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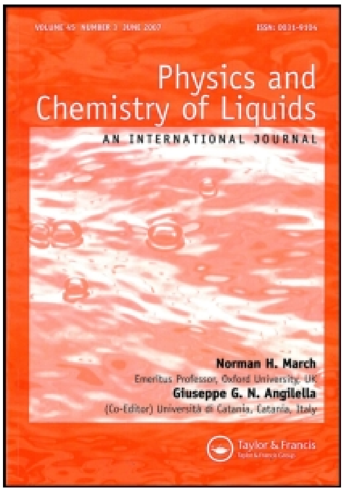

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Water and Electrode-Solution Interfaces

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Water and Electrode-Solution Interfaces†

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Contents

1 INTRODUCTION

Water is so common, yet so complex. Our understanding of this substance has not matched its ubiquitous nature. The presence of water in any region results in a host of unsolved problems. This view is abundantly true at the electrode-solution interfaces which are the scene of the bulk of electrochemical phenomena. This report therefore is aimed at a discussion of water at electrode-solution interfaces. In particular, attention is directed towards the various ways in which interfacial water commands consideration in electrochemistry:

1) as a reference component in the thermodynamics of interfaces;
2) as a "water jacket" for the electrode;

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4) as a competitor with neutral organic molecules for adsorption on the electrode; and finally

5) as a crucial participant in the process of interfacial charge transfer.

The logical structure of this report is based on a foundation consisting of some aspects of the thermodynamics of interfaces. The *raison d'être* of this foundation is that invariably there is an accumulation/depletion at the interface of the various species constituting the bulk electrolyte, and the experimental measurement of this "adsorption" involves water as a reference species. From the methodology for the quantitive treatment of accumulation/depletion of substances at interfaces, the report turns to the invariably occurring accumulation of water on an electrode. Several aspects of this accumulation (which may be termed the "water jacket" or "hydration sheath" of the electrode) require discussion. For instance, it is fruitful to consider the thickness of the water layer, its electrode charge-dependent orientation and orientability and its dielectric constant. To the extent that the water jacket is penetrated, populated and "doped" with either ions or neutral molecules, it next becomes necessary to deal with ionic adsorption and with the adsorption of organic molecules. Finally, a treatment is accorded to the manner in which the solvent participates and influences charge transfer at electrode-solution interfaces.

Several cautionary notes may be sounded here. Firstly, this report will be characterized by the omission of important contributions if it is judged as an exposition of the electrochemical double layer and electrode kinetics; the justification, however, is that an attempt has been made to include only those theories and viewpoints which explicitly and directly bring out the role of water at electrode-solution interfaces. Secondly, try as one may, one cannot but deal largely with mercury-solution interfaces though these are not *hetero*-interfaces in the strict sense of the term. Such a restriction is more or less inevitable because the bulk of our knowledge of the structure of electrode-solution interfaces has come from a study of mercury electrodes which have the virtues of homogeneity and reproducibility. It is hoped that the understanding gained from a study of mercury-solution interfaces can be extended, with suitable modifications, to interfaces formed by solid electrodes in contact with aqueous solutions and that the basic picture of the role of water is unlikely to change.

2. WATER AS A REFERENCE COMPONENT IN INTERFACIAL THERMODYNAMICS

The interfacial region formed when an electrode and an aqueous solution are brought into contact is populated with the same species existing in the bulk electrolyte, but the interfacial concentrations are in general different from the bulk concentrations. This fact implies that there is either an accumulation or depletion of the various constituents of the solution in the interfacial region.

The accumulation/depletion has been quantified since Gibbs with the aid of the concept of surface excess which may be defined thus.

$$\Gamma_i = \frac{n_i - n_i^0}{A} \tag{1}$$

where n_i is the number of moles of the species i in a column of solution contacting A cm^2 of the electrode surface and n_i^0 is the number of moles of i in an identical volume of solution situated in the bulk of the electrolyte, i.e., sufficiently far from the electrode so that the interfacial properties do not manifest themselves. Alternatively, one can distinguish the real interfacial system from a hypothetical Gibbs system in which the bulk properties of the electrode phase and solution phase are preserved right up to the surface of contact. From this point in view, n_i and n_i^0 are the moles of species i in the real and hypothetical systems respectively.

Another approach[1-3] to the understanding of the surface excess is in terms of the way the excess molar concentration, $c_i - c_i^0$, (i.e., the deviation in concentration from the bulk value) varies with distance x from a reference plane, x_R. In terms of this distance-dependent excess concentration, the definition of surface excess assumes the equivalent form

$$\Gamma_i(x_R) = \int_{x_R}^{x} (c_i - c_i^0)\mathrm{d}x \tag{2}$$

The definition shows clearly that the value of the surface excess is a function of the position of the plane of reference. When this plane coincides with the metal surface and $x_R = 0$, the quantity $\Gamma_i(x_R = 0)$ corresponds to the total surface excess. Any value $x_R > 0$ yields only a part of the total surface excess and will be termed the surface excess reckoned at the plane x_R.

One way of determining the total surface excess is to evaluate the integral in Eq. (2), but such a process requires a knowledge of the function $c_i = f(x)$. Direct experimental methods of determining this function are unavailable, and theory comes to the rescue in one case only, viz., when the solution only contains surface-*inactive* ions. In such a case, it turns out from Gouy-Chapman theory for a $z - z$ electrolyte that

$$\Gamma_i = \frac{B}{z_i F}\left[\exp\left(-\frac{z_i F\phi_2}{2RT}\right) - 1\right] \tag{3}$$

where

$$B = (\varepsilon RTc_i^0/2\pi)^{1/2}, \tag{4}$$

i represents an anion or a cation, and ϕ_2 is the potential at the plane of closest approach of the surface-inactive ions to the electrode, i.e., at the Outer Helmholtz Plane (OHP) designated by the subscript 2. In the case of a solution containing surface-inactive ions, the region between the metal surface ($x = 0$) and the OHP (x_2), is ion-free. It follows therefore that Eq. (3) yields the *total* surface excesses of the anions and cations even though these surface excesses are reckoned at the OHP which is different for each ion-type due to differences in the closeness of approach.

When, however, the aqueous solution contains surface-*active* ions or molecules, the distribution function $c_i = f(x)$ is not known either theoretically or experimentally. In such a situation, the surface excess cannot be obtained with the help of Eq. (2) and it is usually evaluated by insertion of electrocapillary data into the thermodynamic equation:

$$-\mathrm{d}\sigma = q_M \mathrm{d}E^+ + \Gamma_- \,\mathrm{d}\mu_\pm + \Gamma_W \,\mathrm{d}\mu_W \qquad (5)$$

where E^+ is the electrode potential with respect to a reference electrode reversible to the cationic species in solution, q_M the electrode charge, μ the chemical potential, W stands for water and it is assumed that $\mu_\pm = \mu_+$. When the above Eq. (5) is combined with the Gibbs–Duhem relation:

$$n_{\mathrm{salt}} \,\mathrm{d}\mu_{\mathrm{salt}} + n_W \,\mathrm{d}\mu_W = 0, \qquad (6)$$

the result is

$$-\left(\frac{\partial\sigma}{\partial\mu_\pm}\right)_{E^+} = \Gamma_{-(W)} = \Gamma_- - \frac{n_{\mathrm{salt}}}{n_W}\Gamma_W$$

$$= \Gamma_- - k\Gamma_W \qquad (7)$$

The experimentally accessible term $-(\partial\sigma/\partial\mu_\pm)_{E^+}$ leads therefore, not to the value of the *absolute* surface excess of the anions, but to a quantity which includes the surface excess of water. The quantity ($\Gamma_- - k\Gamma_W$) is known as the surface excess of the anions relative to the solvent water, or simply as the relative surface excess, $\Gamma_{-(W)}$.

Whereas the absolute surface excess, Γ_- and Γ_W, depend upon the position of the reference plane, several authors, for example, Mohilner,[2] have shown that the value of the relative surface excess, $\Gamma_{-(W)}$ is independent of the reference plane. It does not seem to have been stressed, however, that this invariance of the relative surface excess with respect to the reference plane x_R, requires that

$$\frac{\partial\Gamma_-}{\partial x_R} = k\frac{\partial\Gamma_W}{\partial x_R} \qquad (8)$$

and therefore that, at any x_R,

$$\frac{\partial \Gamma_i}{\partial \Gamma_W} = k \tag{9}$$

Thus, by serving as a reference component, water at the electrode-solution interface ensures that experimentally determined surface excesses are invariant with respect to a change of reference plane. The accompanying disadvantage is that the experimental surface excesses are not absolute, but only relative, quantities.

The intrusion of the surface excess of water into the experimentally determined (relative) surface excesses of other species leads to the following equation:

$$\Gamma_{-(W)} - \Gamma_{-} = k\Gamma_W \tag{10}$$

from which it may be concluded that the difference between the absolute and relative surface excesses is mainly dependent on the salt concentration and increases with the latter.

The magnitude of this difference is also dependent on whether the total (absolute) surface excess or only a part of this total is under investigation. For instance, if one is studying that part, $\Gamma_-^{(1)}$, of the total surface excess which consists of specifically adsorbed ions, then

$$\Gamma_-^{(1)} = \Gamma_- - \Gamma_-^{(2)} \tag{11}$$

where $\Gamma_-^{(2)}$ is the part of the surface excess distributed in the diffuse layer, and from (10)

$$\begin{aligned} \Gamma_-^{(1)} &= \Gamma_{-(W)} + k\Gamma_W - \Gamma_-^{(2)} \\ &= -\left(\frac{\partial \sigma}{\partial \mu_\pm}\right)_{E} + k\Gamma_W - \Gamma_-^{(2)} \end{aligned} \tag{12}$$

Quite often, the second term in Eq. (12) is neglected and the specifically adsorbed surface excess, $\Gamma_-^{(1)}$, is obtained from Eq. (12) after using Gouy-Chapman theory to substitute for $\Gamma_-^{(2)}$. In this case, the neglect of the term containing the surface excess of water leads to an error which may be significant in comparison with $\Gamma_-^{(1)}$ which itself is ordinarily quite small (5–50 μcoul cm^{-2}). Since $\Gamma_-^{(1)}$ is used to develop adsorption isotherms and test double layer theories, it is clear that the error introduced by neglecting the thermodynamic role of water may be significant enough to distort the isotherms and vitiate comparison between theory and experiment. The significance of this reference role of water is enhanced at high salt concentrations and for low values of $\Gamma_-^{(1)}$, i.e., for ions which undergo weak specific adsorption, such as fluoride and perchlorate ions.

