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DOUBLE LAYER AND DIELECTRIC THEORY

A discussion of problems

By

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Abstract

The effect of double layer structure on various phenomena observed at the perfectly polarizable electrode is considered. The potential drop across the double layer is critically discussed and evaluated, the contribution of the χ -potential is assessed, and the dielectric constant is shown to vary little as long as the solvent is not eliminated from the double layer. Reorientation of solvent dipoles is important for relaxation phenomena but has little effect on the capacity of the double layer. The anodic rise of the capacity is explained by an adsorption mechanism in which the separation of the planes of charge (metal and anions) is eventually reduced to zero.

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1. Introduction

The fundamental problems of the electric double layer at the metal-electrolyte interface are studied in a number of laboratories. Accordingly, the field has been reviewed often in recent years^{1,2)}, with stress variously on kinetic

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effects, equilibrium adsorption of ions and neutral species and its thermodynamics, the polarisability of interfaces, discreteness-of-charge-effects, and the observed features of capacity and pseudocapacity. Water, the most frequent double layer constituent, has emerged as a key to the explanation of many observations. However, it has not found a consistent place in double layer models. Its fractional surface coverage, its orientation and its dielectric properties have been inferred, usually, in an indirect way, and it is called into action, as it were, on a stand-by basis.

The present paper attempts some discussion on problems where the presence or absence of water (or a solvent in general) in the double layer matter. The unresolved questions or the suggestions will certainly require exact solutions in future theoretical work. Some of the quantities or concepts presented may be a starting point for new experimental work. The problems are, in particular: dielectric dispersion, potential differences and total potential drop in the double layer, the χ -potential, the dielectric constant in the double layer, the energy of the double layer capacitor, and the charge density as electric variable.

2. Dielectric dispersion of the solvent in the double layer

This has been inferred experimentally³⁾ and theoretically⁴⁾ with specific reference to the water in the double layer, and it has also met with criticism^{2,5)}. Dielectric dispersion will, of course, occur under a variety of conditions. Most of the observable phenomena are artifactitious, but some are related to inherent causes, to processes that cannot be separated from the functioning of the double layer as such. If one accepts at all the concept of water (or any polar solvent) acting as double layer dielectric, then he *must* expect dispersion phenomena at some frequency, by simple analogy to the behaviour of bulk dielectrics. Present evidence indicates that the *mean* relaxation time corresponds to frequencies not normally attained in double layer capacity measurements, and calculations have shown that the effects observed are consistent with dipole relaxation³⁾. Other double layer constituents, alone or in combination, may produce further relaxation phenomena; in this respect, definite conclusions must be left to new experiments. In particular, the importance of *inhomogeneity dispersion* in the sense of WAGNER's theory⁶⁾ is uncertain at present. The question should be answered whether, at liquid electrodes, a distinction between relaxation processes and the effect of inhomogeneities is meaningful in the monolayer concerned.

In the present context, reference to these dispersion phenomena is important

mainly because they are *one* aspect of solvent reorientation in the electric double layer. This reorientation is part of the following discussion.

3. Potential differences in the double layer

3.1 GRAHAME's various potentials

Figure 1 shows an idealised electrostatic model of the double layer, and many of the potentials that have been defined are inscribed. The idealisation consists in the assumption of a two-dimensionally uniform charge distribution in infinitely thin planes parallel to the metal surface, and the assumption of uniform dielectric properties at least in the two regions between planes *M* and

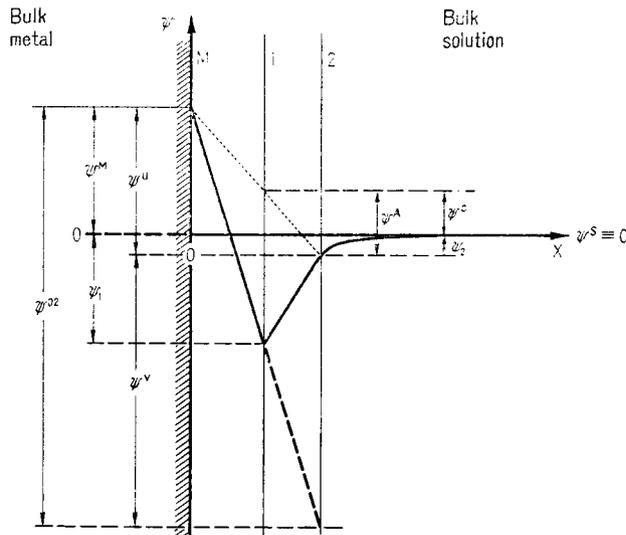


Fig. 1. Potential-distance profile of the electric double layer. Charges at planes *M* (metal), *1* (contact-adsorbed ions) and *2* (plane of closest approach of ions which are part of the diffuse layer) are smeared out uniformly.

1 and between *1* and *2*. The symbols in the figure correspond largely to GRAHAME'S^{7,8)}, the definition of the corresponding quantities is evident from the figure. The potential ψ_1 , for example, is that at the plane of ions in contact adsorption (specifically adsorbed) and does not include any contributions due to the discreteness of an ion at the point under consideration. This latter restriction poses the problem (which has received attention in discreteness-of-charge calculations, *e.g.* by KRYLOV⁹⁾) that the picture drawn applies directly only to infinitely small test charges—even where the averaging condition is

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observed.

The picture of Fig. 1 should be useful where macroscopic quantities such as capacity, charge density and potentials relating them are concerned. Under the assumptions made, all the potential drops are related to respective charge densities by relations of the type

$$\phi_{ij} = 4\pi q_{ij}(x_j - x_i)/\epsilon_{ij}. \quad (1)$$

Here, ij stands for any of the indices in Fig. 1, except S ; q_{ij} is the part of charge density common to plates i and j of parallel plate capacitors (which are in series for any additive ϕ_{ij}), x is the separation between a plane, i or j , of charge and plane M , and ϵ_{ij} is the dielectric constant of the region between planes i and j . (In the following, $\phi_2 - \phi^S \equiv \phi_2$ will be neglected.)

It is evident that some of the charge densities thus defined, for example q^{02} and q^v , lack physical significance, *i.e.* cannot be related to definite parts of ionic surface excesses. Any capacities related to them, *e.g.* C^{02} and C^v , will hence also be physically meaningless. Lastly, if ϕ^M was the total potential drop between the metal and the solution (developing in excess over any potential drop present at the potential of zero charge), one is wondering where the much-discussed variable χ -potential comes in. As far as Fig. 1 is concerned, such a dipole potential could only enter as a *constant* by way of fixing the solution potential $\phi^S \equiv 0$ at some potential of zero charge. This problem is further considered in Section 3.2.

3.2 Dielectric constant, χ -potential, and total potential drop in the double layer capacitor

The properties of a parallel plate capacitor are determined by the separation of the plates, $x_j - x_i = \bar{x}$, and the behaviour of the dielectric between the plates. For the double layer capacitor, one might conventionally take the separation between M and 1 (Fig. 1) as an ionic radius, that between M and 2 as a hydrated ion's radius. (As long as water is a prime constituent of the double layer, the effective dielectric constant will be near six³.)

BOCKRIS *et. al.*¹⁰ have introduced arguments that x_2 actually includes the distance across a hydration layer on the electrode. On the other hand, x_1 —as defined above—has received little criticism. In fact, tests of ionic adsorption isotherms¹¹ have confirmed its value quantitatively except for iodide. This ion is the only one, however, for which the anodic rise of the capacity-potential relation¹² occurs near enough to the point of zero charge to have a pronounced effect on the isotherms (*cf.* also the irregularity in the plot of ϕ_i —here in Fig. 1 denoted ϕ^c —against potential found by GRAHAME⁸). This may actually give a clue as to the properties of the double layer capacitor on the anodic side

which so far are the subject of considerable controversy (*cf.* the discussion of DEVANATHAN and TILAK²⁾; DEVANATHAN advocates a constant inner layer capacity, GRAHAME^{7,13)} took it to vary strongly with potential); see below.

