2RT}\int_{q^*}^{q}\int_{q^*}^{q}\left[\frac{\partial\,(1/C)}{\partial \ln a_\pm}\right]_q dq^2, \qquad (2)$$

where q^* is the negative charge on the electrode (large enough to suppress the specific adsorption of anions), and $a_\pm$ is the mean activity of the electrolyte. The quantities $(\Gamma_-)_{q=q^*}$ and $(\partial\Gamma_-/\partial q)_{q=q^*}$ in Eqn. (2) are calculated by the formulae of the theory of the diffuse layer[29,30]. In order to use Eqn. (2) we must first of all determine the charge on the electrode by numerical integration of the C,E curves and plot $1/C$ against $\ln a_\pm$ for different (constant) values of q. The differentials $[\partial(1/C)/\partial \ln a_\pm]_q$ are then found by numerical or graphical differentiation of these curves.

The binary electrolyte method can be used if the following conditions are met. Firstly there must be a region of charge such that the charge of specifically adsorbed ions is $q_1^- = 0$. Secondly we must assume that the specific adsorption of counter-ions is negligible, and therefore that the charge q_1^+ of these ions in the fixed part of the double layer is zero. The condition $q_1^+ = 0$ must be met in the presence as well as in the absence of specific adsorption of anions. This is equivalent to assuming that the specifically adsorbed anions do not "drag" cations from the base electrolyte into the fixed part of the electrical double layer.

The second method relies on the use of a mixed electrolyte of constant ionic strength. To study the adsorption of the surface-active anion A* we use the system

$$mc\,\mathrm{KA^*} + (1-m)\cdot c\,\mathrm{KA}, \qquad (3)$$

where c is the total concentration of the solution, and m is the mole fraction of the surface-active anion A^* in the mixture with the inactive anion A. To study the adsorption of the surface-active cation K^* we use the system

$$mc\,\mathrm{K^*A} + (1-m)\cdot c\,\mathrm{KA}, \qquad (4)$$

where K is the surface-inactive cation. The characteristic C,E curves for systems (3) and (4) are shown in Fig. 1.

When the mixed electrolyte method is used to treat the experimental results there are two possible approaches. The first approach, used almost exclusively in the work reported so far, consists in the following. The q,E curves are first calculated by the reverse integration method, and then the change in the reciprocal of the differential capacitance $\Delta(1/C) = 1/C_0 - 1/C$ as between the inactive and the active electrolyte is calculated for a given charge on the electrode. The following equation is used:

$$q_1 = (zF/RT)\frac{\partial}{\partial \ln m}\int_{q^*}^{q}\int_{q^*}^{q}\Delta\left(\frac{1}{C}\right)\mathrm{d}\,q^2, \qquad (5)$$

where F is the Faraday and z is the charge on the ion. The second method of treating the experimental data in the mixed electrolyte method is proposed in Ref. 32, but it does not appear to have been used to date. It consists in plotting the reciprocal of the capacitance against the logarithm of the mole fraction in the mixture for q = const: these plots are then differentiated, and the differential is integrated twice with respect to charge:

$$q_1 = -(zF/RT)\int_{q^*}^{q}\int_{q^*}^{q}[\partial\,(1/C)/\partial \ln m]_q\,\mathrm{d}\,q^2. \qquad (6)$$

In principle Eqns. (5) and (6) should give the same value for the charge of specifically adsorbed ions (q_1).

The following assumptions are implicit in the mixed electrolyte method: 1) the surface-inactive reference ion can exist over the whole of the range of charges[31,33,34]; 2) the degrees of dissociation of the inactive and the active electrolyte are equal (note that substantial errors can arise if this assumption is not valid[35]); 3) the activity coefficients of the two electrolytes in the mixture are approximately equal[15,31] (the errors associated with the infringement of this condition, and ways of applying suitable corrections, are discussed in Refs. 36 and 37).

In order to describe the adsorption of ions we must not only determine the surface activity of various types of particle but also evaluate the adsorption characteristics of the double layer such as the ion–electrode interaction (the free energy of adsorption ΔG_A) and the ion–ion interaction in the adsorption layer (the repulsion interaction coefficient B). Hence the measured charge of specifically adsorbed ions is usually compared with the values calculated by using the adsorption isotherms. A detailed examination of experimental data and a theoretical discussion of the various types of isotherm[38-42] suggest that the most appropriate equation for the binary electrolyte is

$$\ln(q_1/zc) + zF\psi_0/RT = \ln\beta - 2Bq_1/z \qquad (7)$$

whereas the analogous isotherm

$$\ln(q_1/zmc) + zF\psi_0/RT = \ln\beta - 2Bq_1/z \qquad (8)$$

is the best for the mixed electrolyte. In these expressions the quantity $\ln\beta$, which is usually a linear function of the charge, i.e.

$$\ln\beta = a + bq, \qquad (9)$$

characterises the free energy of adsorption. The quantity ψ_0 is the potential of the outer Helmholtz plane, which can be calculated by the theory of the diffuse double layer. Thus for a 1,1 electrolyte we have

$$\psi_0 = (2RT/F)\,\mathrm{arcsinh}\left(\frac{q+q_1}{2Ac^{1/2}}\right), \qquad (10)$$

where $A = (\epsilon RT/2\pi)^{\frac{1}{2}}$ and ϵ is the dielectric constant of the solvent. The quantity B in Eqns. (7) and (8) is a measure of the repulsion interaction between the specifically adsorbed ions.

Eqns. (7) and (8) are a variant of the virial isotherm equation with the concentration of the ion in the bulk of the solution replaced by the concentration of the same ion in the outer Helmholtz plane. Thus the isotherm takes account of the so-called buffer action of the diffuse part of the electrical double layer, consisting in a contribution to the energy of an ion passing from the solution to the surface (since such an ion has to pass through the potential jump in the diffuse layer).

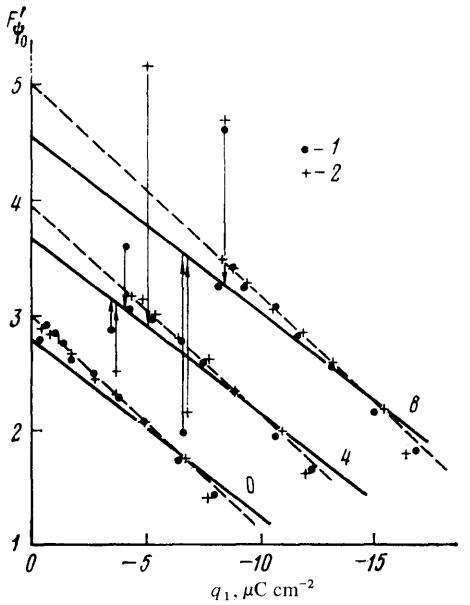


Figure 3. Plots of the quantity $F'_{\psi_0} = [\lg(q_1/zc) + zF\psi_0/2.3RT]$ against charge of specifically adsorbed anions for different electrode charges (stated against each curve in μC cm^{-2}). Full lines are theoretical plots obtained from Eqn. (7) with $a = 6.4$, $b = 0.51$, $B = 0.175$; the points and the broken curves are calculations by Eqn. (2) assuming the following uncertainties in the capacitance values: *1*) 0.1, *2*) 0.01 μF cm^{-2} (from Ref. 43).