Considerable progress towards the elimination of the nuisance value of water in leading to relative, rather than absolute, surface excess, was recently achieved by Hurwitz[4] and independently by Dutkiewiez and Parsons.[5] This achievement has not been explicitly claimed in the work of these authors which was intended primarily to avoid the sometimes-questioned use of Gouy–Chapman theory in calculating $\Gamma_-^{(2)}$ and thus evaluating the specifically adsorbed excess charge $\Gamma_-^{(1)}$. The essence of the technique developed by these authors is to study the specific adsorption of A^- ions from constant ionic strength mixtures of the salts KA and KB after ensuring that B^- ions are *not* specifically adsorbed.

The case when both A^- and B^- are specifically adsorbed has been treated recently by Lakshmanan and Rangarajan.[6]

In such a situation the basic electrocapillary equation becomes

$$-(\partial\sigma)_{E_+,I} = \Gamma_A\,\mathrm{d}\mu_A + \Gamma_B\,\mathrm{d}\mu_B + \Gamma_W\,\mathrm{d}\mu_W \qquad (13)$$

which upon introducing

$$\mathrm{d}\mu_A \approx RT\mathrm{d}\ln m_A \qquad (14)$$

$$\mathrm{d}\mu_B \approx RT\mathrm{d}\ln m_B = -RT\frac{m_A}{m_B}\mathrm{d}\ln m_A \qquad (15)$$

$$\mathrm{d}\mu_W \approx 0. \qquad (16)$$

$$\Gamma_A = \Gamma_A^{(1)} + \Gamma_A^{(2)}\text{ (specific adsorption)} \qquad (17)$$

$$\Gamma_B = \Gamma_B^{(2)}\text{ (no specific adsorption)} \qquad (18)$$

reduces to

$$-\frac{1}{RT}\left(\frac{\partial\sigma}{\partial\ln m_A}\right)_{E_+,I} = \Gamma_A^{(1)} + \Gamma_A^{(2)} - \Gamma_B^{(2')}\frac{m_A}{m_B} \qquad (19)$$

The plane of closest approach to the electrode by B^- ions is denoted by 2′ At this stage, the following assumption is made:

$$\frac{\Gamma_A^{(2)}}{\Gamma_B^{(2)}} = \frac{m_A}{m_B} \qquad (20)$$

in which case

$$-\frac{1}{RT}\left(\frac{\partial\sigma}{\partial\ln m_A}\right)_{E_+,I} = \Gamma_A^{(1)} + \frac{m_A}{m_B}[\Gamma_B^{(2)} - \Gamma_B^{(2')}] \qquad (21)$$

Thus if the outer Helmoltz planes for the A and B ions coincide

$$-\frac{1}{RT}\left(\frac{\partial\sigma}{\partial\ln m_A}\right)_{E_+,I} = \Gamma_A^{(1)} \qquad (22)$$

indicating that, by this elegant method, the *absolute* surface excess contributed by the specifically adsorbed ions can be determined without having to rely on water as a reference component. Further, it is clear from

$$\Gamma_A^{(1)} = \int_{x=0}^{x=2} (c_A - c_A^0)\mathrm{d}x \qquad (23)$$

that this part of the total surface excess is independent of the reference plane.

3 THE 'PRIMARY HYDRATION SHEATH' OF THE ELECTRODE

3.1 Thickness of the primary hydration layer

The distinction between relative and absolute surface excesses has been taken advantage of by the schools of Randles[7] and of Frumkin[8] to compute the *amount* of water adsorbed in the so-called *inner layer*, i.e., in the region between the metal surface and the OHP. The experimental technique involves the use of conditions under which none of the ionic species are specifically adsorbed and therefore the absolute surface excesses of these species can be calculated from Gouy–Chapman theory. Since specific adsorption consists of the penetration of ions into the inner layer, the absence of specific adsorption implies that an *ion-free* water layer is present in the region between the metal surface and the OHP. This ion-free water layer may be looked upon as a "primary hydration sheath" for the electrode.

The amount of water in the ion-free water layer at a given charge on the mercury electrode seems to be constant up to solution concentrations of ~ 2M and to have a value of $\sim 1.4 \times 10^{-9}$ equiv cm^{-2} for Li$^+$, Na$^+$ and K$^+$ ions. Assuming the bulk density of water, this amount of water corresponds to a hydration sheath thickness of ~ 2.5 Å, which is about the thickness of a monolayer of adsorbed water molecules. Mg^{++} ions yield a thickness of 4.4 Å for the inner layer water. In very concentrated solutions, the thickness appears to decrease probably because the ions are starved of hydration water.

The work on the ion-free water layer has an important bearing on the well known observation that, in the absence of specific adsorption, most cations yield a constant, concentration-independent cathodic capacity. The latter capacity has been ascribed by Devanathan[9] to the solvent, but in estimating this solvent capacity two alternative models have been used for the inner layer. In one model urged by Devanathan[9] the OHP is considered as the plane through the centres of non-specifically adsorbed, hydrated cations in contact with the electrode, i.e., the OHP is taken as the closest distance of approach of hydrated cations to a *bare* electrode. In this case, the thickness of the water layer would be around one molecular diameter, ~2.76 Å. According to the second model, which was proposed by Bockris *et al.*[10] the OHP is taken as the closest distance of approach of hydrated cations to a layer of water molecules, in which case the thickness of the water layer would be more than two molecular diameters. It is clear that the above-mentioned work of the schools of Randles and of Frumkin is more consistent with the model of Devanathan[9] than with the model of Bockris *et al.*[10]

Whereas the constant capacity has hitherto been considered as concentration independent, the recent work of Takahashi and Tamamushi[11] has yielded an interesting result, viz., the capacitance minimum on the cathodic side of the ecm (electrocapillary maximum) falls progressively with a decrease in the concentration of the electrolyte ($NaClO_4$, $HClO_4$, NaOH). This effect is marked when the electrolyte concentration is below 10^{-3} M and does not appear to be an experimental artifact. One possible implication of the observation of Takahashi and Tamamushi is that, in very dilute solutions ($\lesssim 10^{-4}$ M), two or more ion-free layers of water molecules may be present between the electrode and the OHP for reasons yet to be elucidated.

Under the conditions of very low salt concentration, and of weak anion hydration, it is reasonable to expect that the region adjacent to the electrode should be populated mainly by water molecules on both the anodic and cathodic sides of the ecm, and therefore that the observed capacity should be due to a water capacitor. The capacitance curves should as a consequence be nearly symmetric on either side of the capacitance minimum (pzc) in extremely dilute solutions. The experimental data[11] appear to bear out this conclusion.

In conclusion, therefore, when the electrode charge is negative, the thickness of the hydration sheath of the electrode appears to be less than about one mole thick in solutions which are more concentrated than ~2 M, a constant one molecule thick in solutions between 2 and 10^{-4} M, and perhaps two or more molecules thick when the solution concentration falls below 10^{-4} M. When, however, the electrode charge is zero or positive, the effective thickness of the inner layer of water may well be less than one molecule thick due to the penetration by specifically adsorbing ions of the erstwhile ion-free inner layer.

3.2 The orientation of adsorbed water molecules

The dipolar nature of the water molecule and the existence of an electrical field across the electrode-solution interface lead naturally to the question of the orientation of water molecules on the electrode. In particular, the orientation of water at the electrocapillary maximum on mercury has been the subject of considerable discussion.

There is now widespread support[12,13,14] for the suggestion of Frumkin *et al.*[15] that at the potential of zero charge there is a residual orientation of the water dipoles with the oxygen of the water towards the mercury surface. In other words, the water-electrode interaction is not purely electrostatic in which case there should be no net orientation of the water molecules when the charge on the electrode is zero.

Further evidence, though indirect, has come from recent electrocapillary studies on the adsorption of dipolar ions (amino acids, for example).[16,17] The dipolar ionic forms of simple straight-chain amino acids possess such large dipole moments, e.g., leucine has a dipole moment of about 30 D, that image interactions may be considered to predominate and the dipolar ions assumed to adsorb flat on an uncharged mercury surface. With such species, any Esin–Markov shift, i.e., any shift in the pzc on adsorption (at low coverages), may be attributed to a decrease of the dipole potential ($\Delta\chi = 4\pi N_W \mu W/\varepsilon$), where N_W is the net number of oriented water molecules desorbed out of the adsorbed and oriented water molecules initially present. The observed positive shift of the pzc is thus in agreement with a water orientation at the pzc in which the negative (oxygen) end of the water dipoles is towards mercury.

One of the implications of such a residual orientation of water molecules at the pzc on mercury is that a weak, specific adsorption of strongly hydrated ions such as fluoride ions may go undetected in the Esin–Markov test. This is because any slight negative shift in the pzc due to specific adsorption is compensated by a positive shift caused by a decrease in the dipole potential due to water. A similar effect may be observed at other potentials of constant charge, and therefore on the generalized Esin–Markov shifts described by Parsons.[18] This compensation effect is of course unimportant for strongly adsorbed ions or weakly hydrated ions.