The situation is complicated by the likelihood of compensation between the effects of compression of the double layer (electrostriction) and of reduction of the value of the dielectric constant as the polarisation increases, *i.e.* possibly $\epsilon/\bar{x} \simeq \text{const.}$, and thus a constant integral capacity of any layer with dimensions governed by constituent particles:

$$K = \epsilon/4\pi\bar{x} \quad (2)$$

(in cm/cm²; if $\epsilon=6$ and $\bar{x}=2.78 \times 10^{-8}$ cm, $K=19\mu\text{F cm}^{-2}$ —a rather realistic value*), justifying essentially the direct application of parallel plate capacitor relations to a double layer filled with water molecules).

An exact theory of the dielectric constant, ϵ'' , in the double layer has not been given, but this is a problem somewhat different from those normally encountered in dielectric theory. Consider first the case where the double layer is water-filled. The atom and electron polarisabilities, $\alpha_a + \alpha_e$, of the water molecule add up to 4.17×10^{-24} cm³, equivalent to a dielectric constant of 5.2. Using the simplest expression, only valid for a gas at moderate pressure,

$$\frac{\epsilon-1}{\epsilon+2} = \frac{4\pi N}{3} (\alpha + f(\mu)), \quad (3)$$

one finds that $f(\mu)$ (a simple function of the molecular dipole moment, μ) is much smaller than α : If $\epsilon''=6$, $f(\mu)=0.29 \times 10^{-24}$ cm³, if $\epsilon''=10$, $f(\mu)=1.19 \times 10^{-24}$ cm³. According to a more appropriate relation, *e.g.* ONSAGER's¹⁴⁾,

$$\frac{\epsilon-1}{4\pi\epsilon} = \frac{n^2+2}{2\epsilon+n^2} N\alpha + \frac{(n^2+2)^2(2\epsilon+1)}{(2\epsilon+n^2)^2} \frac{N\mu^2}{9kT}, \quad (4)$$

with $n^2=1.78$, $\mu=0.57$ D***) for $\epsilon''=6$; $\mu=0.91$ D for $\epsilon''=10$ ($\mu=3.1$ D for $\epsilon=80$; from this last value one might conclude that these estimated moments are correct to the order of magnitude).

These results indicate that the contribution, ϵ_0 , of orientation polarisation to the double layer dielectric constant is small. But they give no indication how this contribution varies with potential. Calculations on the reorientation of water in the double layer^{10,15)} show that it is "slow" (*i.e.* its variation with

*) This should, strictly speaking, be the capacity of two metal plates separated by a monolayer of water adsorbed on them.

**) This is a value for the dipole moment of an individual molecule, and must be distinguished from an average value such as might be calculated from some value of the γ -potential.

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the field), and that saturation is incomplete within the experimental range. Thus, ϵ_0 is not reduced to zero in this range, and one may conclude that ϵ_0 plays no significant part in the observed changes of the dielectric properties of the double layer (its capacity); moreover, it varies with electric polarisation in a sense opposite to that observed with the capacity (*e.g.* the inner layer capacity of GRAHAME^{7,13}).

It is not known with any certainty what happens to the contributions of electron polarisation, ϵ_e , and atom polarisation, ϵ_a , as the immense double layer fields are built up ($240/\epsilon$ megavolt per cm at $20 \mu\text{C cm}^{-2}$ charge density). If, speculatively, ϵ_a is related to the displacement of the relevant nuclei along a MORSE curve, an ultimate rise, rather than any saturation, is expected for this quantity; thus *if* water remains as dielectric in the double layer, ϵ'' might rise with electric polarisation, after an initial decrease corresponding to the parabolic part of the potential energy-distance curve. But, two arguments speak against an effect of this on the observed dielectric properties of the double layer on the anodic side. First, anodic films of mercury *salts* are formed in neutral or acid solutions before decomposition of water occurs (with increasing anodic polarisation), indicating chemical stability of the water molecules within the experimental range of double layer studies; secondly, most of the anions, or probably all, become specifically adsorbed and expel water from the part of the interface where the field is strongest, at least to such an extent that the water molecules escape electric break-down.

This leads to considerations on a second case, that where the double layer capacitor does *not* remain water-filled. One may then argue to use a dielectric constant appropriate for ions, as suggested by STERN¹⁶. This will be correct for ions which behave as "solvent", rather than as charged particles. According to the idealisations of Fig. 1, they would have to form ion pairs oriented parallel to the interface. In molten salts, such a configuration can be imagined. In aqueous solutions, both experiments on the adsorption behaviour of ions² and statistical treatments^{17,18} indicate the formation of alternately charged layers, each of like ions, parallel to the interface, as far as the solution side of the double layer is concerned; and a statistical de-coupling of ions with different adsorption properties¹⁹ is predicted.

Thus, as the solvent is expelled from the inner layer under high anodic polarisation, a lower dielectric constant becomes applicable, either that of "solvent ions" or one of unity, *viz.* when there are layers of charged species not separated by any solvent. This effect should more than compensate any effect of increasing ϵ_a . [Of course, within the experimental range, the coverage of the electrode by ions remains far short of unity¹¹, unless bulky ions are

considered²⁰). In many instances, therefore, the inner layer field as an average may be validly calculated as

$$E^{in} = 4\pi q^M / \epsilon^{in}, \quad (5)$$

where q^M follows from experiment, and ϵ^{in} will be between five and six when averaging over the total dielectric space in the inner layer (in Fig. 1, between M and I).] The ultimate rise of the capacity on the anodic side remains, at any count, unexplained on the basis of dielectric theory.

Further below, this sharp rise¹²) will be considered. Before, the problem of potential differences across the interface should be examined. This examination is connected with the postulate of a variable χ -potential due to (re-)orientation of water or any polar solvent or adsorbate. We admit at first that this gives rise, in any given system, to a constant contribution, χ_0 , to the potential drop at the potential of zero charge. At this point, considerable uncertainty arises whether or not to use a relation applicable to the situation at the metal-gas interface, *viz.*

$$d\varphi = d\psi + d\chi, \quad (6)$$

or an integrated form of it, where changes in the total potential drop, φ , between the inner of a phase and a point at infinity in vacuum are considered as the sum of changes in outer (ψ) and surface (χ) potential. OVERBEEK²¹) has discussed some of the difficulties connected with the use of this equation when the metal-gas interface is replaced by a metal-solution interface and when, in a narrower sense, ψ is attributed to the distribution of charged species (*cf.* eq. (1)) and χ to that of polar species. In view of the molecular structure of the interface, this redefinition of ψ and χ can be admitted but, unless the dielectric constant is also redefined, eq. (6) should now, in the present author's opinion, not be used at all. One has *either*

$$d\varphi = d\psi \quad (7 a)$$

where $\psi = f(q, \epsilon, \bar{x})$, in form of a combination of equations such as eq. (1), q being a function of the adsorption isotherms of ions which in turn depend on several experimental parameters including q ; ϵ is a function of the composition and polarisation of the interface and *includes* a part due to orientation polarization, α_0 , arising with the variable orientation of the solvent (and/or other polar species); *or*

$$d\varphi = d\chi \quad (7 b)$$

where χ is a function involving induced (αE^{in}) as well as permanent dipole moments of all neutral constituents of the double layer; and in principle,

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$$\chi_i = 4\pi N_i(\mu_i + \alpha_i E_i^{eff}) / \epsilon_{i,eff}^{eff} \quad (8)$$

where N is the number of species i per unit area, ϵ_{eff} the dielectric constant applicable effectively in such a calculation (*cf.* Ref. 15).