The precision of the various methods has been assessed[32,43] by using Eqns. (7) and (8) under conditions of a charge of specifically adsorbed ions in excess of the charge on the electrode (in absolute value). As had already been pointed out[44,45], under the opposite conditions (i.e. $|q_1| < |q|$) the binary electrolyte method cannot be used to determine the specific adsorption of ions, and only the mixed electrolyte method offers reliable results. Hence it was interesting to compare the two methods under the condition $|q_1| > |q|$. This was done by assigning arbitrary values to the parameters a, b, and B, and using Eqns. (7) and (8) to calculate (on a computer) the variation of q_1, with q for various concentrations of the active component in the binary[43] or the mixed[32] electrolyte. The equation[43]

$$1/C = 1/C_{02} + (RT/FM)\left[2 - \frac{(2 - zbM)^2}{2 + M(z/q_1 + 2B)}\right] \qquad (11)$$

(where $M = [4A^2c + (q + q_1)^2]^{\frac{1}{2}}$ and C_{02} is the differential capacitance of the fixed layer at $q_1 = 0$) was then used to calculate the differential capacitance curves. The C values were rounded off to within 0.1 or 0.01 μF cm^{-2}, and the capacitance curves were then interpreted by the method described above[32,43]. This enabled the theoretical values of the parameters to be compared objectively with those obtained from the differential capacitance curves.

Table 1. Comparison of standard and calculated values of the parameters a, b, and B.

Parameter	Binary electrolyte method		Mixed electrolyte method	
	given	found	given	found
a	6.400	6.79	8.1500	8.24
b, cm^2 μC^{-1}	0.510	0.59	0.5900	0.61
B, cm^2 μC^{-1}	0.175	0.22	0.2125	0.23

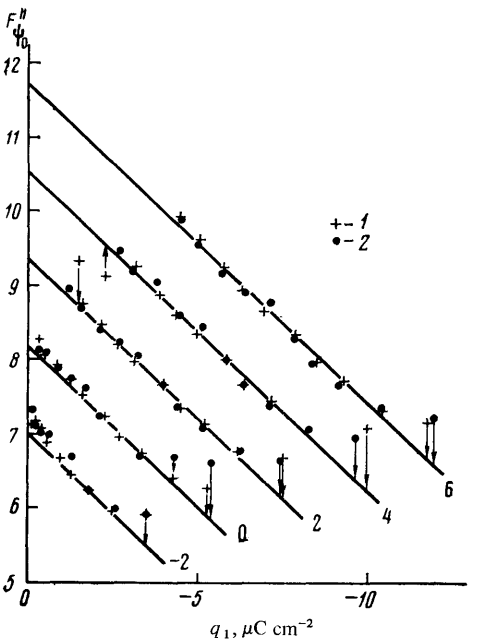


Figure 4. Plots of $F''_{\psi_0} = [\ln(q_1/zmc) + zF_{\psi_0}/RT]$ against charge of specifically adsorbed anions for different electrode charges (stated against each curve in μC cm^{-2}). Full lines are theoretical plots obtained from Eqn. (8) with $a = 8.15$, $b = 0.59$, $B = 0.2125$, and $c = 0.1$; the points were calculated by the mixed electrolyte method [*1*) by Eqn. (5), *2*) by Eqn. (6)] (from Ref. 32).

Fig. 3 shows plots of F'_{ψ_0} against q_1, where F'_{ψ_0} is the left-hand side of Eqn. (7), based on results obtained for a binary electrolyte[43]. The full lines are the initial plots,

corresponding to given values of the parameters a, b, and B, and the points were obtained from the C,E curves by the binary electrolyte method. Points *1* and *2* denote two different levels of precision in rounding off the differential capacitance values. We note a strong deviation of the "experimental" points from the ideal straight line, irrespective of the rounding off precision. Even the points which lie near the straight lines can be seen to fall on different straight lines, with a different slope and a different intercept. In other words, the binary electrolyte method can lead to serious errors in the determination of the parameters a, b, and B. We have shown[43] that the error of the binary electrolyte method can be minimised by increasing 1.5–2-fold the number of concentrations for which the differential capacitance curves are determined. Analogous data for a mixed electrolyte[32] are shown in Fig. 4. Though some of the points lie well away from the straight lines, most of the points lie exactly on the lines, and the experimental values of the parameters a, b, and B agree very well with the values assumed in the theoretical plots.

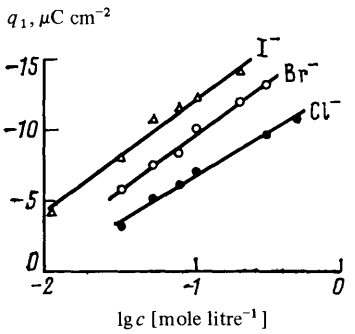


Figure 5. Specific adsorption isotherms of the Cl^-, Br^-, and I^- anions on a mercury electrode at a charge of +2 μC cm^{-2} from binary solutions in DMSO (from Ref. 30).

Our estimates of the precision of the binary electrolyte and the mixed electrolyte method are summarised in Table 1. We note that when $|q_1| > |q|$ the specific adsorption of ions is more accurately described by the mixed electrolyte method. Thus its use is recommended if the necessary conditions are met. In this respect the bismuth electrode has an important advantage, since it is easier to select a surface-inactive reference ion for the bismuth electrode than for the mercury electrode. This is due partly to the semiconductor properties of bismuth (which tend to lower the affinity of bismuth towards all anions) and partly to the fact that oxygen-containing solvent molecules are more strongly adsorbed on bismuth[13,14]. In the case of the mercury electrode there are systems for which no surface-inactive reference ion can be chosen[46]. Thus the results obtained on a bismuth electrode are currently the most appropriate for quantitative comparison of the specific adsorption of ions from non-aqueous solvents.

III. SPECIFIC ADSORPTION OF IONS AT THE METAL–NON-AQUEOUS SOLVENT INTERFACE

Let us examine first of all some experimental results. Fig. 5 shows the specific adsorption isotherms of the anions Cl^-, Br^-, and I^- at the interface between mercury and dimethylsulphoxide (DMSO) for $q = +2$ μC cm^{-2}. The isotherms have the characteristic semilogarithmic form, the surface activity of the anions increasing in the sequence $Cl^- < Br^- < I^-$ (i.e. as in aqueous solutions). Fig. 6 shows the specific adsorption isotherms of the Br^- anion for a range of solvents and an uncharged mercury surface.

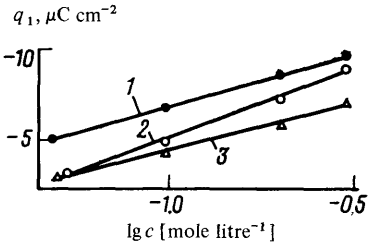


Figure 6. Specific adsorption isotherms of the Br^- anion on an uncharged mercury surface from binary solutions in different solvents: *1*) DMSO,[103] *2*) water[104], *3*) DMFA.[47]

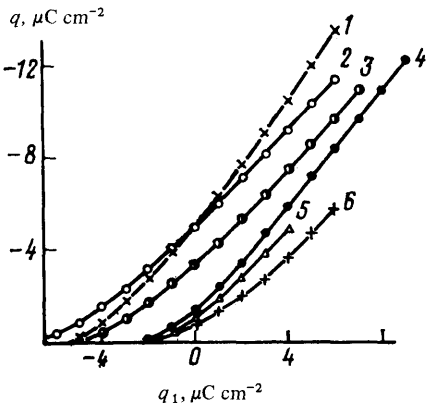


Figure 7. Charge of specifically adsorbed Br^- anions against charge of the Bi electrode (at $m = 0.1$) for the following solvents: *1*) AN, *2*) DMFA, *3*) DMSO, *4*) ethanol, *5*) methanol, *6*) water (from Ref. 14).

We note that the surface activity of Br^- increases from dimethylformamide (DMFA) to water and to DMSO, but the differences are not very large. Fig. 7 shows plots of q_1 against q for the adsorption of Br^- anions on Bi from six different solvents. We can see that for sufficiently high values of $q > 0$ the adsorbability of Br^- anions increases in the sequence water < methanol < ethanol < DMSO < DMFA < acetonitrile (AN).