To the extent that the residual orientation of water molecules is a manifestation of non-electrostatic interactions, it must depend upon the nature of the electrode material. The recent work of Trasatti[19] on the dependence of the degree of orientation of adsorbed water on the nature of the electrode is an important step in the quantitative characterization of this relationship. Work in such directions is bound to prove vital in the extension of our understanding of water on mercury-solution interfaces to other electrode systems.

3.3 The orientational freedom of adsorbed water molecules

It has been stressed that a metal in contact with an aqueous solution is covered to a large extent with water molecules and that at the pzc, there appears to be a residual (net) orientation of these molecules. Hence the rotational freedom of an adsorbed water molecule is a maximum, not at the pzc, but at some other potential at which there is no residual (net) orientation. This question of the rotational freedom or orientability of water molecules in the hydration sheath of the electrode is a vital matter because it is closely related to the interpretation of the experimentally observed "humps" on the capacitance-potential curves for mercury in contact with aqueous solutions.

The main features of this capacitance hump have been the subject of many works[10,14,20–22] and therefore the following salient features are highlighted here:

1) the hump usually occurs on the positive side of the ecm;
2) it is observed even after correcting for the diffuse layer capacitance[23];
3) it is independent of the nature of the cation in solution;
4) it is influenced by the nature of the anion in solution;
5) it has a negative temperature coefficient.

Interpretations of the various phenomena associated with the capacitance hump have been the result of three main streams of thought which are in the nature of a thesis, an antithesis and a synthesis.

Mott and Watts-Tobin proposed[24] what is in essence a water re-orientation model according to which the capacitance hump is associated with a re-orientation of water molecules at the hump maximum and a decrease in rotational freedom on either side. An over-simplified water re-oreintation model is obviously inconsistent with the facts. In particular, the model does not explain the influence of the nature and concentration of the anion on the hump characteristics. Neither does it explain why the hump does not occur at some charge negative to the pzc at which negative charge the residual orientation of water molecules at the pzc disappears and the water *does* re-orient.

Bockris, Devanathan and Muller[10] virtually eliminated adsorbed water from any contributory role and saw in the lateral repulsion of specifically adsorbed anions an explanation of the hump. The critical experimental evidences claimed in support of the lateral-repulsion model depends on the identification of the electrode charge (q_M) at which the hump maximum occurs with an inflection on the $q_1 - q_M$ curve (where q_1 is the specifically adsorbed charge). This however is no easy task as the $q_1 - q_M$ plots are virtually inflexion-free straight lines. The validity of a simple anion repulsion model must also be examined in the light of recent work[25] which shows that most anions of the structure-breaking type (BF_4^-, PF_6^-, ClO_3^-, NO_3^-, ClO_4^-

CF_3COO^-, etc.) give rise to capacitance humps having nearly the same characteristics despite the different shapes and adsorbabilities which these ions are bound to have. It appears that the only common factor in all these systems, viz., adsorbed water, must have an important role in determining the hump.

In the simple water re-orientation model, it is only the field due to the electrode charge which is considered to influence the net orientation of adsorbed water molecules. The field-induced re-orientation of adsorbed water has been quantitatively analysed by Damaskin on the basis of a parallel-plate capacitor model.[26] In this water capacitor, water molecules are considered to possess different dielectric properties corresponding to their two possible orientations on the electrode, viz., an orientation with the oxygen (negative) end towards the electrode and another orientation with the hydrogens (positive) toward the electrode. It turns out that there is good qualitative agreement between the model and experiment, and that even with a net negative orientation of water towards mercury at the pzc, the model indicates that the area occupied by one water molecule is 33 $Å^2$ of electrode surface, i.e., about three times the true cross-sectional area of a water molecule. One interpretation of this large cross-sectional area is in terms of clusters of water molecules on the electrode surface, but such two-dimensional clusters are unlikely to have a net dipole moment. Hence, it is not clear why such clusters should reorient in an electric field. Moreover, the model denies a role to anions, and all anions show at least a weak adsorption on mercury. Thus recent studies show that even strongly hydrated ions such as F^- and $H_2PO_4^-$ ions are specifically adsorbed[27–29] on mercury and that capacitance humps are observed in the presence of these ions.

The point is that the reorientation of adsorbed water molecules can also result from the interaction with the field of specifically adsorbed anions. This was realized a decade ago by the Frumkin school in proposing[30] a synthesis of the simple water-reorientation and anion interaction models in the form of what may be called an *anion*-induced *water-disorientation* model. The main view point of this model has since been emphasized by Payne[17] by Devanathan *et al.*[32] and by Hills.[33]

Let us consider how the anion-induced water-disorientation model fits the experimental trends in the case of ions which undergo weak specific adsorption. (In the case of strongly adsorbing ions such as bromide, the degree of quasichemical interaction with the mercury surface probably over-shadows the electrostatic interaction with the inner layer water and the characteristics of the capacitance hump will be determined to a large extent by the "quasi-chemical" interaction).

As the electrode charge is made more and more positive starting from the pzc, there are two main effects:

a) the direct effect of the increasingly positive electrode charge is to set up an increasingly strong field which in turn will increasingly orient the water molecules parallel to the field;

b) the indirect effect is to increase the extent of anion specific adsorption and therefore to increase the fraction of first layer water molecules bound in the hydration sheaths of the anions.

Since the water molecules in the anion hydration sheaths may be expected to adopt orientations which compromise between the aligning influences of the electrode field and the field of the anions, the effective role of the specifically adsorbed ions is to inhibit the orientation induced by the field, i.e., to act as a disorienting influence on the water molecules in the first layer. Such a disorientation leads to an increase in capacity. The disorientation and the capacity cannot however increase indefinitely because of two factors:

1) with increasingly positive charge, the orienting influence of the field becomes stronger and stronger, and

2) the rate of increase in the specific adsorption of anions must show a decrease with increasing electrode charge (this is a central point in the anion lateral interaction model) not only because of spatial restrictions arising from increasing coverage[32] but also because of increasing lateral repulsion.[10]

The resultant effect of these two factors is that, after attaining a maximum disorientation corresponding to the hump peak, the net orientation starts increasing with increasing positive charge—this corresponds to a fall of capacity.

On the basis of the above anion-induced water disorientation model, several consequences emerge.

1) The anions specifically adsorbed on the electrode surface are considered to be partially hydrated, i.e., dehydrated in the direction of the electrode surface. The relatively large surface area occupied by such partially-hydrated adsorbed ions enhances hump formation by a spatial saturation effect. Incidentally, the cross-sectional area of a partially dehydrated anion is in fair agreement with the area of 30–40 Å^2 derived by theory on the basis of a field-induced reorientation mode.[26]

2) The stronger the hydration of the anion (for example, F^-), the less pronounced will be the hump because of the reduced freedom of rotation of water molecules in the hydration sheaths of ions.

3) The maximum adsorption of simple aliphatic molecules should occur at some negative charge on the electrode. This is because the adsorption of organic molecules is competitive, not only with adsorbed water molecules (as expected in the simple theory,[10] but also with the invariably present

specifically adsorbed anions which are desorbed only on the cathodic side of the ecm.

4) In dilute solutions of weakly adsorbed anions, the capacitance hump should occur at *positive* rational potentials if adsorbed water molecules have a residual negative orientation at the pzc. This is because the anion-induced disorientation of inner layer water (arising from the water of hydration of adsorbed anions) at positive electrode charges will increase the capacitance initially. However, with increasing positive electrode charge, the enhancing effect on the capacity is more than compensated by the capacitance fall due to stronger electrode fields and due to diminishing disorientation from an increasing coverage by like-charged, large-sized anions adsorbed. In sufficiently concentrated solutions of weakly adsorbed anions, the hump can even occur at negative rational potentials[34] due to the increased probability of adequate anion adsorption required to produce hump effects.

3.4 The dielectric constant of interfacial water

The dielectric saturation of water adjacent to the electrode due to the intense electric field at the interface has been well recognized[35] by the use of a dielectric constant of 6–7. It is clear, however, from the above discussion that this saturation value of the dielectric constant is applicable only at values of electrode charge sufficiently negative to ensure an ion-free oriented water layer. At other values of electrode charge, $q_M \gtrsim 0$, the penetration of the ion-free layer by specifically adsorbed anions is bound to perturb the dielectric constant, and to introduce the conceptual problem of the dielectric constant of a water layer interspersed with the charges of specifically adsorbed ions. Under these conditions, the dielectric constant of a region one water molecule thick becomes more of a parameter than a quantity which has been given a theoretical basis. One point, however, is clear—the bulk dielectric constant of water has little bearing on phenomena at the electrode-solution interface because the water structure in this region is so different from that of bulk water. In this context, some recent work on non-aqueous solvents is worth noting. It has been shown that the differences in the solvent capacity observed in the constant capacity region are far more sensitive to the size of the solvent molecule than to the bulk dielectric constant.[36,37]

4 THE INFLUENCE OF WATER ON THE SPECIFIC ADSORPTION OF IONS

Bockris and coworkers have emphasized[10,38,39] sufficiently the qualitative relationship between the degree of specific adsorption of ions (especially the halide and alkali metal ions) and the energy of ionic hydration. The basic model used in the discussion of such relationships is one in which the state of specific adsorption involves a partially dehydrated ion in "contact"—hence the more illustrative term "contact adsorption"—with an electrode locally dehydrated in the direction of the ion.[21,38,39] Thus the model requires a partial dehydration of the specifically adsorbing ion, and consequently ions with sufficiently stable primary hydration shells remain in the OHP and do not specifically adsorb.