Upon integration, both equations (7) will yield a constant, φ_0 , which in the case of eq. (7 a) is a χ -potential in the restricted sense (χ in absence of charges), in the case of eq. (7 b) a ψ -potential in the restricted sense (ψ in absence of net polarisation of the dielectric); but except for these constants*), any combined use of (7 a) and (7 b) must rest on an arbitrary separation, for example, of induced and permanent polarisation of the dielectric in the double layer or, in other words, an integration using a variable integration constant—a rather unusual situation. Physically, such a procedure would amount to an arbitrary combination of two work terms, one due to charging of the capacitor plates in presence of some dielectric, and one due to the polarisation of the dielectric between the plates, both incomplete.

Consider now the case of a double layer containing two dielectrics, *e.g.* water as solvent and an organic substance as adsorbate. Contact adsorption and diffuse layer effects will both be neglected now. Figure 2 shows a model of the interface for this case. Plane M is the same as in Fig. 1. Plane 1 has become meaningless because of the assumption just made. Plane 2 is split into an outer HELMHOLTZ plane for the solvent molecules, denoted 2_{H_2O} , and an outer HELMHOLTZ plane for the organic adsorbate molecules, 2_A . The three planes of charge are at M , at 2_{H_2O} and at 2_A ; they divide the double layer dielectric in two layers, I and II. One must expect four contributions to the potential: one each due to water and to A in region I, and one each due to water and A in region II. The potential drops across consecutive layers are additive. As to the potential drop across one layer (*e.g.* region I), it will *not* be assumed here that the planes 2 are equipotential planes on a molecular scale; or that the charge is smeared out over these planes uniformly, except where their "H₂O" or "A" fractions are concerned. Rather, the contributions of individual molecules or parts thereof to the total potential drop across any one region are taken to be additive, in connexion with eq. (8), and the respective fractional capacitors are in series. The four potential drops and their sums are shown in Fig. 2. The assumptions made are $\epsilon_{H_2O}^I \ll \epsilon_{H_2O}^{II}$, $\epsilon_A^I = \epsilon_A^{II}$. For the potential drop between M and 2_A , one can write (φ_0 is a constant, see above; $\theta_{H_2O} = 1 - \theta_A$):

$$\varphi - \varphi_0 = (1 - \theta_A)\chi'_{H_2O} + \theta_A\chi'_A \quad (9)$$

*) which in principle, of course, also contain a contribution of other interfaces in the circuit; but this is here considered to be eliminated by reference to appropriate zero charge potentials.

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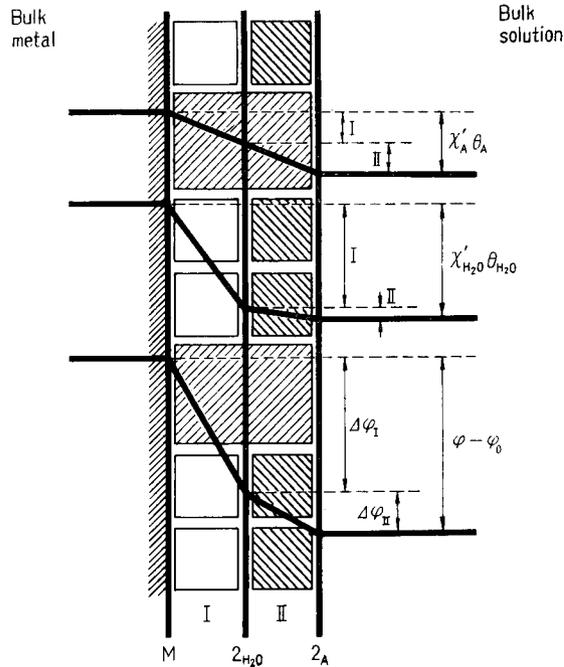


Fig. 2. Potential-distance profiles of the electric double layer with variable dielectric material. Small white figures: water in contact with the electrode. Small shaded figures: water between the planes 2_{H_2O} and 2_A . Large shaded figures: neutral organic adsorbate.

χ'_{H_2O} and χ'_A are the potentials between plates of hypothetical double layer capacitors containing water (practically a monolayer only since the contribution of layers further away from the plane M is much smaller) or substance A exclusively, but in the orientations typical for given values of θ_A and q ; θ_A is the fractional coverage of the electrode by A , a neutral organic species competing with H_2O for the electrode surface. The model resulting is a series combination of the two fractional capacitors; other arguments for this combination have been advanced²²⁾.

The detailed evaluation of the various potential drops should be based on the charge distribution functions, *i.e.* the probabilities of finding components of charge associated with the different adsorbed species, and on the ensuing distribution of the field across the microscopic regions of different dielectrics. This is not attempted here. Instead, the total potential drop across the water-filled double layer capacitor will be evaluated from an adsorption experiment.

Differentiating eq. (9) at constant charge with respect to coverage one

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obtains

$$\frac{d\varphi}{d\theta_{\text{H}_2\text{O}}} = -\frac{d\varphi}{d\theta_{\text{A}}} = \chi'_{\text{H}_2\text{O}} - \chi'_{\text{A}} + \theta_{\text{A}} \left(\frac{d\chi'_{\text{H}_2\text{O}}}{d\theta_{\text{A}}} - \frac{d\chi'_{\text{A}}}{d\theta_{\text{A}}} \right). \quad (10)$$

FRUMKIN *et al.*²³⁾ have shown experimentally that χ'_{A} and $d\chi'_{\text{A}}/d\theta_{\text{A}}$ become quite small at small coverages of such molecules as pentanoic acid or butanol; this should be connected with the random orientation of the polar group of a lone molecule and the small probability to find ions associated with it, rather than with any given water molecule adsorbed around it at the electrode. It may be assumed, on the other hand, that $\chi'_{\text{H}_2\text{O}}$ does not depend on θ_{A} when this is small. In this limiting case, eq. (10) may, therefore, be written (t denoting total, used because of a necessary distinction, see below)

$$\lim_{\theta_{\text{A}} \rightarrow 0} \frac{d\varphi}{d\theta_{\text{H}_2\text{O}}} = \chi'_{\text{H}_2\text{O}}, \quad (11)$$

where $\chi'_{\text{H}_2\text{O}}$ is a particular value of $\chi'_{\text{H}_2\text{O}}$.

The differentiation has been carried out graphically with the plots shown in Fig. 3, from BLOMGREN *et al.*'s data²⁴⁾ for the system mercury/0.1 N HCl

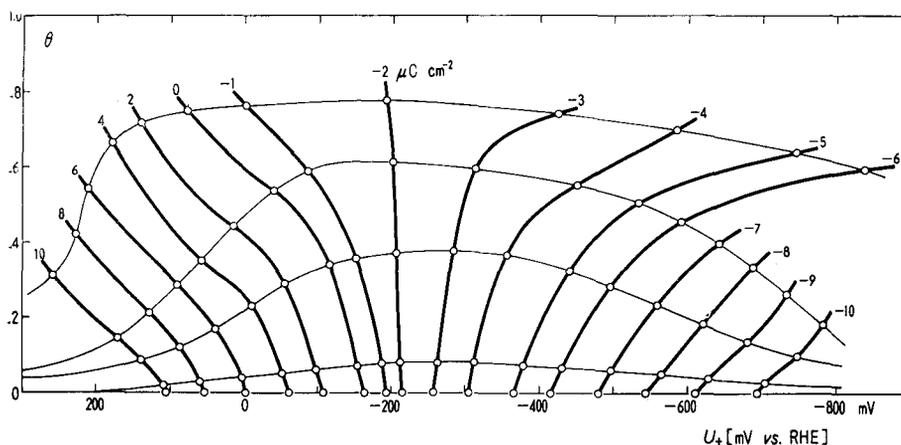


Fig. 3. Coverage of a mercury electrode by butanol. Adsorption from 0.1 N HCl aq., containing (from top to bottom) 0.5 M, 0.1 M, 0.05 M, 0.01 M, and no butanol. Bold lines connect coordinates corresponding to the charge densities indicated in the figure (in $\mu\text{C cm}^{-2}$). Potentials against a hydrogen electrode in 0.1 N HCl aq. (without butanol).