In Figs. 8 and 9 we show some measurements of the specific adsorption of Cs^+ cations from various solvents on a negatively charged surface of bismuth or mercury. We note that the surface activity of the Cs^+ cations is greater at the mercury than at the bismuth interface for all solvents, i.e. that the nature of the metal has a marked effect. On the other hand the specific adsorption of Cs^+ on both metals (bearing a sufficiently negative surface charge) increases on going from water to DMFA, methanol, and ethanol. These results should be interpreted in conjunction with the changes in double-layer capacitance of sodium and caesium salts in various solvents. By comparing Figs. 9 and 10 we see that the increase in capacitance can be correlated qualitatively with the specific adsorption of caesium cations at the appropriate interface.

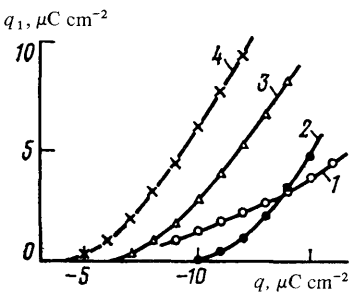


Figure 8. Charge of specifically adsorbed Cs^+ cations against charge of the Bi electrode (at $m = 0.1$) for the following solvents: *1*) water, *2*) DMFA, *3*) methanol, *4*) ethanol (from Ref. 14).

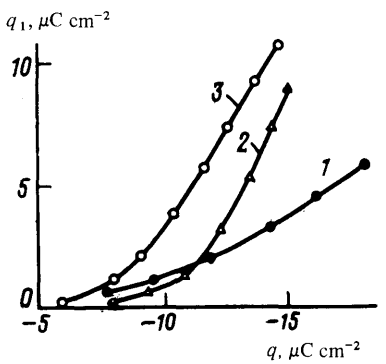


Figure 9. Charge of specifically adsorbed Cs^+ cations against charge of the Hg electrode (at $m = 1$) for the following solvents: *1*) water,[57] *2*) DMFA,[105] *3*) methanol[60].

It is interesting to consider the factors which determine the adsorption energy of the ions and the way in which this energy varies with the nature of the metal, that of the solvent, the charge on the electrode, and lastly the amount of adsorption already present on the electrode. A general solution of this problem must take account of the following interactions: metal and ion, metal and solvent, ion and solvent, adsorbed ions with themselves, and solvent molecules with themselves. We must also allow for the influence of the field due to the electrical double layer on all these interactions. Thus we can expect any general solution to be rather cumbersome.

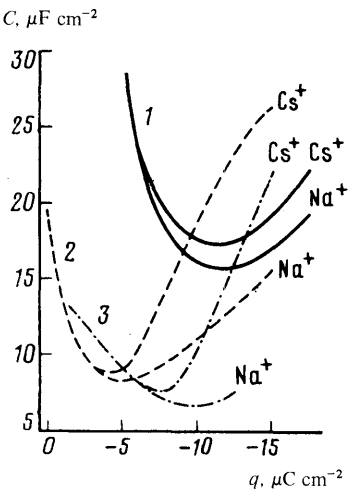


Figure 10. Cathodic portions of the plots of differential capacitance against electrode charge in 0.1 N solutions of sodium and caesium salts at the following interfaces: *1*) Hg/H_2O (chlorides)[57], *2*) Hg/CH_3OH (chlorides)[60], *3*) Hg/DMFA (perchlorates)[44].

Let us examine in detail the factors which influence the adsorbability of ions in different solvents. Since the specific adsorption of anions causes solvent molecules to be displaced from the surface, we can treat the adsorption process as a reaction in which solvent molecules are replaced by ions:

$$n\,S_{ads} + A_{bulk} \rightarrow A_{ads} + n\,S_{bulk}, \qquad (12)$$

where S denotes a solvent molecule, A is a specifically adsorbed ion (anion in this case), and n is the average number of solvent molecules displaced from the surface by one ion ($n \neq 1$). Evidently, the energy of adsorption of the ion from a given solvent ($\Delta G_{ads}^{(S)}$) will be greater, the stronger the interaction between the metal and the ion (ΔG_{M-A}), and it will be smaller, the stronger the interaction between the metal and the solvent (ΔG_{M-S}) as a result of the displacement of solvent molecules from the surface. It will also be smaller, the stronger the interaction between the ion and the solvent (ΔG_{A-S}), because the bonds between the ion and the solvent molecules are partially broken, and it will be greater, the stronger the interaction between the solvent molecules themselves (ΔG_{S-S}), because of the interaction between the displaced solvent molecules when they are transferred to the bulk of the solution. Thus the energy of adsorption of the ion A from the solvent S_1 can be written, according to Eqn. (12),

$$\Delta G_{ads}^{(S_1)} = \Delta G_{M-A} - n_1 \Delta G_{M-S_1} - \Delta G_{A-S_1} + n_1 \Delta G_{S_1-S_1}. \qquad (13a)$$

An analogous expression can be written for the solvent S_2 on the assumption that the quantity ΔG_{M-A} is independent of the solvent:

$$\Delta G_{ads}^{(S_2)} = \Delta G_{M-A} - n_2 \Delta G_{M-S_2} - \Delta G_{A-S_2} + n_2 \Delta G_{S_2-S_2}. \quad (13b)$$

We shall characterise the quantity ΔG_{M-S} by the work of adhesion referred to the limiting adsorption of solvent ($\Gamma_\infty^{(S)}$).[4,5] Using the Dupre equation we have

$$\Delta G_{M-S} = (\sigma_M + \sigma_S - {}_M\sigma_S)/\Gamma_\infty^{(S)}, \quad (14)$$

where σ_M is the surface tension (reversible surface work of the metal M), σ_S is the surface tension of the solvent S, and ${}_M\sigma_S$ is the interfacial tension (reversible surface work) of the M/S interface. If we equate[4,5] the quantity ΔG_{S-S} to one-half of the work of cohesion, also referred to $\Gamma_\infty^{(S)}$, we have

$$\Delta G_{S-S} = \sigma_S/\Gamma_\infty^{(S)}. \quad (15)$$

Subtracting (13b) from (13a), and using (14) and (15), we obtain

$$\Delta(\Delta G_{ads})^{(S_1-S_2)} = (\Delta G_{A-S_2} - \Delta G_{A-S_1}) + n_2(\sigma_M - {}_M\sigma_{S_2})/\Gamma_\infty^{(S_2)} - n_1(\sigma_M - {}_M\sigma_{S_1})/\Gamma_\infty^{(S_1)}. \quad (16)$$

But since $\Gamma_\infty^{(S_1)}/n_1 = \Gamma_\infty^{(S_2)}/n_2 = \Gamma_\infty^{(A)}$, where $\Gamma_\infty^{(A)}$ is the limiting adsorption of the anion A, Eqn. (16) simplifies to

$$\Delta(\Delta G_{ads})^{(S_1-S_2)} = (\Delta G_{A-S_2} - \Delta G_{A-S_1}) + ({}_M\sigma_{S_1} - {}_M\sigma_{S_2})/\Gamma_\infty^{(A)}. \quad (17)$$

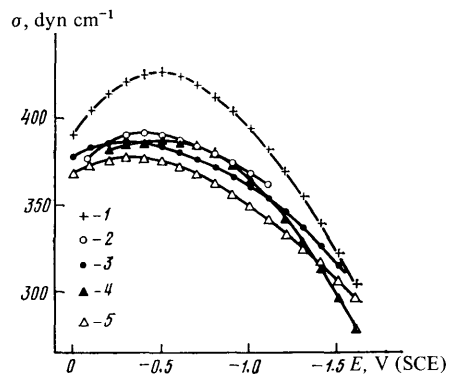


Figure 11. Electrocapillary curves of the mercury electrode for 0.1 *N* solutions of: *1*) Na_2SO_4 in water[18], *2*) NaCl in methanol[2], *3*) $NaClO_4$ in ethanol[2], *4*) KF in formamide[9], *5*) $NaClO_4$ in DMFA.[44]

Thus to the approximation of our present model the change in energy of adsorption of an ion on going from one solvent to another is determined by two factors: the difference in solvation energy and the different in surface tension of the metal in the two solvents, referred to the limiting loading of the surface by adsorbate. This conclusion had been arrived at earlier[47] for the transition from water to DMFA, but equality of the areas occupied by the ion and by the solvent molecule had been assumed (i.e. $n_1 = n_2 = 1$). The above argument does not rely on this assumption. Thus the use of Eqn. (17) to discuss the influence of the solvent on the adsorption energy of ions seems to be fully justified.