That the energy of desolvation is a major factor determining adsorbability has been further confirmed by recent studies[26] of the adsorption of ions on mercury from different non-aqueous solutions such as water, formamide, DMF, alcohols, DMSO which show that the sequence of adsorbability, viz., $I^- > Br^- > Cl^- > SCN^- > NO_3^- > ClO_4^- > BF_6^- > PF_6^- > F^-$ is practically unaffected by the solvent.

In view of the importance of hydration, one can understand the absence of a simple corelation of the adsorbability with the strength of the covalent bond between the electrode metal and the adsorbable ion.[38] There is, however, some unexpected evidence that certain strongly hydrated cations such as Cd^{++} show significant specific adsorption at the metal-solution interface. This indicates that there may be other ways of looking at the forces of specific adsorption.

In this context, mention may be made of other relationships which have been noted. For instance, a reasonable correlation has been shown[40] between the adsorbability of halide ions and the electronegativity difference between these ions and mercury. Again, in a recent work,[41] Barclay has suggested a possible link between the adsorbability of a given ion and the electron affinity of different electrode metals, indicating that the strength of electrosorption of ions on metals seems to be that of a semi-polar bond.

It appears therefore that there is a need for a more comprehensive correlation involving both hydration and bonding parameters with adsorbability. Such a correlation may require a consideration of the semi-polar bond between a partially dehydrated ion and a metal.

5. WATER AND ORGANIC ADSORPTION

The fact that the electrosorption of organic molecules from aqueous solutions involves the displacement of water molecules adsorbed on the electrode was emphasized and treated quantitatively from the molecular point of view by Bockris, Gileadi and Müller.[42] However, in this theory, the change in the free energy of adsorption with a change in the electrode charge is assumed to be determined entirely by lateral interactions among adsorbed water molecules in two orientations. The validity of this assumption has been questioned.[43] In particular, it has been pointed out[20,43] that the theory cannot account for the effect of the size of the adsorbate molecules on adsorption, and that the theory ignores the energy change of the ionic double layer with adsorption.

In view of the mounting evidence that all anions are specifically adsorbed at least to some extent, it is reasonable to suppose that the adsorption of organic molecules from aqueous solution involves competition with adsorbed water molecules alone on the far cathodic side of the ecm, and with both adsorbed water molecules *and* partially hydrated anions around the ecm as well as on the anodic side. Support for this mechanism of adsorption is available from the observed dependence of *anodic* peak capacitance[44] and *anodic* peak potential[45] on the nature and concentration of the anion. In contrast, the *cathodic* desorption peaks (peak capacitance and peak potential) are virtually independent of the nature of the supporting electrolyte.

It follows that the organic molecule should displace during its adsorption at least one adsorbed, partially hydrated anion on the far anodic side of ecm, and at least one adsorbed H_2O molecule on the far cathodic side. An intermediate type of displacement should prevail around ecm. A molecular theory of adsorption is desirable which takes into account the interaction of a weakly hydrated organic molecule with the electrode field under the above conditions of competitive adsorption.

The actual number of adsorbed water molecules displaced on the adsorption of one organic molecule has been a subject of some controversy. Areawise, an aliphatic molecule, normally oriented to the electrode, must displace 3 to 6 H_2O molecules in order to interact with the electrode. However, since the Frumkin isotherm has been found to fit very well the adsorption data of a variety of organic molecules[46,47] and since this isotherm implies that one water molecule is displaced per organic molecule adsorbed, it has been inferred [and confirmed by other arguments[46]] that adsorbed water is present as clusters on the electrode surface. On the other hand, adsorption from mixed solvents has shown[48] the desirability of considering adsorbed water to be present as monomers. Moreover, as stated before, it is difficult to visualise the orientational freedom (as evidenced by capacitance humps) of two dimensional clusters of water molecules at the interface. There appears to be a need for reconciling the broad applicability of the Frumkin adsorption isotherm with the displacement area of inner layer water during competitive adsorption.

6 WATER AND CHARGE-TRANSFER PROCESS

The discussion has dealt thus far with interfaces under conditions quiescent in so far as electron transfer is concerned. Turning now to charge transfer at interfaces, naive considerations may lead to the view that there are only two participants (the electron and the oxidant/reductant particle) and that the water molecules of the aqueous solution serve as a subdued backdrop. The picture however is quite different and it is now generally recognized that water plays a central role in the phenomenon of charge transfer at interfaces.

In a sense, the crucial role of the solvent was seen over 40 years ago when Gurney discussed "the quantum mechanics of electrolysis" as his paper was entitled.[50] Fresh from his independent treatment (with Condon) of tunnelling in the alpha-decay of nuclei, Gurney saw interfacial charge transfer as an electron-tunnelling phenomenon. From the standpoint of the radiationless tunnelling of an electron from an energy level in the electrode to a level of *equal* energy in the oxidant particle, the main problems are two-fold:

1) to specify the electron energy levels in the electrode and in the oxidant particle; and

2) to describe the energy barrier through which the electron tunnels.

The energy levels in the electrode are a comparatively simple matter in that well-known distribution laws can be used, e.g., the Fermi–Dirac distribution. The electronic energy levels in the oxidant particle involve more complications essentially because (as Gurney realized) the positions of electronic levels of ions *in aqueous solution* are different from those *in vacuo*, the difference arising from the essentially electrostatic interactions of ions with water. It is in this way that water enters the picture with regard to the energy barrier confronting the electron in the metal, Gurney synthesised it from the image interaction energy between an electron and the metal and from the coulombic interaction between an electron and an ion. Such a synthesis, the electron analogue of the synthesis of two Morse curves for pseudotriatomic systems, involves two assumptions:

a) the electron interaction with the metal is unaffected by the proximity of the ion and the environmental water, and

b) the electron interaction with the ion immersed in water is unperturbed by the presence of the metal.

Taking the case of H_3O^+ discharge,

$$H^+ - H_2O + e \longrightarrow H + H_2O$$

Gurney specified the electron energy in the metal by Φ the work function, and the electron energy in the hydrogen ion by $I - L - R$ where I is the ionization potential, L, the hydration energy of the proton and R, the $H - H_2O$ repulsion energy. The condition for radiationless electron tunnelling becomes

$$\Phi = I - L - R$$

Gurney's statement of the tunnelling condition is valid only for weak interactions between the metal and hydrogen atoms, and therefore Butler[51] incorporated the M—H adsorption energy, A by writing the condition in the form

$$R(x) - A(x') = I - L(x) - \Phi$$

where it has been emphasized that $R(x)$ and $L(x)$ are functions of the $H—H_2O$ and $H^+—H_2O$ distance x, and $A(x)$ depends on the M—H distance x'. This condition corresponds to electron tunnelling at the intersection of the Morse curves for the $MH + H_2O$ and $M(e) + H_3O^+$ systems. In other words, electron transfer cannot take place to the $H^+ - H_2O$ bond.

Notwithstanding the wide separation between the $H^+ - H_2O$ vibration levels in the *gas* phase, Gurney assumed that these levels "are sufficiently blurred by the interaction with adjacent (water) molecules to be treated as forming an almost *continuous* spectrum of levels." It followed from this assumption that the H_3O^+ system is thermally excited according to the Boltzmann distribution into a state appropriate for tunnelling. Thus, the aqueous medium has a crucial role in the Gurney approach—the role of conferring thermal excitability to the reactant particle. In this simple picture, the electron becomes the only quantum sub-system and the H_3O^+ and the water are the classical parts of the system. Further, the classical sub-systems are responsible for the activation of the total system with the quantum sub-system (the electron) being responsible for the transition probability.

After some decades of oblivion, several authors[51,53] resurrected the Gurney approach in particular Bockris and coworkers.[53] As the situation stands today, it appears that the Gurney approach has the appeal of a simple and elegant picture which facilitates qualitative understanding of situations involving interfacial charge transfer.

The case with which electron transfer can be pictured in the Gurney model is perhaps because the approach is almost wholly classical except for the use of the well-known quantum mechanical formula for tunnelling. In particular, it stresses that, before electron tunnelling can take place to a H_3O^+ ion, for example, the environmental water has to blur the vibrational levels of $H^+ - H_2O$ into a continuum and the hydration bond between the proton and its water molecule must undergo suitable stretching. Qualitatively, one can visualize an analogous distortion of the primary hydration shell as a pre-condition to electron transfer in redox reactions. One of the major problems in the Gurney model concerns the energy level scheme in the reactant particle and how this scheme is converted into a continuum by the electrostatic action of the surrounding water. Even in the case of the $H^+ - H_2O$ system, the mode of conversion of the vibrational levels into a continuum has not been worked out, and therefore in case of more complicated systems, the problem would be even more difficult. Another problem involves the accurate representation of the electron energy barrier and a rigorous calculation of quantum transition of an electron through this barrier. Answers to these questions generate difficulties in the way of numerical calculations with the Gurney treatment.

Over the past decade and a half, several workers noteworthy amongst who are Marcus,[55,56] Hush,[57] Hale[58] and the Levich school[59,60,65] have adopted a different line of attack on the problem of charge transfer at electrode-aqueous solution interfaces. As in the Gurney model, this second approach looks upon the reorganization of the water structure in the immediate neighbourhood of a reactant particle as a major factor in the activation process. The need for this water reorganization becomes obvious[61] if one considers a simple redox reaction which does not involve bond breaking, e.g., $Fe^{+++} + e \rightarrow Fe^{++}$. Since the structure of the hydration sheaths around these ions depends upon the ionic radius and charge, it is clear that the conversion of an Fe^{+++} to a Fe^{++} involves not only electron transfer but also reorganization of the hydration sheaths. Thus, water rearrangement becomes a pre-condition for electron transfer.