aq. + *n*-butanol. The results are given in Fig. 4; they represent approximately the χ -potential across a monolayer of water as a function of charge density. The same figure shows the potential measured in the system without butanol,

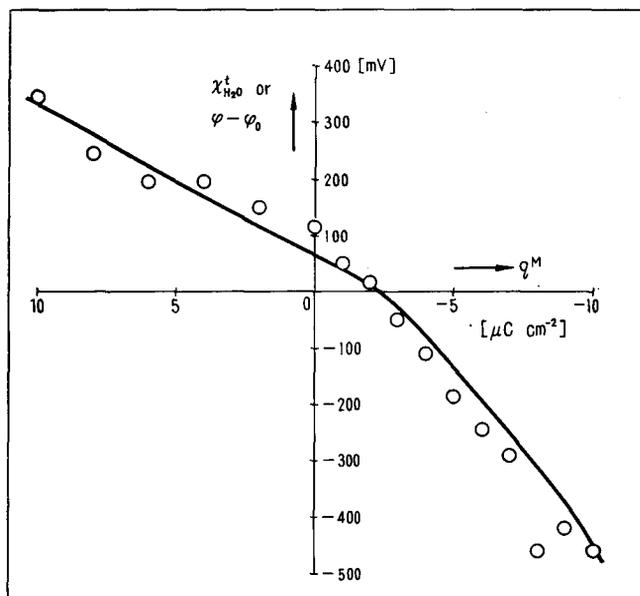


Fig. 4. Potential drop across the double layer capacitor filled with water. $\varphi - \varphi_0$ as measured directly, except for the constant; $\chi_{\text{H}_2\text{O}}^t$ as obtained from Fig. 3 by eq. (11); both as functions of the charge density on the metal, q^M .

setting φ_0 at a value of -225 mV so that $\varphi - \varphi_0 = 0$ at a charge density $q^M = -2.3 \mu\text{C cm}^{-2}$. This is also, because of the relation ($\Gamma_{A(1)}$ is the surface excess of A, μ_A its chemical potential, $U = \varphi + \text{const.}$):

$$(\partial \Gamma_{A(1)} / \partial U)_{\mu_A} = (\partial q^M / \partial \mu_A)_{U}, \quad (12)$$

the charge density of maximum adsorption, q_{max}^M ²⁵). The adsorption maximum of organic substances such as butanol was expected to occur where water has no preferential orientation^{10,27}.

It should be stressed again that the quantity shown in Fig. 4 is the total χ -potential, and was therefore denoted χ^t . It includes induced polarity. The much-discussed quantity $\chi_{\text{H}_2\text{O}}$ ^{1,2,10,15,21,28-30} is contained in $\chi_{\text{H}_2\text{O}}^t$. In the light of dielectric theory (see above), it is expected that, since $\chi \propto \alpha_0$ but $\chi^t \propto \alpha(\alpha = \alpha_e + \alpha_a + \alpha_0)$ and $\epsilon^{dl} \approx 6$,

$$d\chi_{\text{H}_2\text{O}} \leq 0.15 d\chi_{\text{H}_2\text{O}}^t. \quad (13)$$

Correspondingly, the lowering of the capacity of a water-filled double layer beyond the region of dipole relaxation should not exceed 15%.^{3,26}

Incidentally, consistent use of the relation between eq. (7 a) and eq. (7 b)

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should make it possible to decide experimentally whether in double layer problems, in relations of the type

$$\chi = c\pi N\mu/\epsilon, \quad (14)$$

$c=4$ or less (*cf.* eq. (8) and Ref. 2).

3.3 DAMASKIN'S theory of the hump

DAMASKIN³¹⁾ has put forward a quantitative theory of the well-known hump observed on many capacity-potential curves in aqueous solutions. In the present context, his work should be briefly reviewed.

It is interesting to have a value of 41 \AA^2 per adsorbing water species. DAMASKIN takes this result from his hump theory as confirmation of findings in his work on the theory of the potential-dependence of the adsorption of organic molecules³²⁾. It appears that this consistency arises from consistent neglect of interaction of water molecules among themselves at the interface. Since DAMASKIN'S theory is mathematically correct, these interactions must show up in unrealistic parameters. BOCKRIS *et al.*^{25,33)} who took the interaction into account explicitly could use molecular ratios of displacement of water by organic molecules in agreement with expectations from the molecular size of a single water molecule ($\sim 10 \text{ \AA}^2$).

A second observation is the following. DAMASKIN'S treatment appears to amount to taking $\chi_{\text{H}_2\text{O}} = \chi'_{\text{H}_2\text{O}}$. Thus his values of μ and ϵ , in particular their ratio, must be taken as effective figures: If ϵ is put at a realistic value of six, instead two, μ must be raised by the same factor and will hence include induced polarisation. But if this is so, then the agreement found cannot be taken as proof for the correctness of the hypothesis that the hump is due to dipole rotation. Of course, in the sense of Fig. 4 above, the approach is feasible in principle; there should be an inflexion on the $q^M - \chi'_{\text{H}_2\text{O}}$ curve in exactly the same shape and position as the one on the $q^M - \varphi$ curve. But in order to assess the contribution of reorientation of permanent dipoles on this, χ and χ' must be distinguished. The effect of the adsorption of ions on χ' or φ was suggested to prevail over that of the dipole reorientation^{10,11)}, in agreement with eq. (13), and thus to govern the humps.

The difference in hump properties quoted by DAMASKIN regarding various anions can be understood as follows. Ions of the chloride type displace oriented water (this produces $\Delta\chi'_{\text{H}_2\text{O}}$), just as do ions of the nitrate type (structure breaking ions). But, their effect on the orientation of water remaining beside them in the double layer is quite different, because the former are small and have a large field around them, while the latter are large and have a relatively weak field. Both effects (displacement and reorientation) are neglected in the

theories compared. To take account of this in a χ -type theory (DAMASKIN) would require to consider in detail the changes in induced and permanent polarisation of the water layer when ions become adsorbed, in fact this should be a quantitative function of the adsorption curve (amount adsorbed against electric variable at constant concentration) of the ions. To account for this in a ϕ -type theory (*cf.* eq. (1); BOCKRIS *et al.* gave expressions in terms of q_1 , the amount of ions specifically adsorbed) would require to consider in detail changes in ϵ as a function of adsorption. These improvements should await a HARRIS-ALDER type theory of the double layer dielectric (which, incidentally, should be less complicated than the theory for a bulk dielectric³⁴).