Let us consider first of all the effect of changes in interfacial tension. Fig. 11 shows the electrocapillary curves for a mercury electrode in solutions of various salts in water, methanol, ethanol, formamide, and DMFA. The σ, E curve for water (at low surface charges) lies significantly higher than the curves for the other solvents. Thus if we consider only the second factor we conclude that anions should be more readily adsorbed from aqueous than from non-aqueous solutions. However we see from Figs. 6 and 7 that this conclusion does not agree with experiment, and therefore the energy of solvation of the ions appears to play the predominant role.

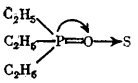
This result is not surprising if we remember that the change in energy of solvation of anions between water and various polar solvents is usually between 2 and 12 kcal mole^{-1}.[48] At the same time, putting $\Gamma_\infty^{(A)} \simeq 5 \times 10^{-10}$ mole cm^{-2} and noting from Fig. 11 that ${}_{Hg}\sigma_{H_2O} - {}_{Hg}\sigma_S \leq 40$ dyn cm^{-1}, we conclude that the ratio $({}_{Hg}\sigma_{H_2O} - {}_{Hg}\sigma_S)/\Gamma_\infty^{(A)}$ cannot be greater than 1.9 kcal mole^{-1}. On the other hand if we consider the adsorption of cations, which is most marked at high negative charges (when the surface tension is approximately the same in different solvents), we find that the second factor can be ignored to a first approximation. In this case the adsorption is determined only by the difference in solvation energy.

Let us examine the factors which determine the energy of solvation of ions and its change as between different solvents. The major part ($\geq 80\%$) of the energy of solvation accompanying the transfer of the ion from the gas phase into the solvent consists of the Born term, i.e. the energy gain due to purely electrostatic interactions between the charged particle and the medium (whose dielectric constant is substantially greater than unity[49]). However we are not concerned with the overall solvation energy, but with the difference in solvation energy as the ion is transferred from one solvent to another. The contribution of the Born term to this difference is quite small. Indeed, the well known Born formula for the solvation energy[50] gives the relative change in solvation energy on transferring the ion from a solvent of dielectric constant ϵ_1 to a solvent of dielectric constant ϵ_2 as $(1/\epsilon_2 - 1/\epsilon_1) \cdot 100\%$, i.e. less than 4% if the dielectric constants are greater than 25.

Thus the most important contribution to the change in solvation energy on transferring an ion from one polar solvent to another must come from factors other than the Born term. These could include, for example, hydrogen bond formation with anions in protonic solvents, whose effect should be most marked when the ion is transferred to an aprotic solvent (in which this factor is absent). Another relevant factor is the effect of the ion on the structure of the solvent, which may give rise to energy effects and thus contribute to the difference in solvation energy of the ion between two different solvents. Lastly we must allow for donor–acceptor interactions between the ion and the solvent molecule.

Up to recently it has been customary to characterise donor–acceptor interaction with allowance for hydrogen bond formation in terms of the donor number *DN*. According to Gutmann[48,51] the donor number is determined by the enthalpy of the reaction between a solvent molecule and $SbCl_5$ (i.e. of the reaction S + $SbCl_5$ = S.$SbCl_5$), in which the solvent S acts as a donor and $SbCl_5$ as an acceptor of electrons, thus: $DN \equiv -\Delta H_{S \rightarrow SbCl_5}$. However the experimental information most commonly available in studies of the specific adsorption of ions from non-aqueous solvents

concerns the adsorption of anions, which are themselves electron donors. Therefore the donor number is not a convenient way of comparing the adsorption of anions, and we prefer to use the acceptor number *AN*, recently proposed by Gutmann and coworkers[52,53]. The acceptor number can be determined by considering the interaction between solvent molecules and triethylphosphine oxide, which is an electron donor. As a result of donor–acceptor interactions of the type of



we observe a chemical shift of the ^{31}P signal in the NMR spectrum: it is suggested that the *AN* is proportional to $\delta^{31}P$. The acceptor number is normalised by the condition that the chemical shift $\delta^{31}P$ for the reaction $(C_2H_5)_3$. .PO + $SbCl_5$ corresponds to $AN = 0$ in hexane and $AN = 100$ in dichloroethane.

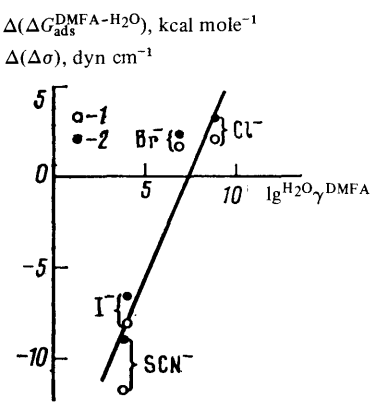


Figure 12. Change in surface activity of the anions Cl^-, Br^-, I^-, and SCN^- when transferred from water to DMFA against distribution coefficient of the ions between these two solvents. The surface activity of the anions on a mercury electrode is characterised by: *1*) the energy of adsorption at zero charge for $\Gamma_- \to 0$, *2*) the decrease in surface tension at the electrocapillarity maximum for $c = 0.1\ M$.

Gutmann has pointed out[52] that the acceptor number shows a good correlation with the energy of transfer of a chloride ion from acetonitrile to 12 different solvents. This observation confirms the validity of the acceptor number as an indicator of the change in solvation energy of a given ion on being transferred to different solvents. Of course, the donor–acceptor interaction is characterised by the properties of the ion as well as by those of the solvent (charge on the ion, and structure of the electronic shells[48,49]). Therefore the change in solvation energy of different ions being transferred from one solvent to another is not identical, and hence the corresponding change in the energy of adsorption of the ions is also not identical.

The change in solvation energy of ions of a given type being transferred from one solvent to another is conveniently characterised by the distribution coefficient of the ions between the two solvents. Fig. 12 shows a plot of the change in energy of adsorption of different ions on an uncharged mercury surface between water and DMFA against the logarithm of the distribution coefficient the ions between the same two solvents. These results suggest a good correlation between the change in solvation energy and the change in adsorption energy under the condition $M^{\sigma}S_1 - M^{\sigma}S_2 = \text{const}$. As Fig. 12 shows, the quantity $\Delta(\Delta G_{ads})(DMFA-H_2O)$ on the vertical axis can be replaced by the change in the lowering of surface tension $\Delta(\Delta\sigma)$ produced by the ion at the maximum of the electrocapillary curve. If the vertical scale is properly chosen the plot against $\lg {}^{S_1}\gamma^{S_2}$ is practically unchanged.

Unfortunately the distribution coefficients are not available for all the ions (and certainly not for all the solvents). Therefore we should look for a more general correlation between the energy of adsorption of the ion on the given electrode at $q = 0$ and the *AN* value of the solvent. If the potential of the outer Helmholtz plane (ψ_0) does not vary appreciably at $q = 0$ when the ion is transferred to a different solvent we can combine the term $zF\psi_0/RT$ in Eqns. (7) and (8) with the parameter $a_b = a + zF\psi_0/RT$, and use the latter parameter (a_b) to characterise the adsorption energy of the ion. Values of the parameter a_b for the adsorption of various ions on a bismuth electrode from various solvents are plotted in Fig. 13 against the acceptor number of the solvent. We note a good correlation between the change in adsorbability of the ion on bismuth and the acceptor number of the solvent, the difference in adsorbability between water and DMFA being greatest for the Cl^- anion and decreasing in the sequence

$$Cl^- > Br^- > I^- > SCN^-,$$

which reflects the effect of the nature of the ion. The small Cl^- anion is strongly solvated in aqueous solution as a result of hydrogen bond formation, whereas in aprotic solvents this ion is poorly solvated. As the size of the ion increases, so does its polarisability in dipolar aprotic solvents, thus compensating the solvation effects accompanying the transfer of the ion from water to DMFA. In the case of the large SCN^- anion the compensation is almost complete (see Fig. 13).