The work (E_W) of water rearrangement is a crucial component of the free energy of activation of an interfacial charge transfer process, and its calculation has occupied the attention of the contributors to this point of view. Instead of a simple Born model in which the ion is taken as a uniformly charged sphere interacting electrostatically with a dielectric continuum, the Marcus-Hush treatment has involved a division of the aqueous environment of an ion into a primary hydration sheath containing water molecules fully oriented in the ionic field, and the water outside which is treated as a continuum. The inner region—the primary hydration shell—is treated microscopically in some appropriate manner, and the Born equation for the free energy of hydration has been frequently used for the water outside the primary shell. However, such a macroscopic approach is not unavoidable, and microscopic treatment of the interaction between the solvent and the primary hydrated ion has been developed in detail by the Levich school.[59,60,65] In their view, the crucial point is the thermally-induced fluctuations in the specific polarization of the aqueous polar medium viewed as a continuum. These fluctuations can be represented by optical polarization waves or alternatively by optical phonons. The activation of the ion occurs by interaction with the phonons in a multiphonon process.

In their treatment, the Levich school have taken the view that the vibrations within the primary solvated ion, e.g., the $H^+ - H_2O$ vibrations, have a $h\nu \gg kT$ and therefore these vibrations are not thermally excitable. This view has turned out to be an important bone of contention with the Bockris school[62,63] which argues the Gurney cause and asserts that these H^+ –

H_2O vibrations are thermally excitable because they have been smeared into a continuum by interaction of the H_3O^+ with the surrounding water. In the gas phase, the position is clear—the $H^+ - H_2O$ vibrations have $h\nu \gg kT$. It is also certain that the vibrational levels will be squeezed together by interaction (essentially electrostatic) with the surrounding water. Whether they are in fact blurred into a continuum must be decided by spectroscopy which however has not settled the problem unequivocally. It appears, however that the bending modes in water are classical, but this would mean that the stretching modes are unlikely to be classical.

In asserting that the $h\nu$ for the $H^+ - H_2O$ stretching is large compared to kT, the Levich school is forced to take up the double adiabatic approximation, i.e., the electron is a fast (quantum) sub-system compared with the proton which is in turn a fast sub-system compared with the classical solvent. An unfortunate feature of the Levich work is that, in contrast to experiment, it has not yielded the overpotential-log current density straight lines (Tafel lines) over the large number of decades observed in experiment. It is not clear, however, whether this descrepancy arises from the fact that the $H^+ - H_2O$ stretching was treated as non-classical in which case it must be stressed that the Levich formalism is generalized enough not to compel treatment of the $H^+ - H_2O$ vibration as being classically frozen i.e., thermally unexcitable.

In the case of charge transfer in *metal deposition* process, there are several additional features involving water.[64] These features emerge by noting that metal deposition must be represented by

$$M(H_2O)_n^{z+} + ze\ (\text{from battery}) = M^{z+} + ze\ (\text{in metal}) + n\, H_2O$$

rather than the usual:

$$M^{2+} + ze = M$$

The former scheme emphasises that the process of metal deposition is in fact a process of conversion of a fully hydrated ion in the solution into a fully *de*hydrated ion incorporated into the metal lattice. Thus metal deposition involves dehydration and lattice incorporation. It is generally accepted that the dehydration and lattice incorporation are not accomplished in a single step. Rather, the existence on a solid surface of atomic planes, steps, kinks and edge vacancies and holes facilitates a step-wise process in which the ion initially with its full complement of hydration water molecules is progressively dehydrated as it is transferred from the OHP to the plane, from the plane to the step, from the step to the kink, then on to the edge vacancy and finally it is incorporated into a hole.

The mechanism for this stepwise dehydration is yet unclear but perhaps it has to do with the differences in the symmetry of the electrode field at the different sites; and the influence of these symmetry differences on the interaction between the water molecules in the primary hydration sheath and the ion. Another fundamental problem concerns the stage (during the stepwise dehydration) process at which electron transfer occurs. Related to this problem is the question of the partial charge on the depositing ion during the intermediate stages of deposition.

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Discussion of the Report of A. K. N. Reddy and S. Sathyanarayana

R. Parsons. I should like to say a little bit more about the calculation of dielectric constants ε and thickness x_2 in the inner layer of an electrode. If the capacity is regarded as a parallel plate condensor, its value gives only the ratio of ε to x_2. As far as I know there are only two experimental routes to these quantities separately.

1) The value of ε may be deduced from the adsorption of a dipole molecule (Schapink *et al.*, *Trans. Faraday Soc.*, **56**, 415 (1960) Parsons, *Proc. Roy. Soc.* **A261**, 79, (1961) like thiourea. From the Helmholtz formula $\Delta\phi = -4\pi N\mu/\varepsilon$ and the assumption that μ has its value in the bulk, an effective value of ε can be obtained.

It ranges from 6–14 with a hump near the capacity hump (R. Parsons and P. C. Symons, *Trans. Faraday Soc.* **64**, 1077 (1968). Together with the capacity this leads to a thickness (x_2) of 3–4 Å.

2) As Reddy has discussed, the thickness can be estimated in the absence of specific adsorption by comparing experimental surface excesses with those calculated from Gouy-Chapman theory in a way analogous to the calculated of the ion-free layer at the air-water interface discussed by Randles. For NaH_2PO_4, Dr. Zobel and I (*J. Electroanal Chem.*, **9**, 333 (1965)) found values between 2.5 and 3.5 Å in reasonable agreement with the values obtained by the route above.

I must say that I have doubts about the results of Takahashi and Tamamushi.[1] Measurements in 10^{-4} M HCl were made in 1939 by Frumkin *et al.*[2] and in very dilute NaF solutions by Delahay[3] using the coulostatic method method more recently. There was no evidence of a decrease in the capacity of the inner layer from these results.

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J. E. B. Randles. I would like to ask Dr. Parsons how his results for the adsorption of thiourea lead to a value for the dielectric constant of the region close to the mercury independent of layer thickness.

R. Parsons. I think that the screening by the diffuse layer and the higher bulk dielectric constant confines the lines of force largely to the inner layer. Thiourea is a notably small molecule which fits nicely into the inner layer.

J. E. B. Randles. I was thinking of the fact that the lines of force from the thiourea dipoles are likely to penetrate to appreciable distances out of the layer (say one or two water molecules thick) adjacent to the mercury surface.

The distance to which the field will penetrate will be greater the greater the separation of the thiourea dipoles. It is my feeling, therefore, that the dielectric constant appearing in the formula is an average value over a layer whose thickness depends on the surface concentration of thiourea.

R. Parsons. If the adsorption of thiourea is represented in terms of a two-dimensional imperfect gas model, the second virial coefficient can be reasonably well interpreted (Parson, *Proc. Roy. Soc.*, **A261**, 79 (1961)) in terms of dipole-dipole interaction using the dielectric constant obtained as above. This tends to support the simplified approach.

M. Mandel. In the equation which Parsons used in his first method to compute ε, appears the dipole moment μ of thiourea which he took equal to the bulk value in the solution. It should however be emphasized that this bulk value is not well known and certainly differs from the permanent dipole moment of the isolated molecule because of the inducent moment due to some reaction field. For the same reason it is not to be expected that the dipole moment in the bulk will be equal to the dipole moment of the adsorbed molecule at the surface, as the reaction field at the surface certainly will differ from this field in the bulk.

So the calculation of ε in the surface layers involves so many assumptions that it does not look different than adjusting this parameter straight away.

M. Magat. I think we must be very cautious in using notions like dipoles or dielectric constant when distances of the order of 3 Å are concerned. Dipoles are the first term of a development of the electrical field due to a charge distribution in a molecule and can be used only at distances R much larger than the "length" of the dipole that, at least in the case of water, is of the order of 1 Å. It is even more dangerous to speak for such distances of the dielectric constant which is a macroscopic notion. I fear we have to use "molecular" models of water and do numerical "calculations," which I grant are difficult but are the only ones that can have a sense.

M. Mandel. I wonder if it would not be better to drop the concept of dielectric constant altogether in as far as surface layers are concerned and rather use the much better definable concepts of position-depending polarization or even position-depending average dipole moment etc.

A. K. N. Reddy. Firstly, the observation of Takahashi and Tamamushi may be due to the fact that they used systems (perchlorate solutions) different from those used by Frumkin and Delahay. Secondly, Takahashi and Tamamushi observed an intial increase of capacity with concentration followed by a constant capacity at higher concentration. If the limiting concentration above which there is a constant capacity depends on the electrolyte, then it may be that the concentrations used by Frumkin and Delahay were not low enough. In any case, it is not easy to explain the concentration dependence of the cathodic capacity—perhaps the dependence is because at such low concentration ($\simeq 10^{-5}$ M), the diffuse charge region is so diffuse (large Debye reciprocal length) that the effective thickness of the parallel-plate capacitor is increased.

R. Parsons. Yes, I agree that the idea of a dielectric constant is oversimplified. A much more elaborate treatment has been given by Macdonald and Barlow (*Adv. Electrochem.*, Vol. **6**, 1 (1967)) but I do not think that it has yet been related to experiment convincingly.

H. G. Hertz. The reorientation time of a water molecule in pure water as well as in the ionic hydration sphere is fairly wellknown. My question is: Does one know anything regarding the reorientation time of the water molecule when it is at the Hg-surface?

R. Parsons. Experimental measurements of double layer capacity (Armstrong *et al.*, *Electrochim. Acta*, **13**, 215 (1968)) show no evidence of a relaxation effect up to 1 MHz. This suggests that the relaxation time of water in the inner layer is not much different from that in bulk water.

G. Careri. Perhaps one can use attenuated infrared absorption, or better the laser Raman scattering, to detect spectroscopic properties of the adsorbed layer provided they are vastly different from the ones of pure water.

R. Parsons. Raman spectra of species adsorbed at the electrode surface have now been obtained. (M. Fleischmann, P. J. Hendra, and A. J. McQuillan, *J. C. S. Chem. Comm.*, 80 (1973)).