3.4 The anodic rise of the capacity curve and the orientation of water on gallium

FRUMKIN *et al.*³⁵ have stated that they cannot explain the rise of the capacity curves on Ga by the adsorption of ions, and attributed it to the adsorption of water. The comparison of the adsorption of various ions in 1 N solutions leaves no doubt that water adheres more strongly to Ga than it does to Hg. However, on capacity curves, only the adsorption of charged species ($z \neq 0$) can be observed directly. One has always^{22,36}

$$C = \sum z_i F C_{i(1)} \quad (15)$$

where $C_i = -(\partial I_{i(1)} / \partial U)_\mu$. For the above hypothesis to hold, water on Ga would have, (i) either to adsorb under charge transfer—but then the capacity should vary significantly with frequency; it does not, and therefore this possibility must be ruled out; (ii) or it would have to affect the adsorption of anions, by its dielectric properties, in such a way that $C_{-(1)}$ ($-$ denotes the anion) in eq. (15) becomes much larger than in the case of mercury—but this explanation differs in important detail from the one advanced in the work mentioned.

The situation can be understood as follows. The quantities of ions adsorbed on Ga are smaller than on Hg at low double layer fields, but they rise faster with anodic potential. The charge density also rises fast with anodic potential, as seen from the data published. As a function of charge, the adsorption of ions on Ga will resemble more closely that on Hg, but, the potential changes caused by the same increase of $I_{z_{-(1)}}$ (the amount of anions adsorbed in contact with the electrode) differ for the two metals, and are smaller for Ga.

If adsorbed water had a higher dielectric constant in the case of Ga, and hence a higher value of χ' , then a larger potential shift upon its desorption (opposed to that in U), and a smaller net change of the potential due to adsorption of ions, could indeed be observed. But this assumption is in disagreement with

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the observed capacity values on the cathodic side which are equal to those observed on mercury. The differences between Ga and Hg must, therefore, be explained by the behaviour of the adsorbed ions.

This proposition is developed here in two stages. The first stage is designed to explain the differences between Ga and Hg as a whole and also an observed anomaly in the adsorption of iodide on Hg^{11,37}. The second stage is designed to explain the ultimate anodic rise on either metal. No sharp boundary between these stages of adsorption, nor in the transition from ordinary contact adsorption to these stages, is implied. The second stage is discussed in Section 4.4, the first stage is described in the following.

When, on a liquid metal or a metal near the ~~melting~~ ^{melting} point, particles are adsorbed which are comparable in atomic weight and size to the adsorbent

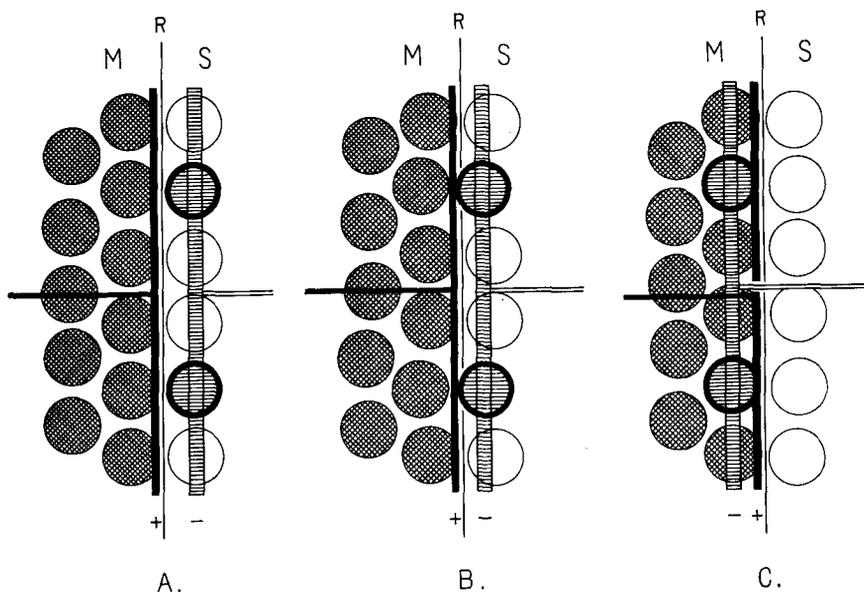


Fig. 5. Ions in contact with the electrode.

- M*: the metal; *S*: the solution; *R*: a plane tangent to metal atoms carrying no adsorbed ions; +: the positive plate of the double layer capacitor (charge associated with the metal surface); -: the negative plate of the double layer capacitor (charge associated with anions in contact with the metal). Cross-hatched: mercury atoms; shaded with horizontal lines: anions (bold circles); empty circles: water molecules.
- Part A: Ordinary contact (or specific) adsorption
 Part B: Intensified contact adsorption (ions piercing the metal surface 'R'): Reduction of $(\psi^M - \psi_1)$ (cf. Fig. 1)
 Part C: Intrinsic contact adsorption (ions and metal atoms in the same plane): Further reduction of $(\psi^M - \psi_1)$ to zero and reversal of its sign

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metal atoms, then they will push into the metal surface (given by a plane through some point of reference in the periphery of metal atoms without adsorbed particles*). This will lead to a smaller value for x_1 , figure 1, and a smaller increase of potential with charge by the simple electrostatic relation (1). Considering atomic weights, this 'piercing' of the metal surface is likely for Hg with I^- only, but it is likely for Ga with Cl^- and Br^- as well. The absence of the effect for ClO_4^- follows from the geometry of this ion. Ordinary contact adsorption and intensified contact adsorption are shown in figure 5, parts A and B, respectively; the + and - plates of the inner layer capacitor are drawn closer together when ions pierce the surface. (The position of the + plate in the metal is somewhat arbitrary; it will be close to the 'tangent' surface 'R' if the dielectric constant inside the metal is very high up to 'R'.) This effect seems more reasonable than the very considerable compression of I^- ions which otherwise must be assumed, *cf.* Ref. 11.

4. Charging of the double layer

4.1 Choice in the expressions for the energy of the charged double layer capacitor

On the basis of the comments in Section 3.2, one may choose between the state of charging (charge density and potential across the double layer capacitor) and the state of polarisation (the energy of adsorbed particles in the double layer field), in order to describe the energy content of the double layer and its variation with potential or charge density. FRUMKIN's theory of the potential dependence of adsorption³⁸⁾ follows the first line of approach, with the modification that the charge density is expressed by capacity and potential which are both 'over-all' quantities which cannot easily be related to a molecular picture. BUTLER's³⁹⁾ and BOCKRIS *et al.*'s^{10,25-27)} theories follow the second line, which by its nature is closer to a molecular picture, they use, however, some strong approximations which will have to be reexamined when the dielectric theory of the double layer has been developed beyond its present state. DEVANATHAN and TILAK²⁾ use what appears a combined expression.

A new theoretical development appears possible in connexion with Figure 2; *viz.*, to determine φ_0 as shown, and to use the values $(\varphi - \varphi_0) = \chi'$ as basis in the state-of-charging approach, accounting at practical coverages, where χ' must be replaced by χ' (eq. (9)), for the obvious condition that there is then a contribution of the dipole moments (permanent and induced) of increasingly

*) or with adsorbed particles of much smaller weight, such as the solvent molecules; these cause, as it were, no recoil when they collide in thermal motion with the metal surface atoms.

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oriented adsorbate molecules. In this theory, the variation of χ' across the double layer would be calculated as a function of coverage over the available range of charge densities. By integration of equation (12), adsorption curves can be arrived at theoretically.

Of the approaches outlined, only the last one will give room to predict the variation in the components of charge upon adsorption of neutral molecules, or conversely to predict the variation of adsorption when increasing the specific adsorbability of the ions of the base electrolyte, because the potential due to such ions may be accounted for separately, adding another term to equation (9).