As expected, the adsorbability of anions increases as the acceptor number decreases. For the Cs^+ cations we note the opposite relationship (Fig. 13): the adsorption energy decreases on going from water to DMFA. Since a decrease in acceptor number should increase the solvation energy of cations, this result is not unexpected. However a comparison of the change in adsorbability of cations at zero charge with the results given above for high negative charges (Figs. 8–10) produces an apparent contradiction: the results for an uncharged surface are consistent with the change in acceptor number, whereas those for high negative surface charges are not. This discrepancy arises because the adsorption energy depends on the charge on the electrode as described in formula (9), where the parameter *b* is related to the structure of the electrical double layer.

Using the simple model of Grahame and Parsons[54,55] we obtain the following expression for the parameter *b* (see Ref. 38):

$$b = -zF/RTK_{12}, \qquad (18)$$

where K_{12} is the integral capacity of the space between the outer and the inner Helmholtz plane. Replacement of water by an organic solvent causes a relative displacement of the charged planes of the double layer, and K_{12} decreases whilst b increases. Therefore at high negative charges the adsorbability of cations in organic solvents can be greater than in H_2O, in spite of the smaller value of the a parameter. This effect is illustrated in Table 2 for the special case of the adsorption of Cs^+ cations at the Bi/H_2O and Bi/CH_3OH interfaces.

Table 2. Adsorption energy of Cs^+ and parameters of the double layer at the Bi/H_2O and Bi/CH_3OH interfaces for $q \leqslant 0$.

Interface	$a = (\ln \beta)_{q=0}$	K_{12}, $\mu F\ cm^{-2}$	b, $cm^2\ \mu C^{-1}$	$(\ln \beta)_{q=-15}$
Bi/H_2O	−1.4	93	−0.42	4.9
Bi/CH_3OH	−1.6	46	−0.85	11.2

Thus by allowing for the effect of the electric field on the adsorption energy of the ions we find that the changes in adsorption energy between different solvents are determined not only by the factors which appear in Eqn. (17) but also (and to a large extent) by a geometric factor: the relative size of the solvent molecules.

We should note that geometry considerations apply not only to the change in adsorption energy but also to the repulsion interaction between specifically adsorbed ions located in the inner Helmholtz plane. In practice the counter-ions reside in the outer Helmholtz plane, where they partially screen this repulsion effect, so that the screening effect is greatest (and the repulsion between the specifically adsorbed ions is weakest) when the inner and the outer Helmholtz plane are closest together. Since the molecules of non-aqueous solvents are larger than water molecules we expect the strongest repulsion effects in non-aqueous solvents[56]. As Fig. 14 shows, this expectation is borne out in a large number of systems[13,14]: the Figure is a plot of the virial coefficients B (which characterise the repulsion interaction in the adsorption of anions and cations on a Bi electrode from a number of solvents) against the quantity $(x_2-x_1)/x_2$, where x_1 and x_2 are the distance from the electrode surface to the inner and the outer Helmholtz plane respectively. Since the parameter B allows for the variation of the adsorption energy with the amount of pre-adsorbed particles this dependence of B on the ratio $(x_2-x_1)/x_2$ demonstrates one aspect of the influence of the nature of the solvent on the adsorption energy of ions.

Thus we have a fairly complex relationship between the specific adsorption energy of ions and the nature of the solvent, determined by the interaction of the solvent with the electrode surface, by ionic solvation effects, and by the geometry of the solvent molecules.

IV. SPECIAL FEATURES OF THE DOUBLE-LAYER MODELS FOR NON-AQUEOUS SOLUTIONS

As we have already pointed out, the isotherm which most rationally describes the adsorption of ions is one which allows for the buffer action of the diffuse double layer [see Eqns. (7) and (8)]. This can be illustrated by

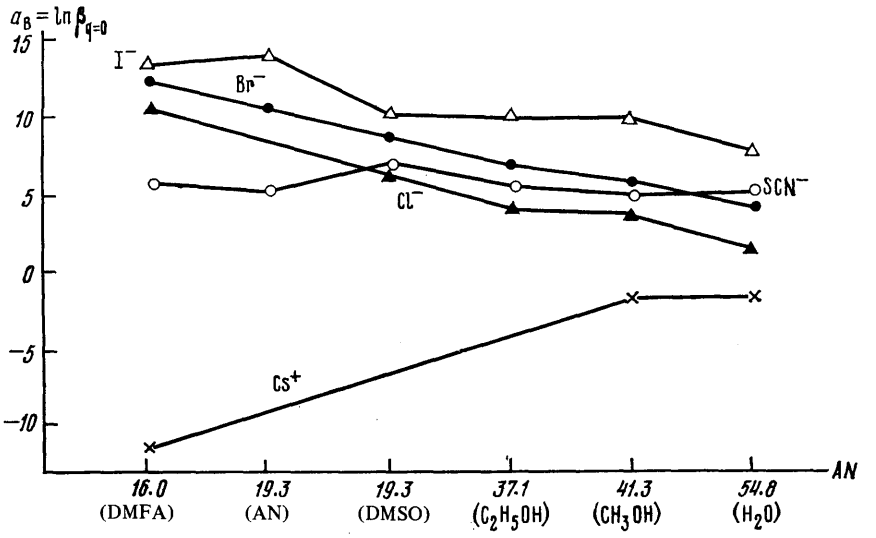


Figure 13. Adsorption of various ions on an uncharged bismuth surface against the acceptor number (AN) of the solvent. (a_b values taken from Ref. 14, AN values from Ref. 52).

considering the adsorption of caesium cations at the Hg/H_2O interface[38,57]. If we ignore the diffuse layer the adsorption isotherms in co-ordinates of $\ln(q_1/zmc)$ against q_1 give straight-line plots (Fig. 15). However these straight lines are not indistinguishable for systems with different ionic strength, and therefore the free energy of adsorption at $q_1 \to 0$ is a function of the concentration of the solution. This conclusion lacks physical significance, since there can be only one value of the energy of adsorption (which defines the system) for each value of the surface charge. However if we introduce a correction for the diffuse layer as in Eqn. (8) all the experimental points for systems with different ionic strength fall on a single straight line, and we obtain a unique value of the free energy of adsorption for each surface charge (Fig. 16). Similar results were obtained for the adsorption of K^+ and Rb^+ cations at the Bi/CH_3OH and Bi/C_2H_5OH interfaces[58].

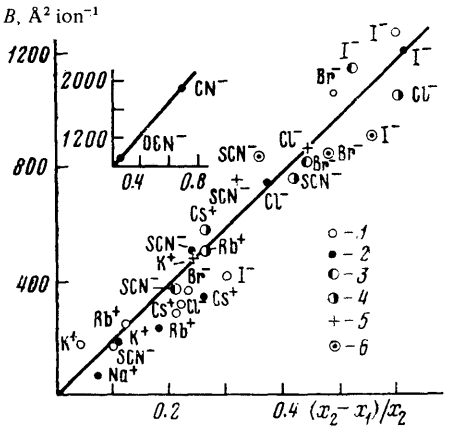


Figure 14. Plot of the second virial coefficient against the ratio $(x_2 - x_1)/x_2$ for the adsorption of various ions on the surface of a Bi electrode from the following solvents: *1*) water, *2*) methanol, *3*) AN, *4*) DMFA, *5*) ethanol, *6*) DMSO (from Ref. 14).