H. D. Hurwitz. The point has been stressed by different authors that the value of the excess surface entropy at the ideally polarized interphase can give many indications on the structure of the electrochemical double layer and especially on the local structure of the water adsorbed at the electrode. This surface entropy is directly related, by means of Gibb's equation, to the temperature coefficient of the surface tension γ. Keeping the density of charge q of the electrode constant, it is convenient to use the differentiation of the function introduced by Parsons, $\xi = \gamma + qE$, instead of the differentiation of the surface tension, the electromotive force E being measured, for example, with reference to a calomel electrode. Under these conditions, the expression:

$$\left[\left(\frac{\delta\xi}{\delta T}\right)_{q,p,m_{\mathrm{Cl}^-}} - qE'_T\right] \tag{1}$$

where E'_T is the temperature coefficient of the reference electrode, leads directly to the excess surface entropy at the ideal polarized electrode.

Determination of these values, at 25°C have been performed in our laboratory by Dr. D'Alkaine and Miss Charles for NaCl and NaF solutions. Such results, expressed in function of q, are shown in Fig. VI.1. For 0.1 molal solutions of NaCl and NaF, the shape of the curves are similar to those presented by G. Hills and R. Payne (*Trans. Farad. Soc.*, **61**, 326 (1955)).

Inspection of the curves shown in Figure VI.1, indicates a maximum at about -3μ Cb/cm^2 and some effect of specific adsorption of the Cl^- ion is apparent from a comparison with the F^- system where the anion is not appreciably adsorbed in the inner Helmholtz layer. It is therefore tempting to discuss the influence of the Cl^- ions in terms of some competition between water molecules and ions specifically adsorbed. Let us emphasize however that such matter should be treated with reserve since the expression (1) yields a complex quantity depending on the contribution of the diffuse part of the double layer, of ions and water coadsorbed in the inner layer and finally on the contribution of the mercury side of the electrochemical interphase. In order to get a better interpretation of surface excess extropies, we have therefore suggested

1) to proceed with measurements of temperature effects in systems composed of mixed electrolytes of the type NaF—NaCl at constant ionic strength,

2) to choose a model of a rather compact monolayer for the inner Helmholtz layer and to adopt the Gouy–Chapman theory for the diffuse layer.

As indicated by Professor Reddy in his talk, the first condition yields direct knowledge of absolute excess of chloride ions, specifically adsorded Γ_{Cl^-}. Therefore, it is possible to rewrite expression (1), keeping, in the partial differentiation $\Gamma^i_{\mathrm{Cl}^-}$ constant instead of the molality m_{Cl^-}

$$\left[\left(\frac{\delta\xi}{\delta T}\right)_{q,p,\Gamma^i_{\mathrm{Cl}^-}} - qE'_T\right] = \frac{\dot{S}^i_0 - \dot{S}^{s\,\mathrm{ln}}_0}{\Omega_0} + F(\Gamma^\circ) + F^1(\Gamma^{\mathrm{Hg}}) \tag{2}$$

The second condition, thus the monolayer model, may now be used in order to derive properly the right hand side of Eq. (2) where $\dot{S}^{s\,\mathrm{ln}}_0$, $\dot{S}^i_0$ and Ω_0 are respectively the partial molar entropy of water in the bulk and in the monolayer and the partial molar area of water in the monolayer, the two latter thermodynamic quantities being function of 9 and $\Gamma^i_{\mathrm{Cl}^-}$. Furthermore, the term $F(\Gamma^0)$ represents the effect of the diffuse layer which can be calculated and $F'(\Gamma^{Hg})$ the contribution of the Hg on the metal side of the interphase, is unfortunately unknown. The values given by Eq. (2) have been plotted in Figure VI-2 as a function of q.

The method described above is most informative if the difference

$$\left(\frac{\delta\xi}{\delta T}\right)_{q,\,\Gamma^{i}_{\mathrm{Cl}^-},\,p} - \left(\frac{\delta\xi}{\delta T}\right)_{q,\,p} = -\left(\frac{\dot{S}^{i}_{0}}{\Omega_0} - \frac{\dot{S}^{s\,\ln}_{0}}{\Omega^{0}_{0}}\right) \tag{3}$$

is computed, where the subscript indicates the absence of specifically adsorbed ions (the pure NaF system). The measurements shown in Figure VI-2 suggest, at small values of $\Gamma^{i}_{\mathrm{Cl}^-}$, a partial molar entropy of the type

$$\dot{S}^{i}_{0}(q, \chi_0) = \dot{S}^{i}_{0\,\circ}(q) - f(\lg \chi_0) \tag{4}$$

where χ_0 is the molar fraction of water in the inner layer and the function $f(\lg \chi_0)$ does not depend on q. Such behavior of S^{i}_{0} resemble that expected in an ideal mixture such as would occur in the Henry region of an adsorption isotherm. A similar pattern of $\dot{S}^{i}_{0}(q, \chi_0)$ in function of q is observed at larger $\Gamma^{i}_{\mathrm{Cl}^-}$ but the slope of the curve is significantly larger than that at small ionic specific adsorption. This change might be attributed to different values of $S^{i}_{0}(q)$. Considering the effect of $\Gamma^{i}_{\mathrm{Cl}^-}$ at larger as well as at small specific ionic adsorption, it appears as if the presence of specifically adsorbed ions was adding an entropy of mixing but did not influence the configuration of adsorbed water. Indeed, it is probable that any change of configuration of field dependent oriented water molecules, promoted by the anions, should be a function of q. Further rather straightforward thermodynamic considerations show that the condition:

$$\frac{\delta}{\delta q}(\dot{S}^{i}_{0} - \dot{S}^{i}_{0})_{p,\,T,\,\Gamma^{i}_{\mathrm{Cl}^-}} = 0 \tag{5}$$

is fulfilled as soon as the free energy of adsorption of Cl^- ions becomes a linear function of q. Such adsorption isotherms, congruent with respect to q, have been frequently encountered.

One could conclude in pointing out that no particular effect is observed in the region of the differential capacity hump at positive values of q. As noticed by Hills, the maximum of partial molar entropy at $-3,8\mu$ C/cm^2 is found near to the value of the charge where it has been suggested that the water molecules in the inner layer are not oriented in any preferential direction.

R. Parsons. I would like to express my agreement with Reddy's thesis, antithesis and synthesis of the theories of the hump. I believe that examples of each theory exist.

In fluoride solutions the capacity of Hg shows a hump in a region where there is no specific adsorption. This seems to be due to water orientation.

Similar effects occur in other halides if one analyses the data so as to eliminate the effect of the specific adsorption (cf. Grahame's work in JACS **80**, 4201 (1958)).

On the other hand a good example of a hump due almost entirely due to specific adsorption is that of benzene-m-disulphonate (Parry and Parsons, *Trans. Faraday Soc.*, **59**, 241 (1963)). In fact any adsorption isotherm taken up to saturation must produce a hump. For many simple inorganic anions only the lower values of surface coverage are accessible and no pure adsorption hump is seen.

Finally there is clear evidence of the effect of adsorbed ions on the water orientation hump in the curves for ClO_4^-, HSO_4^-, $H_2PO_4^-$, isoelectronic ions which are increasingly solvated in this order and decreasingly hump generative.[1] There is also a gradation in their adsorption properties, in that ClO_4^- is adsorbed well on the negative side of the pzc, the amount of adsorption growing slowly with increase of positive charge. In contrast $H_2PO_4^-$ is not adsorbed, until the charge becomes positive and the adsorption increases rapidly with increase of positive charge.

The geometrically isomeric maleate and fumarate ions also have strikingly different hump-forming properties. The hump is strongly marked with maleate and almost non existent with fumarate. Reilly and I (*J. Electroanal Chem.*, **24**, (1970) App. 23) have suggested that the charges on the fumarate are close to the Hg surface and interact less with the water than the maleate whose charges can project into the solution.

Reference

1. R. Parsons, *Rev. Pure and Appl. Chem.*, **18**, 91 (1968).

J. E. Desnoyers. The excess properties of aqueous electrolyte solutions cannot be explained easily if we only use arguments based on long-range forces between ions, association and coulombic hydration of ions. Since a charged mercury surface can be considered as a large ion, the phenomena existing in electrolyte solutions should also be present near electrodes. As the ions approach the surface there should be some extra ordering or disordering of the water structure and this should cause extra attraction or repulsion between the ions and the electrodes. I therefore agree with Prof. Parsons that structural changes near ions can very well be involved in the peculiar behaviour of the capacity curves.

J. E. B. Randles. Referring to the different capacity curves for mercury in solutions of fumarate and maleate ions, may I ask Dr. Parsons if he is sure that this difference is not due to a difference in the adsorption isotherms of the two ions.

R. Parsons. In fact we have made measurements in the maleate and fumarate systems at various concentrations and there is no great difference between the adsorption isotherms. In particular the plots of the specifically adsorbed charge against the charge on the electrode seem to have a similar slope.

E. Gileadi. I would like to ask Dr. Parsons what his opinion is regarding the orientation of water molecules adsorbed at the surface of the uncharged electrode (i.e. at the potential of zero charge). A model taking into account only two possible orientation is convenient from the mathematical point of view and has been adopted by several authors. It may be argued that several more orientations are possible and any model must take into account the sum over all such orientations. On the other hand, if the water molecule can take many positions at the surface, which differ only slightly from each other then its rotational motion would not be hindered and a high dielectric constant would result at or near the potential zero charge.

R. Parsons. This is only an opinion, but it seems to me more likely that the surface layer consists not of water oriented strongly in two directions but rather of molecules oriented weakly in the two or more directions. Perhaps there is rather strong two-dimensional interaction and rather weak interaction between this layer and the water further from the electrode as suggested by Watts-Tobin, *Phil. Mag.*, **6**, 133 (1961).