4.2 Rational potential and differential potential

Potential differences across interfaces are usually referred to an arbitrary zero, for example to the potential of zero charge in a solution "without adsorbing ions" (the rational potential, U_r , of GRAHAME⁷⁾), or to the potential of zero charge in the same solution^{*)} (U_s). Thermodynamically meaningful potentials⁷⁾, U_i , on the other hand, refer to electrodes corresponding reversibly to the activity of one of the constituents, i , of the solution; and the scheme

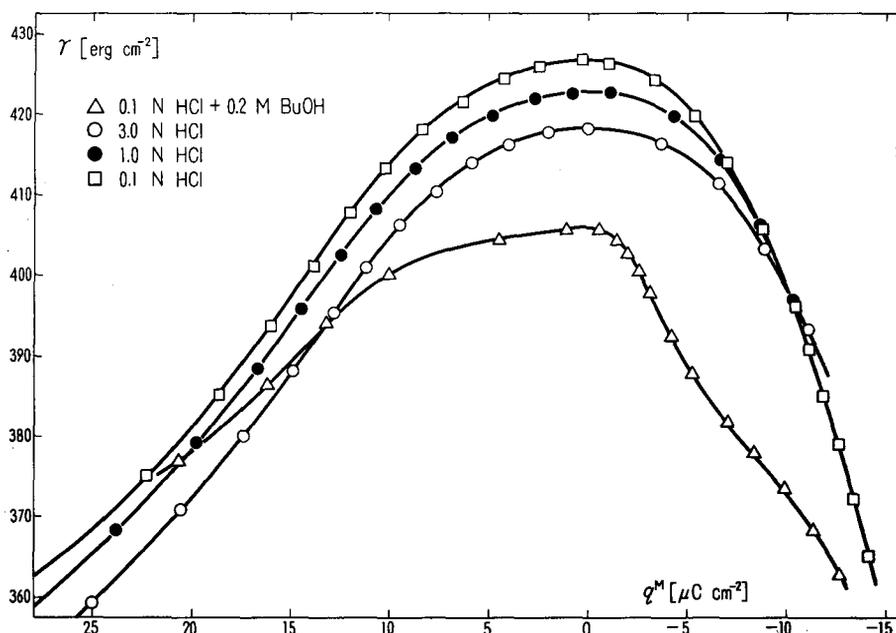


Fig. 6. Interfacial tension plotted against charge density, q^M , for the interface between mercury and the solutions indicated in the figure.

*) $U_s = U - U^{zc}$ where U^{zc} is the potential of zero charge in the same solution and is measured against the same reference electrode as U .

of thermodynamic relations between interfacial tension, surface excesses, charge density, differential capacity and other quantities²²⁾ is built on the use of the U_i scale of potentials.

It may be argued^{22,25,26,40)} that neither U_r and U_s nor U_i are satisfactory electric variables when more than thermodynamic information about the interface is desired. The charge density, q^M , can be held *constant*, instead of potential, to evaluate adsorption.⁴⁰⁻⁴²⁾ It will be interesting to see what happens when substituting q^M as a *variable* for the potential. The interfacial tension varies with q^M thus (see Figure 6):

$$(\partial\gamma/\partial q^M)_\mu = -U_a, \quad (16)$$

a quantity not hitherto defined. Equation 16 is the equivalent of the LIPPMANN equation where the electric variable is changed from U to q^M . U_a as a function

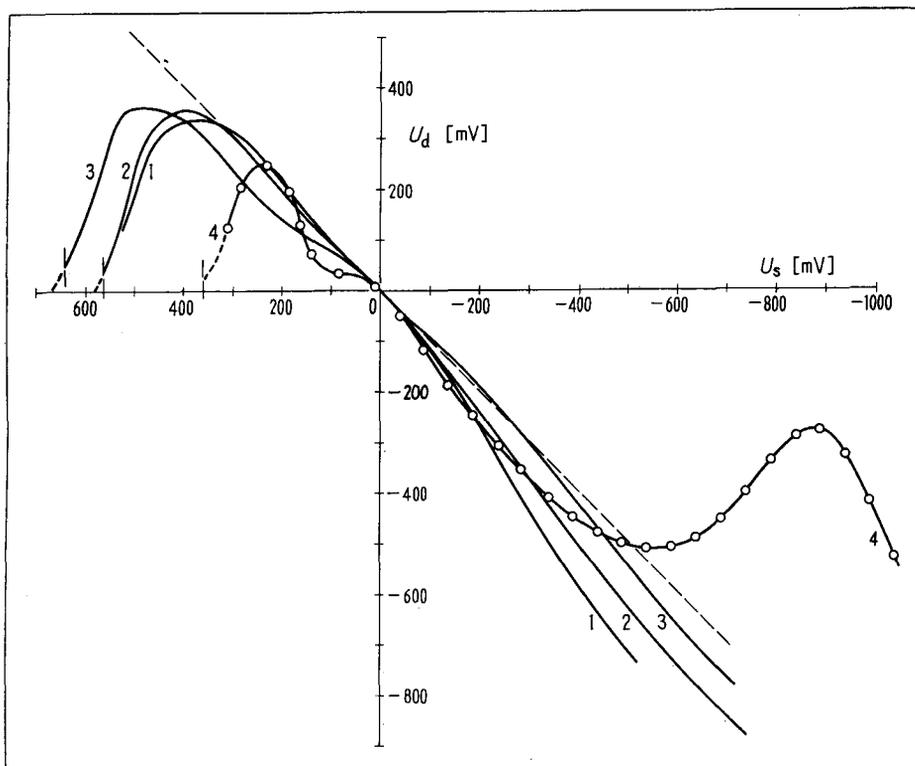


Fig. 7. The differential potential, U_d , at the interface between mercury and various aqueous solutions: 1: 1.0 N HCl; 2: 0.1 N HCl; 3: 0.01 N HCl; 4: 0.1 N HCl+0.2 M butanol. Potentials U_s referred to those of zero charge in the particular solution. Broken line for the ideal case $U_d=U_s$.

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of U_s is shown in Figure 7. The quantity shows an unusual behaviour, it becomes very small again on the far anodic side, contrary to q^M . It will be appropriate to call U_d the *differential* potential, by analogy as follows: The potential, U_s , and the integral capacity, K , are related by

$$K = q^M/U_s, \quad (17)$$

whereas it is easy to show that the differential capacity is given as

$$C = q^M/U_d. \quad (18)$$

U_s could thus be called the integral potential.

Here, an important point must be made. GRAHAME has made it quite clear that what one measures in an a. c. method is the differential capacity, and in its definition,

$$C = (\partial q^M/\partial U)_\mu, \quad (19)$$

the integral potential appears ($dU = dU_r = dU_s = dU_e$ at const. μ). Now the energy of a charged double layer capacitor is

$$W = \frac{1}{2} q^M U_s, \quad (20)$$

and can be rewritten

$$W = \frac{1}{2} K U_s^2. \quad (21)$$

But, as a component in a circuit, the capacitor behaves as one with the capacity C , and therefore eq. (21) should be more properly written as

$$W = \frac{1}{2} C U_d U_s. \quad (22)$$

Significant deviations of U_d vs. U_s from the straight line of unit slope in Figure 7 are then a direct measure for the malfunction of the double layer as a capacitor in this circuit.

In the interpretation of double layer phenomena, U_s is an experimental quantity, and C can be given in terms of the adsorption curves of charged components of the solution as a function of U_s (cf. eq. (15)). In a way, U_s may be considered as an external quantity, impressed by experiment on the system. Now the question arises often how it comes that $I_{-(1)}$ rises so quickly with U_s upon strong anodic polarisation (see above Section 3.4). Equations (20) and (21) do not supply any answer but from eq. (22) it can be seen that there is a significant potential which becomes small under these conditions. In

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fact, it decreases faster than U_s increases. Thus, the charging of the double layer condenser does not occur against a constant (or constantly rising) potential drop *inside* of it! (Actually, these statements should be made in the reverse sense, *viz.* as more ions become adsorbed, they cause changes in U_s , U_d and C , among them least significantly in U_s). It must also be noted that C and U_s are over-all quantities referring to an existing double layer structure so that U_d emerges as a meaningful quantity where *changes* in this structure are concerned; as it were, it accounts for the changes in double layer structure after the "double layer effect" has been taken into account.