However complications arising from the incorporation of counter-ions into the fixed part of the double layer are often encountered in non-aqueous solvents. This process is favoured by the relatively smaller difference in dielectric constant (as compared with an aqueous medium) between the fixed and the diffuse part of the double layer, which allows ion pairs to be formed not only in the bulk but also within the fixed part of the double layer. The incorporation of counter-ions into the fixed part of the double layer can be illustrated by the adsorption of Cl^- on a bismuth electrode from ethanol[59]. The application of the isotherm equation (8) to the experimental results is shown in Fig. 17. We note that in the absence of a correction for the diffuse layer the plots of $\ln(q_1/zmc)$ against q_1 are rectilinear, but the straight lines for different concentrations do not coincide, and therefore different values of the adsorption energy are obtained for different concentrations at $q_1 \to 0$. On the other hand if the diffuse layer correction is applied, as in Fig. 17, the adsorption energy at $q_1 \to 0$ ceases to be a function of the ionic strength of the solution, though serious deviations from linearity are introduced.

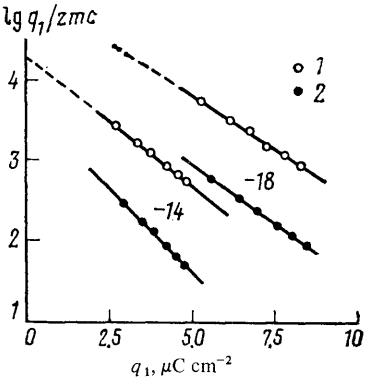


Figure 15. Plots of $\lg(q_1/zmc)$ against charge of specifically adsorbed Cs^+ cations in the system mc CsCl + $(1-m)c$ LiCl at the Hg/H_2O interface: *1*) $c = 0.01$ *M*, *2*) $c = 0.1$ *M*. The numbers against the curves denote the electrode charge in $\mu C\ cm^{-2}$ (from Ref. 57).

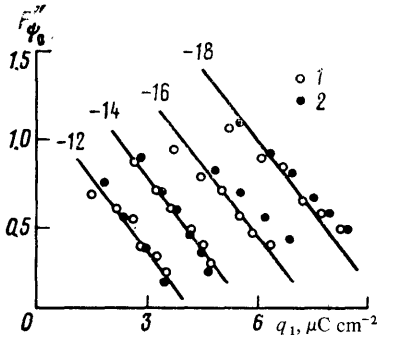


Figure 16. Plots of $[\lg(q_1/zmc) + zF\psi_0/2.3RT] = F''_{\psi_0}$ against charge of specifically adsorbed Cs^+ cations for the system mc CsCl + $(1-m)c$ LiCl (from Ref. 38).

These deviations from linearity can be explained by postulating that counter-ions (in this case Li^+ cations) are attracted into the fixed layer by the specifically adsorbed Cl^- anions. In the calculation of the potential of the outer Helmholtz plane (ψ_0) which appears in Eqn. (8) we had assumed that $q_1^i = 0$, i.e. that the Li^+ cations are not attracted into the fixed layer. This assumption appears to be unjustified. We shall now assume that the system is correctly described by Eqn. (8), and that the deviations from linearity are due to the incorporation of Li^+ cations into the fixed part of the double layer. We can therefore calculate the true potential of the outer Helmholtz plane from the magnitude of these deviations, and hence arrive

at the value of q_1^+. The number of cations (calculated in this way) is plotted in Fig. 18 against the number of specifically adsorbed anions. We can see that the points corresponding to different charges on the electrode all lie on the same curve, i.e. a definite relationship exists between the incorporation of cations and the specific adsorption of anions. This observation confirms the validity of our previous assumption, i.e. that the deviations from linearity of the plots of $[\ln(q_1/zmc) + zF\psi_0/RT]$ against q_1^- are due to the incorporation of counter-ions into the fixed part of the electrical double layer. This assumption stems directly from the concept of ion pair formation in the fixed layer, noting that the formation of ion pairs requires a definite stoichiometry of cations and anions.

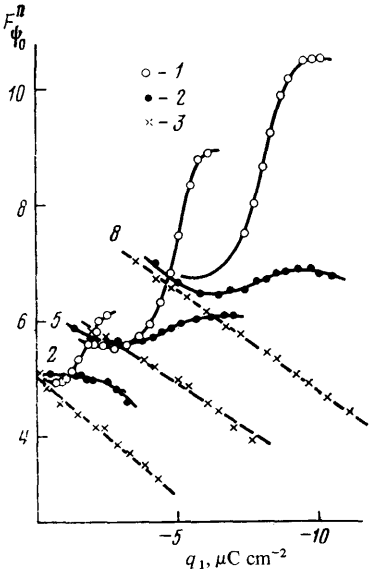


Figure 17. Plots of $[\ln(q_1/zmc) + zF\psi_0/RT] = F\psi_0''$ against charge of specifically adsorbed Cl^- anions in the system mc LiCl + $(1-m)c$ $LiClO_4$ at the Bi/C_2H_5OH interface: *1*) c = 0.01, *2*) c = 0.1, *3*) c = 0.5 *M*. The numbers against the curves denote the electrode charge in μC cm^{-2} (from Ref. 59).

The validity of our assumption can be demonstrated also by calculating the total surface excess of anions (Γ_-) in the double layer. The quantity Γ_- can be evaluated, in the first instance, by adding the charge of specifically adsorbed anions (q_1^-) and the charge due to the anions in the diffuse layer (q_2^-). The quantity q_2^- is calculated either by ignoring the incorporations of cations ($q_1^+ = 0$) or by allowing for the q_1^+ values (as shown in Fig. 18). Alternatively, the total surface excess Γ_- can be calculated by an independent method (the binary electrolyte method). By comparing the two methods we conclude[59] that the agreement between the plots of Γ_- against q is much better when allowance is made for the incorporation of cations in the fixed part of the double layer.

Similar irregularities in the plot of $F\psi_0'' = [\ln(q_1/zmc) + zF\psi_0/RT]$ against the charge due to specific adsorption can be observed in other systems, and in particular for the adsorption of Cs^+ cations at the Hg/CH_3OH interface[60].

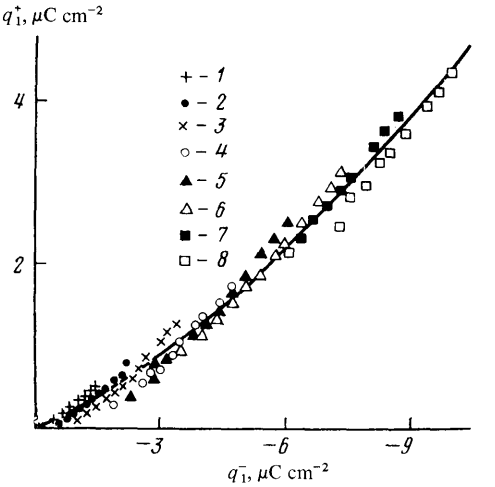


Figure 18. Charge of Li^+ cations incorporated into the fixed layer against charge of specifically adsorbed Cl^- anions in the system mc LiCl + $(1-m)c$ $LiClO_4$ at the Bi/C_2H_5OH interface for c = 0.01 *M*. The numbers denote the charge in μC cm^{-2} to which each type of point refers (from Ref. 59).

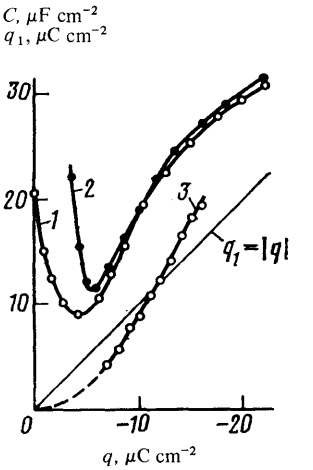


Figure 19. Differential capacity of a mercury electrode in 0.1 *N* methanolic solutions of (*1*) CsCl and (*2*) CsI, and charge of specifically adsorbed Cs^+ cations (*3*) in the same systems as a function of electrode charge.