The relation of the position of the hump with respect to the point of zero charge may be misleading. If the anions and cations have different distances of closest approach, then the parallel plate capacity may be strongly potential-dependent and the combination of this steeply raising curve with a hump may shift the position of the maximum considerably.

H. G. Hertz. In your pictures you have drawn single water molecules and ions but the mercury surface was given as one simple straight line. What are the instantaneous deviations from the exact mathematical plane in a molecular scale? Considering the fluctuations in shape of the Hg surface may also be useful in conjunction with the problem of dielectric net polarisation of the surface water layer when one assumes that the water molecules have a preferred orientation relative to themselves and relative to the Hg atoms.

A. K. N. Reddy. I believe there is an ellipsometric observation of Lord Rayleigh which indicated that the roughness of the surface of liquid mercury is only of the order of one atom diameter. In any case, it is always presupposed that liquid mercury does not have the surface heterogeneities of a solid metal.

H. G. Hertz. If I should estimate the reorientation time of the water molecule (i.e. the "dielectric relaxation time") at the interface water-mercury my first question would be: What is the selfdiffusion coefficient of the Hg atom in liquid Hg?

R. Parsons. I think that the self diffusion coefficient of Hg must be large, perhaps of the order of 10^{-5} cm^2/s. cf A. G. Stromberg, *Dokl. Akad. Nauk. U.S.S.R.*, **85**, 831 (1952).

H. G. Hertz. If this is so, i.e. if $D_{Hg} \simeq 10^{-5}$ cm^2/sec, then every motion in the liquid should as well be fast. This is so because we know that the Hg-water interaction is weak, then, if there is weak interaction and any long time correlations of forces are absent (i.e. Hg-chain also move fast) then there should hardly be anything to cause slow motion of H_2O molecules. Perhaps the guess that the water reorientation time of the surface is 2–3 times that of the bulk water is reasonable.

E. Gileadi. I think that the self diffusion coefficient of mercury may not be relevant with respect to the layer of mercury atom at the interphase, since these may be localized by partial bonds formed with the adsorbed water molecules. Thus, I would still expect the relaxation time for rotation of water molecules at the mercury surface to be longer than in the bulk.

H. G. Hertz. The adsorption energy is the energy required for bringing the water molecule from the mercury surface to infinite separation in vacuo. But in our situation this molecule is never brought in vacuo we have only to do with an energy of "rearrangement" necessary to turn the molecule over *in the liquid*. Usually, one estimates $E_A \simeq \frac{1}{3}E_{vap}$.

J. E. B. Randles. Dr. Hertz has remarked on the possible "roughness" of the interface between mercury and an aqueous solution. This roughness must be related to the excess entropy of the interface. From various measurements, including those mentioned a few minutes ago by Dr. Hurwitz, it emerges that the surface excess entropy of the mercury/aqueous electrolyte interface at the pzc is less than the sum of that of the mercury/gas interface and that of the water/gas interface. The roughness of the mercury/aqueous solution interface is most probably less than that of the aqueous solution/gas interface. The roughness probably increases with increasing charge on the interface (i.e., decreasing interfacial tension) on both sides of the ecm.

I would like to add some remarks about water near the mercury surface. The question has been asked whether a water molecule in contact with mercury is likely to have two or several preferred orientations relative to the mercury. I think that these molecules are influenced at least as much, probably more, by their aqueous neighbours than by mercury. At zero charge on mercury, there is evidence that these molecules, like those at the water/gas interface, have a slight preference for orientations with the protons directed towards the aqueous phase. The reason for this is probably to be found mainly in the structure of the water and the change in it as the interface is approached. At the interface with mercury, of course, considerable modification (i.e polarization) of this structure must occur as a result of charging the interface. The influence of the interface on the water structure, and the rapid change of field strength with distance, in the layer a few molecular diameters thick on the aqueous side of the interface, are such as to make the use of a macroscopic concept such as dielectric constant inappropriate.

However, until we have much more detailed information about the interaction of water molecules with each other, with ions, and with mercury, we may continue to use such concepts as a short-hand expression of the inexact knowledge which we have.

H. D. Hurwitz. Considering the bell-shape curves for the surface excess entropies which I have presented earlier, I must say that I am somewhat puzzled by the values of the ordinate. In some recent experimental data available to us, the temperature coefficient of the surface tension of the pure Hg/vacuum interface has been estimated to be about 4.10^{-9} cal K^{-1} cm^{-2}. However, one observes that the experimental value obtained at the maximum of the ideal polarized mercury interface is less.

If, notwithstanding this fact, one keeps believing that the contribution of the metal of the electrochemical interphase is less than 3.10^{-9} cal K^{-1} cm^{-2}m the resulting positive partial molar entropy of adsorption at the maximum could be interpreted in terms of a larger number of partially hydrogen unbound water molecules at the surface than in the bulk. For example, taking the view-point of Nemethy and Sheraga, that is tantamount to saying that at the surface a given number of H bonds are broken which makes the structure equivalent to bulk water structure prevailing at higher temperature. Under these conditions, the decrease on each side of the maximum could be attributed to the orientation of the water dipoles in the electric field.

It remains that the actual results are very confusing. It seems that today no definite structure of water at the electrode interface can be suggested and that many models are open to question.

A. K. N. Reddy.

1) The act of metal deposition may be viewed as a multi-step process of successive dehydration involving transfer from the OHP to the plane surface diffusion to steps, kinks, etc. culminating in metal deposition. If, after transfer to the plane, the ion is completely discharged, then it should not retain any water of hydration and it should be considered an adatom. If,

however, the entity on the plane is viewed as being partially hydrated, than it should be treated as an adion.

2) There has been work directed towards identifying the rate-determining step in the multi-step successive dehydration process. Bockris and Mehl[1] were of the view that their experiments on deposition established that the surface diffusion of adions is rate-determining, but Rangarajan[2] has recently shown that the experiments would be equally consistent which rate-determining lattice incorporation.

3) The question still remains however as to the mechanism of dehydration, the stage at which electron transfer occurs and the precise meaning of the particle charge on adions. Perhaps the differences in the electric field on the planes and at the steps, kinks, etc. are responsible for the relevant water molecules being squeezed out.

References

1. J. O'M. Bockris and J. Mehl, *Can. J. Chem.*, 37, 190 (1959).
2. R. Rangarajan, *J. Electroan. Chem.*, 16, 485 (1968).

R. Parsons. Simple metal deposition reactions are fast and as a result difficult to interpret. Hence the evidence for the existence of adions as distinct from atoms is uncertain because of the fact that Rangarajan's analysis shows that the same relaxation behaviour is to be expected from a mechanism involving deposition on a plane followed by surface diffusion and from one involving non linear diffusion followed by direct deposition at a growth site.

Conclusions based on theoretical considerations are also questionable. The calculations of Bockris and Conway (*Electrochemica Acta*, 3, 340 (1961) does not take proper account of the levelling of energy curves and so their predictions are of doubtful relevance.

J. E. B. Randles. The discharge and deposition of a metal ion onto an electrode surface should not, I think, be thought of as separate processes. At a mercury electrode, there are no complications due to surface diffusion of "ad-atoms" or "ad-ions" and the activation energy for many metal ion deposition is quite small. For example, for the deposition of Pb^{2+}_{aq} it is only about 5 kcal mol^{-1} whereas the total free energy of hydration of the ions is around 300 kcal mol^{-1}. The fact that deposition can occur with an energy barrier only about 1/60 of this shows that the energy required to distort and then displace the hydration shell of the ion must be very largely supplied by the simultaneous increase of the energy of interaction of the ion with the electrode. At the surface of metals (as shown by thermionic work-function calculation for alkali metals) the "electron gas" of the metal extends significantly beyond the surface plane of atoms. When an hydrated cation approaches such a surface, from the solution phase, there will be a local extrusion of the electron gas towards the ion. The resulting exchange force attracting the ion towards the metal, facilitate the displacement of water molecules from the side of the ion facing the metal. There is no abrupt electron transfer but a gradual extension of the electron atmosphere towards the ion which finally at a solid electrode becomes adsorbed on the surface, or, at a mercury electrode, passes into the metal. This is true, not only for the deposition of monovalent ions, but also for divalent ions such as Pb^{2+} and Cd^{2+} at least at a mercury electrode. Such processes, quantum mechanically speaking, are adiabatic.

On the other hand other processes, such as the reduction of certains anions, are almost certainly non-adiabatic. The reduction of persulfate at a mercury electrode is, as shown by Frumkin, inhibited in solutions of low ionic strength when the potential of the electrode is made more negative than the potential of zero charge. If the electrode potential is increasingly negative, reduction gradually increases again. In these circumstances, I think we must assume that the increased electric field facilitates electron "tunnelling" from the electrode through a few layers of water molecules to persulfate ions in the outer region of the diffuse layer. In the diffuse layer the concentration of persulfate declines steeply as the electrode is approached but conversely the probability of electron tunelling increases.

These two opposing factors probably result in electron jumps occuring to persulfate ions at a range of distances from the electrode surface, within the diffuse layer, but with a maximum frequency at some intermediate distance. The process itself is a discrete electron jump rather than an adiabatic process.

H. G. Hertz. Assume we have a neutral metal alone in the water. Then I would estimate that its self-diffusion coefficient in H_2O is that of the noble gas atom of similar atomic weight (in water). And these self-diffusion coefficient are known. The life-time of such a metal atom in the liquid interface is then given by the simple formula relating mean square displacement, time, and diffusion constant.