If U_d is extrapolated to zero, a potential of about 20 mV anodic to the reversible potential of calomel formation (indicated by vertical lines at the left

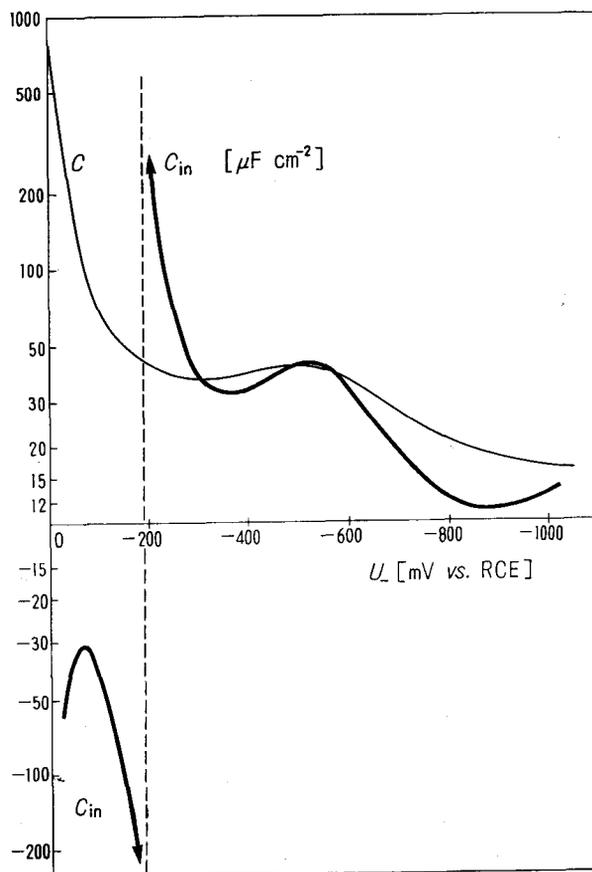


Fig. 8. The intrinsic capacity, C_{in} , and the differential capacity, C , at the interface Hg/1.0 N HCl. Potentials against a calomel electrode in the same solution.

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ends of the curves in Figure 7) is obtained. At this potential, a non-steady transition of C from values of the order of 1000 to values of about $5 \mu\text{F cm}^{-2}$ was observed in all solutions⁴³, and simultaneously a variation in the resistance, indicating that a reaction producing a barrier on the electrode surface occurred; films could also be observed directly. It thus appears that the quantity U_d provides a link between the non-polarisable and polarisable electrode phenomena not provided by any other quantity referring to the polarisable electrode. (The reaction resistance is a quantity referring to the non-polarisable electrode.)

4.3 Differential capacity and intrinsic capacity

From the differential potential, a new quantity of the dimension of a capacity can be found as

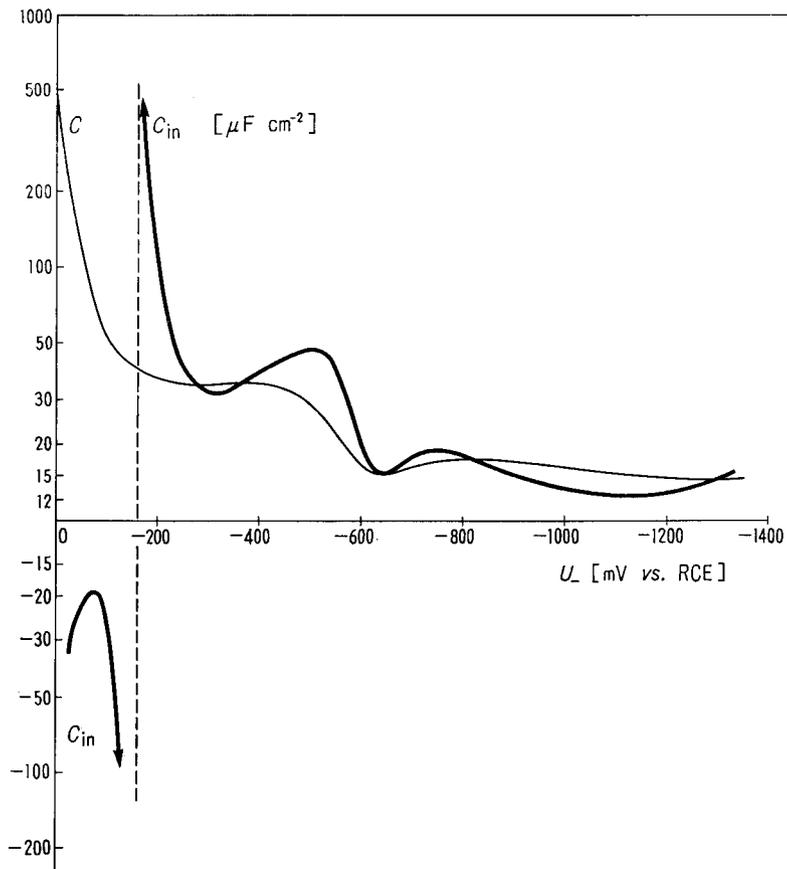


Fig. 9. The intrinsic capacity, C_{in} , and the differential capacity, C , at the interface Hg/0.01 N HCl. Potentials against a calomel electrode in the same solution.

$$C_{in} = (\partial q^M / \partial U_a)_\mu \quad (23)$$

and this is shown for actual systems in Figures 8 and 9. Its significance should be closely related to double layer structure. If U_a can be understood as a net potential^{*}, not containing any "double layer effect", then C_{in} should have a significance (in terms of a component in an equivalent circuit) which reflects directly the behaviour inside the double layer, and it should allow a more direct interpretation of the changes at the interface. In other words, if the adsorption of just one ion was supposed to be determining for the double layer structure—as well-founded for the anodic branch—, then C_{in} should be amenable to an approximate electrostatic interpretation of the adsorption of this ion.

4.4 Intrinsic adsorption

Figs. 8 and 9 show that C_{in} for the Hg/HCl aq. interface assumes (when going anodically) very high values before C rises; then it becomes infinity and finally negative over a region of potentials $U_s < U_{rev}$. This may be explained by the appearance of a new adsorption pattern, as sketched in Figure 5, part C. It is recalled that the first portion of the rise of C (or similarly of C_{in} ; the hump is included in this region) toward the anodic side is explained by contact (or specific) adsorption, Figure 5, part A^{10,44}). In this region, or next to it, one may have an adsorption effect as discussed above, Figure 5, part B. The further and ultimate rise should be due to an adsorption pattern as shown in Figure 5, part C, which is suggested to be called *intrinsic adsorption*, in which the ions move much closer to the metal plane M (in Figure 1), or even beyond it. The anodic rise is characteristic of all ions which ultimately react with the electrode, thus intrinsic adsorption may be considered as the last stage of equilibrium adsorption before the reaction starts.

Such a model of the interface is consistent with the conclusions in the work of BOULT and THIRSK⁴⁵), it would not invalidate the conclusions of BOCKRIS, DEVANATHAN and REDDY⁴⁶), and it is again in agreement with the passivating action of anodic currents on streaming mercury⁴⁷) which cannot be understood with a model of the interface which merely extends that of Figure 5, part A, to full coverage. (Two-dimensional links were found necessary for monolayer induced passivity⁴⁸).