As in the case of the adsorption of Cl^- ions at the Bi/C_2H_5OH interface, this system shows a surface overcharging effect, and therefore we may suggest that the deviations are due to the incorporation of anions into the fixed part of the

double layer. However the iodide anions attracted by the specifically adsorbed caesium cations could be expected to produce a greater increase in double-layer capacitance than the chloride anions. It is clear from Fig. 19 that this effect is not observed: at high negative charges the experimental C, E curves for 0.1 M methanolic solutions of CsCl and CsI are practically indistinguishable.

We can suggest two possible explanations: either the Cs^+ cations specifically adsorbed at the Hg/CH_3OH interface do not attract anions into the double layer (in which case we must look for another explanation of the deviation from linearity of the plot of $F\psi_0''$ against q_1), or the I^- and Cl^- anions have practically no effect on the capacity of the double layer when incorporated into the fixed layer. Anion adsorption (Cl^- or I^-) usually causes a sharp increase in capacitance when these anions are able to approach the surface, whereas the cations remain in the outer plane or are only partly attracted into the fixed layer. At high negative surface charges the caesium cations are apparently closer to the surface than the anions attracted into the fixed layer. If we ascribe the normal increase in capacity in the presence of iodide anions to partial charge transfer during adsorption[61,62], we cannot expect a large change in capacity to result from the incorporation of I^- anions into the fixed layer when the electrode is in the cathodic region and no charge transfer occurs during the adsorption of iodine. However the only rational criterion for choosing between the two alternative explanations is a direct programme of electrocapillary measurements. The problem remains unresolved at the moment.

The incorporation of counter-ions into the fixed part of the double layer cannot fail to complicate the model of the double layer, since the plane in which the counter-ions are located does not coincide (in general) with the plane of the specifically adsorbed ions. Hence we must consider two inner Helmholtz planes: one for the cations and one for the anions. These planes are situated at distances x_1^+ and x_1^- respectively from the electrode surface. This model of the electrical double layer is discussed in Refs. 63 and 64. Assuming additivity of the potential jumps associated with the charges q, q_1^+, and q_1^- we obtain the following expression[63,64] for the total potential jump in the fixed layer (ψ_u):

$$\psi_u = q/K_{02} + q_1^+/K_{1^+2} + q_1^-/K_{1^-2}, \qquad (19)$$

where K_{02} is the integral capacity of the whole of the fixed layer (from $x = 0$ to $x = x_2$), and K_{1^+2} and K_{1^-2} are the integral capacities of the regions between the outer Helmholtz plane ($x = x_2$) and the planes $x = x_1^+$ and $x = x_1^-$ respectively.

Assume that the specific adsorption consists of cations (for example, Cs^+ cations[64]), and that the charge q_1^- is due to incorporated counter-ions. Under these conditions $q_1^+ > |q_1^-|$ (for example, according to Palm and coworkers[64] $|q_1^-|/q_1^+ = 0.27$), and $x_1^+ < x_1^-$, so that

$$K_{1^-2} = \frac{\varepsilon}{4\pi(x_2 - x_1^-)} > K_{1^+2} = \frac{\varepsilon}{4\pi(x_2 - x_1^+)}.$$

Therefore Eqn. (19) can be re-written

$$\psi_u = \frac{q}{K_{02}} + \frac{q_1^+}{K_{1^+2}}(1 - \alpha_+), \qquad (20)$$

where the quantity $\alpha_+ = K_{1^+2}|q_1^-|/K_{1^-2}q_1^+$ is much smaller than unity. An analogous formula is obtained for the specific adsorption of anions:

$$\psi_u = \frac{q}{K_{02}} + \frac{q_1^-}{K_{1^-2}}(1 - \alpha_-), \qquad (21)$$

where the quantity $\alpha_- = K_{1^-2}q_1^+/K_{1^+2}|q_1^-|$ is also much smaller than unity, since under these conditions $q_1^+ < |q_1^-|$, and $K_{1^-2} < K_{1^+2}$.

Thus to a first approximation we can replace Eqn. (19) by the simpler expression of the Grahame–Parsons model[54]

$$\psi_u = q/K_{02} + q_1/K_{12}. \qquad (22)$$

For the specific adsorption of cations we now have $q_1 = q_2^+$ and $K_{12} = K_{1^+2}/(1-\alpha_+)$, and for the specific adsorption of anions $q_1 = q_1^-$ and $K_{12} = K_{1^-2}/(1-\alpha_-)$. It follows that K_{12} as defined in the Grahame–Parsons model[54] under conditions resulting in the incorporation of counter-ions in the fixed layer describes an effective capacity, slightly greater than the true capacity K_{1^+2} or K_{1^-2}. Therefore the simple Grahame–Parsons model can give a formal description of systems in which the specific adsorption of ions is accompanied by the incorporation of counter-ions into the fixed part of the double layer.

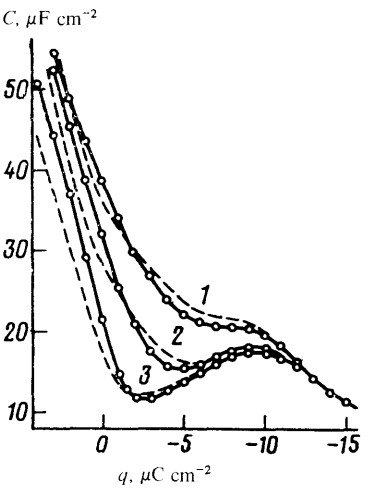


Figure 20. Differential capacity curves for a mercury electrode in *N*-methylformamide solutions of KBr of the following concentrations: *1*) 0.74, *2*) 0.1, *3*) 0.05 *M*. The full curves are experimental, the broken curves are calculated by Eqn. (11) for $a = 6.39$, $b = 0.72$ cm^2 μC^{-1}, and $B = 0.144$ cm^2 μC^{-1} (from Ref. 65).

As an example, we show in Fig. 20 a comparison of experimental C, q curves with the corresponding curves calculated by Eqn. (11) under conditions of specific adsorption of Br^- anions at the mercury/*N*-methylformamide (NMF) interface[65]. As we have already pointed out, Eqn. (11) was derived[43] from the Grahame–Parsons model. Hence the good agreement between experiment and calculation in Fig. 20 shows that the Grahame–Parsons model is formally applicable to the Hg/KBr in NMF system. On the other hand the incorporation of K^+ cations into the fixed part of the double layer through the specifically adsorbed Br^- anions cannot be excluded in this system. In other words, consistency between experimental results

and the Grahame–Parsons model cannot be taken as a general criterion for the absence of incorporated counter-ions in the fixed part of the double layer. A more detailed analysis is needed to establish the absence of counter-ions in the fixed layer[59].

V. SHAPE OF THE DIFFERENTIAL CAPACITY CURVES AND DISTRIBUTION OF SOLVENT MOLECULES IN THE FIXED PART OF THE LAYER IN THE ABSENCE OF SPECIFIC ADSORPTION OF IONS

The differential capacity curves of the fixed layer measured in different solvents can be arbitrarily classified into three groups[66]. The first group is characterised by a single maximum (or "hump"). C,q curves of this shape are obtained in water[67], formamide[9,68], and N-methylformamide[69], with a characteristic increase in capacity in the anodic region. To this group can also be assigned the C,E curves obtained in carbonates, lactones, and in sulpholane[26,70], in which the electrochemical process sets in before the anodic rise in capacity. The second group includes the C,E curves with a minimum, which do not show a "hump". Curves of this shape are typical of methanol[7], DMFA,[68] liquid ammonia[71], and some other solvents. Lastly we have the C,E curves with two "humps", observed in N-methylacetamide and N-methylpropionamide[4] (see curve *2* of Fig. 21).