But I should say one word of warning. We heard the question: if the metal ion is discharged, what holds the water to the neutral particle? It might very well occur that the neutral particle keeps the water much better than the charged one. One example: the self-diffusion coefficient of Xe in water is $\simeq 10^{-5}$ cm^2/sec. But if we charge Xe, we get Cs^+, and here the self-diffusion coefficient is 2.10^{-5} cm^2/sec. This is so because the water around Cs^+ is more fluid, i.e. the water is "held" less. In other words we have the structure breaking effect. What actually occurs, in a simple electrostatic picture, is only determined by the ratio charge/size of the ion.

A. R. Ubbelohde. Question to J. E. Randles.

You may use a quantum mechanical treatment for your electronic cloud of electrons for metal, but otherwise the gradual polarization of the cloud is purely classical in your treatment. Do you need any tunnelling in your treatment?

J. E. B. Randles. In the case of the discharge of a metal ion, I don't think really one could use the classical approach. I think the extension of the ψ function is in fact undistinguishable from tunnelling. Probably, classically speaking, the electrons ought not to be in the gap between the ion and the electrode.

A. K. N. Reddy. Whether the particle on the metal surface is an adatom or an adion, i.e. whether it has a partial charge or not, depends upon

1) at what stage in a step-wise dehydration process the electron transfer takes place, and

2) the extent of localization of this transferred electron on the particle.

If the electron is completely localized on the particle then one has an adatom: if on the other hand there is an electron overlap with the metal, then one has a partially-charged adion.

M. Magat. In support of what Prof. Hertz just said, I would like to recall the Stillinger *et al.*[1] results concerning the "long living" cage that water molecules form around a neutral Neon atom.

Reference

1. M. Losonczy, J. W. Moskowitz, and F. H. Stillinger, Hydrogen bonding between neon and water, *J. Chem. Phys.*, **59**, 3264 (1963).

R. Parsons. It is perhaps worth considering the reaction $Hg_2^{2+} + 2e \rightarrow Hg$ as a metal deposition process without nucleation. This is a fast process with an exchange current $> 1 A cm^{-2}$. The observed relaxation results are not simple to interpret and at one time the existence of an adsorbed intermediate was involved. However, the most recent results seem to prove that no such intermediate is detectable.

Perhaps this sort of process is best regarded as the transfer of an ion from one medium of high dielectric constant (H_2O) to another (Hg) and the role of the electron is less important.

A. K. N. Reddy. Slow deposition processes are invariably complicated by effects due to adsorbed hydrogen atoms.

B. Behr. Prof. Reddy has just mentioned the possibility of partial charge transfer in formation of intermediates in metal ions discharge reactions. The partial charge transfer seems to be much more possible in the case of strong adsorption of anions at metal surfaces. Our measurements concerning Hg in 0.5 MKCl, which were extended up to the equilibrium potential of the calomel electrode, indicated that the charge of the adsorbed Cl^- amounted to ca. 50 $\mu C/cm^2$ which is about 50% of what is needed to form a complete monolayer of calomel. These measurements were not disturbed by the electrode reaction because of the very low concentration of mercurous and mercuric species in the solution under these circumstances. One can hardly imagine such a large adsorption without formation of chemical bonds, although the structure must be different from that of the crystalline salt. Such a process should probably involve partial charge transfer. I should like to ask Prof. Parsons whether he could think of a partial charge transfer in the case of the adsorption of thiourea which he has studied.

R. Parsons. I assumed that there was no change in the charge distribution in thiourea but there is no proof of this. There does not seem to be any change in the dipole moment with coverage, in that the potential change is linear with coverage.

I think it is very difficult to detect a partial charge transfer. The work of Lorenz on this aspect of anion adsorption is not convincing.

H. D. Hurwitz. It is unfortunate, at this point of the meeting, that Professor V. G. Levich is not among us and could neither send his communication, especially since we know that he wished very strongly to come here but was not allowed to.

I think that it is worthwhile to recall some criticism made by Levich as well as by Marcus on the Gurney type of approach used in the treatment of charge transfer processes.

Either we have an adiabatic charge transfer process and then a classical treatment, perhaps refined in the version of Marcus and Levich, is quite valid, or the process is non adiabatic. In the latter case, a coherent quantum mechanical calculation must be used, e.g. of the Landau Zeener type as developed by Levich and his school. The use of the W. K. B. tunnelling approach and the Gamov formula are incorrect in a charge transfer theory as soon as the shape of the potential barrier is a function of the evolution of the charge process itself along its reaction coordinate.

A. K. N. Reddy. It is obvious that the Levich approach is much more general, but even under the conditions of the adiabatic approximation corresponding to the Gurney model, there is a fundamental divergence of opinion with regard to the $H^+ - H_2O$ stretching *in an aqueous medium.* Is the $h\nu$ corresponding to this stretching much greater or much smaller than kT—the former view is taken by Levich who therefore uses the double adiabatic approximation, and the latter view is implicit in Gurney? What do the spectroscopists at this conference have to say on this vital question?

M. Magat. Before the war, Dr. Gueron. Mrs. Reinisch and myself[1] have spent a year looking for O—H bands in H_3O^+. All attempts were unsuccessful. The reason is that the life time of an individual H_3O^+ ion in water is very short $\simeq 10^{-12}$ sec. according to theoretical calculations of Wannier[2] and of the same order of magnitude from experiments of Eigen and coworkers.[3]

References

1. L. Ochs, J. Gueron, and M. Magat, Spectre Raman des solutions aqueuses de gaz chlorhydrique. *J. Phys.*, **1**, 85 (1940).
2. G. Wannier, *Ann der Physik*, **24**, 545, 569 (1935).
3. M. Eigen and L. de Maeyer, Selfdissociation and proton charge transport in water and ice. *Proc. Roy. Soc.*, **A247**, 505 (1958).

R. Defay. I would like to make a general remark on the classical theory of the double layer. I do not like this classical model, where the dielectric constant is assumed to be the same in the diffuse layer and in the bulk of liquid and then to change abruptly from 80 to 7 or 10 units in the Helmholtz layer. It seems to me that this model is too static and that, because of the thermal agitation, the limit between the diffuse layer and the Helmholtz layer cannot be so sharp. I think it is not difficult to establish a thermodynamical formulation for liquid in an electric field with a non uniform distribution of the dielectric constant (see A. Sanfeld monography: Introduction to the thermodynamics of charged and polarized layers; Wiley Interscience Publ. 1968).

Now, in the vicinity of the metal surface, the problem is more complicated, because the scalar pressure in the molecular field is replaced by a tensor or pressure, as it has been shown by A. Steinchen–Sanfeld (Thesis Université de Bruxelles 1970). See also: A. Steichen, R. Defay, and A. Sanfeld: *J. Chim. Phys.*, **68**, 835, 1241, 1223, (1971).

The connection between the theoretical results and the experimental quantities is still to be made, but I think that this connection must be possible.

It seems to me that this manner of thinking will be a good new approach to this old problem.

R. Parsons. I think it is very difficult to detect deviations from the Gouy-Chapman theory because we normally measure average quantities which are not sensitive to these deviations.

We have tried to overcome this difficulty by studying mixtures of mono- and divalent cations arguing that the relative amounts adsorbed should be sensitive to the detailed potential distribution. The first attempt was vitiated by an error, but recent results of Trasatti on KCl + $MgCl_2$ mixtures show that the Gouy–Chapman theory is remarkably good (*Trans. Faraday Soc.*, **65**, 3314 (1969)

B. Behr. I share with Prof. Defay his doubts about the correctness of assuming the bulk dielectric constant over the diffuse double layer. The calculations based on this assumption concerning double layer capacity and specific adsorption made by use of the simple Gouy–Chapman theory seem to give good results which is rather surprising. The theoretical argument for using the bulk dielectric constant is that an electric field of about 10^6 V/cm, like that existing within the diffuse double layer, does not still change much the dielectric constant of water in the bulk.

However, if one considers that the values of local concentrations of ions within the diffuse double layer calculated with the Gouy–Chapman theory from the total charge amount in many cases to 8 to 10 M, and that there are then almost no ions of opposite charge, one can see that the situation is rather unusual. If there are strongly hydrated cations, and their hydration shells cannot be shared, there is practically no water left. What is then the value of the dielectric constant, or can one at all use the dielectric constant for description of a medium like this? It would be very good if the physicists could suggest what should be the theoretical approach in this case.

H. D. Hurwitz. It is worthwhile to recall that by using systems of mixed electrolytes at constant ionic strength and assuming that one of the heteroions (either Li^+ or F^-) is only very slightly specifically adsorbed at potentials in the vicinity of the point of zero charge, it is possible to obtain, in an independent manner, the excess of ions adsorbed in the diffuse layer. Under these conditions, the treatment relies on two assumptions:

1) the same thickness of the inner layer for both heteroions,

2) a ratio of their excesses in the diffuse layer equal to the ratio of their molalities in the bulk.

Both conditions correspond to non specific diffuse adsorption and are less stringent than the approximation of purely long range electrostatic interactions inherent to the Poisson–Boltzman equation as used in the Gouy–Chapman theory.

In this respect, let us recall that Kirkwood and Stillinger,[1] and later Levich and Krylov,[2] have shown that the effect of finite ionic size gives the most significant term in the first order perturbation to the potential of mean force of adsorption at high dilution, in the diffuse layer.

Reference

1. F. H. Stillinger and J. A. Kirkwood, *J. Chem. Phys.*, **33**, 1282 (1960).
2. V. S. Krylov and V. C. Levich, *Zh. Fiz. Khim.*, **37**, 106 (1963).

R. Parsons. The best way of studying the diffuse layer would be to look at the potential profile, but I do not know how to do this.

For calculation of charge from charge, which is what we normally need in double layer studies, the Gouy–Chapman theory seems very accurate and this is confirmed by the work of Hurwitz, Sanfeld and Steinchen–Sanfeld (Electrochimica, Acta, **9**, 929 (1964)).