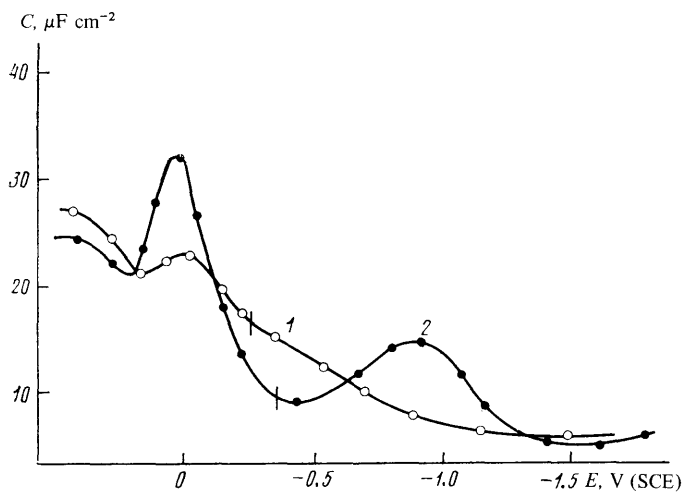


Figure 21. Differential capacity curves for a mercury electrode in 0.1 M solutions of KPF_6 in: *1*) dimethylacetamide, *2*) N-methylpropionamide. The vertical lines denote the position of the zero-charge potential (from Ref. 4).

The models of the fixed layer have been developed primarily for the interface between a metal and an aqueous solution. Thus, several workers[72–77] have discussed the presence of dipoles from the solvent on the electrode surface in two opposite orientations: with their negative pole or their positive pole pointing towards the surface. The relative number of dipoles in the two orientations depends on the charge on the electrode, and the "hump" on the C,q curve denotes equal numbers of dipoles in the two orientations.

Frumkin and coworkers[78,79] proposed a different model to explain the C,E curves of the gallium electrode. They assumed that solvent dipoles are chemisorbed with their negative pole pointing towards the surface: this would explain the experimentally observed increase in capacitance as the potential is made more positive.

Lastly, Damaskin and Frumkin[80] have described a model which combines the assumptions of the two previous models. They suggest that solvent particles can exist on the metal surface in two conditions: either as particles which can be freely oriented by the field of the double layer or as chemisorbed dipoles. Since the freely oriented particles and the chemisorbed dipoles cannot be identical, it is further suggested that the former consist of groups of several (usually three) associated molecules of water. The model was subsequently modified and improved[81–83]. In its most recent form the model describes in a quantitative way the dependence of the capacitance of the double layer on the electrode charge for the case of aqueous solutions of surface-inactive electrolytes on mercury, bismuth, and cadmium electrodes, and it correctly describes the temperature dependence of the capacity of the mercury electrode.

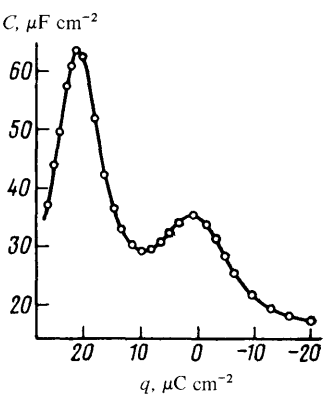


Figure 22. Differential capacity of the fixed part of the double layer against electrode charge according to a model which allows for the simultaneous presence of chemisorbed solvent dipoles and associated groups of dipoles able to orient themselves freely in the field of the double layer (from Ref. 83).

It is easy to show that this model (and none of the other models proposed so far) can account for all three types of differential capacitance curves in non-aqueous solvents[66]. Fig. 22 shows a C,q curve calculated by this model for a wide range of surface charge. If the region of the left-hand peak is not experimentally accessible as a result of electrochemical metal dissolution or solvent oxidation reactions this theoretical curve describes the variations in capacitance in the solvents of our first group. If the ideal polarisability region is even shorter, and only the middle part of the theoretical curve (between the two peaks) is experimentally accessible, the theoretical curve

describes the C,q curves of the second group of solvents. Lastly, for the general case the theory predicts a differential capacitance curve with two peaks as observed in *N*-methylacetamide and in *N*-methylpropionamide (see Fig. 22).

The following observations are also relevant. The position of the theoretical C,q curve along the horizontal axis is determined (if the associated groups of molecules can be freely oriented by the field) exclusively by the difference in energy level between a single solvent molecule forming part of the grouping and the same molecule present as a chemisorbed dipole. Under these conditions the right-hand maximum (or "hump") of the theoretical C,q curve is always found near $q = 0$. In order to shift the theoretical C,q curve towards more negative charges and thus align it with the experimental differential capacitance curves observed in amides we must make the further assumption that the associated groups have different stabilities in the two positions. The physical significance of this assumption is that the orientation of the associated groups depends both on the electric field of the double layer and on the structure of the solvent on the solution side. The structural orientation of the solvent dipoles determines the surface potential at the solution/air interface. The transition from the solution/air to the solution/metal interface causes a change in this surface potential, due both to the field of the double layer and to the specific interaction of the solvent molecules with the metal.

Thus the dipole component of the potential jump at the electrode/solution interface arises not only from the interaction of the solvent molecules with the electrode surface but also from the interaction of these molecules with similar molecules in the bulk of the solution. The work of Bagotskaya and Dubova[84] leads to the same conclusion: these workers compared the change in zero-charge potential of various metals and the change in adsorption-induced potential jump at the solution/air interface[85] for electrodes in water and in non-aqueous solvents respectively.

Studies of the adsorption of thiourea at the non-aqueous solvent/metal interface have helped to establish the structure of this interface. A great deal of information on the adsorption of thiourea on mercury and on bismuth from different solvents is now available[86–91]. However it is difficult to generalise these results because different models were used[86,89,91–93] in their theoretical analysis.

VI. CONCLUSIONS

This review shows that the quantitative study of the structure of the electrical double layer and of ionic adsorption at the metal/non-aqueous solvent interface has allowed us to reach some important conclusions as to the factors which determine the adsorption energy and the charge of specifically adsorbed ions, and also on some special features of the structure of this interface. Nevertheless workers in this field are still faced by many unsolved problems. The following are some of the most important problems currently being examined in the field of the structure of the electrical double layer and of adsorption phenomena at the interface between an electrode and a non-aqueous solution.

1. Further studies of mixed electrolyte systems in the region of $m \to 1$, where anomalous behaviour is sometimes reported (capacitance in a solution with $m = 1$ lower than in a solution with $m < 1$ for the same electrode charge[33,94]).

2. More extensive study of the effects arising from incorporation of counter-ions into the fixed part of the double layer; clarification of the role of the nature of the counter-ion and of the solvent[37,95]; influence of the adsorption of I^- anions (in the second layer) on the measured double layer capacity.

3. Development of a detailed model of the electrical double layer with two inner Helmholtz planes, to take account of the recent theoretical advances in this area[96,97].

4. Acquisition of additional experimental information on the adsorption of thiourea molecules at the metal–non-aqueous solvent interface, especially in dilute solutions (which sometimes show deviations from the classical theory of the diffuse layer[98]); generalisation of existing data on the adsorption of thiourea at various interfaces.

5. Detailed study of the structure of the fixed part of the double layer at the metal–non-aqueous solvent interface in the absence of specific adsorption of ions (measurement of capacity as a function of temperature, application of new relaxation methods with time constants of the order of nanoseconds, quantitative comparison of experimental data with model calculations).

6. Study of systems in which adsorption of ions is in competition with adsorption of solvent dipoles under conditions of strong specific interaction with the electrode surface, where interesting kinetic phenomena have been observed[99] but not fully investigated.

7. Study of systems with very strong chemisorption of solvent molecules on the electrode (for example, Pt or Ni). Only tentative results have so far been obtained[100–102] for systems of this type.

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