Of course, the model does not, as it stands, distinguish between intrinsically adsorbed anions and metal adatoms quantitatively. As anions penetrate into the first layer of metal atoms, which also carry positive charge as one plate of the double layer capacitor, one expects an association of this positive charge with definite metal atoms and hence the formation of $Hg^+ - Cl^-$, or the corres-

*) U_a , at least on the anodic side, ought to be closely related to $(\psi^M - \psi_1)$, cf. Figs. 1 and 5.

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ponding other salts of mercury, gallium *etc.*

If the assumption about the dielectric properties of the metal near its surface, as made above, is correct, then the model of Fig. 5, part C, also explains the negative values of capacity C_{in} observed over a certain region of potentials, *viz.*, as negative plate separation; *i.e.*, this is not an inductance but arises from the sign convention between charge and applied potential in the plate capacitor model. This unusual situation terminates when, *e.g.*, definite Hg^+ ions are formed and the double layer ceases to exist due to the formation of Hg_2Cl_2 as described by BOULT and THIRSK (their structure ii).

In line with this explanation, it must be expected that to incorporate ions of the ClO_4^- type into the metal surface, will be much more difficult; thus the anodic rise begins later, if at all, during increasing anodic polarisation; and ions of the type of benzene-*m*-disulphonate²⁰⁾ should not show a rise of this type at all. This seems to be in agreement with literature data.

5. Conclusions

The dielectric theory of the double layer, here understood as the effect of the structure of the double layer capacitor on its measurable properties, has been discussed from various points of view. Dipole reorientation of the solvent has been found to be important for relaxation phenomena, but to contribute little to the other dielectric properties of the double layer capacitor. Significant changes in the dielectric constant of the double layer should occur only upon elimination of the solvent from it; the most important variable determining the double layer capacity is *then* the distance of the adsorbed ions from the metal. This distance varies strongly when going toward the anodic side, first when ions become specifically adsorbed, then when they become intrinsically adsorbed (in this case the distance of 'separation' may become zero). Therefore, the inner layer capacity also varies strongly.

The effect of variable orientation of permanent dipoles in the double layer on the total potential drop has been assessed and discussed in connexion with theories on the hump and anodic rise on differential capacity-potential curves; it is found to be minor.

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References

- 1) J. R. MACDONALD and C. A. BARLOW, *Proc. First Austral. Conf. Electrochem.* (1963), Pergamon Press, 1965, p. 199, and literature quoted there.
- 2) M. A. V. DEVANATHAN and B. V. K. S. R. A. TILAK, *Chem. Rev.*, **65**, 635 (1965) and literature quoted there.
- 3) J. O'M. BOCKRIS, E. GILEADI and K. MÜLLER, *J. Chem. Phys.*, **44**, 1445 (1966) and literature quoted there.
- 4) K. E. JOHNSON, *Electrochim. Acta*, **9**, 653 (1964).
- 5) R. DE LEVIE, *J. Electroanal. Chem.*, **9**, 117 (1965).
- 6) K. W. WAGNER, *Elektrotechn. Z.*, **36**, 111, 121, 135, 163 (1915).
- 7) D. C. GRAHAME, *Chem. Rev.*, **41**, 441 (1947).
- 8) D. C. GRAHAME, *Z. Elektrochem.*, **62**, 264 (1958); *J. Am. Chem. Soc.*, **80**, 4201 (1958).
- 9) V. S. KRYLOV, *Electrochim. Acta*, **9**, 1247 (1964).
- 10) J. O'M. BOCKRIS, M. A. V. DEVANATHAN and K. MÜLLER, *Proc. Roy. Soc. (London)*, **A 274**, 55 (1963); *Proc. First Austral. Conf. Electrochem.* (1963), Pergamon Press, 1965, p. 832.
- 11) H. WROBLOWA, Z. KOVAC and J. O'M. BOCKRIS, *Trans. Faraday Soc.*, **61**, 1523 (1965).
- 12) *Colloid Science*, ed. H. R. KRUYT, Elsevier, Amsterdam 1952, pp. 153-154 show a summary of GRAHAME's data.
- 13) D. C. GRAHAME, *J. Am. Chem. Soc.*, **76**, 4819 (1954).
- 14) quoted in *Theory of electric polarisation*, by C. J. F. BÖTTCHER, Elsevier, Amsterdam 1952, p. 192.
- 15) J. R. MACDONALD and C. A. BARLOW, *J. Chem. Phys.*, **39**, 412 (1963).
- 16) O. STERN, *Z. Elektrochem.*, **30**, 508 (1924).
- 17) S. LEVINE and G. M. BELL, *J. Phys. Chem.*, **64**, 1188 (1960); F. H. STILLINGER and J. G. KIRKWOOD, *J. Chem. Phys.*, **33**, 1282 (1960).
- 18) V. G. LEVICH and V. A. KIR'YANOV, *Dokl. Akad. Nauk SSSR*, **131**, 1134 (1960), also Ref. 9.
- 19) F. P. BUFF and F. H. STILLINGER, *J. Chem. Phys.*, **39**, 1911 (1963).
- 20) J. M. PARRY and R. PARSONS, *Trans. Faraday Soc.*, **59**, 241 (1963).
- 21) J. T. G. Overbeek, in *Colloid Science*, ed. H. R. KRUYT, Elsevier, Amsterdam 1952, p. 124.
- 22) K. MÜLLER, *Rev. Polarog. (Kyoto)*, in press.
- 23) A. N. FRUMKIN, B. B. DAMASKIN, V. M. GEROVICH and R. I. KAGANOVICH, *Dokl. Akad. Nauk SSSR*, **158**, 706 (1964).
- 24) E. BLOMGREN, J. O'M. BOCKRIS and C. JESCH, *J. Phys. Chem.*, **65**, 2000 (1961).
- 25) J. O'M. BOCKRIS, E. GILEADI and K. MÜLLER, to be published.
- 26) K. MÜLLER, *Electrosorption*, ed. E. GILEADI, Plenum Press, New York 1967, Chapter 6.
- 27) J. O'M. BOCKRIS, M. GREEN and D. A. J. SWINKELS, *J. Electrochem. Soc.*, **111**, 743 (1964).
- 28) A. N. FRUMKIN, Z. A. IOFA and M. A. GEROVICH, *Zh. Fiz. Khim.*, **30**, 1455 (1956).
- 29) B. KAMIENSKI, *Electrochim. Acta*, **1**, 272 (1959).

Double layer and dielectric theory

- 30) A. N. FRUMKIN, *Electrochim. Acta*, **2**, 351 (1960).
- 31) B. B. DAMASKIN, *Elektrokhimiya*, **1**, 1258 (1965).
- 32) B. B. DAMASKIN, *Elektrokhimiya*, **1**, 63 (1965).
- 33) W. HEILAND, E. GILEADI and J. O'M. BOCKRIS, *J. Phys. Chem.*, **70**, 1207 (1966).
- 34) F. E. HARRIS and B. J. ALDER, *J. Chem. Phys.*, **21**, 1031 (1953).
- 35) A. N. FRUMKIN, N. B. GRIGOR'EV and I. A. BAGOTSKAYA, *Dokl. Akad. Nauk SSSR*, **157**, 957 (1964); A. N. FRUMKIN, N. S. POLYANOVSKAYA and N. B. GRIGOR'EV, *Dokl. Akad. Nauk SSSR*, **157**, 1455 (1964).
- 36) D. C. GRAHAME and B. A. SODERBERG, *J. Chem. Phys.*, **22**, 449 (1954).
- 37) D. C. GRAHAME, *J. Am. Chem. Soc.*, **80**, 4201 (1958).
- 38) A. N. FRUMKIN, *Z. Physik*, **35**, 792 (1926); A. N. FRUMKIN and B. B. DAMASKIN, *Modern aspects of electrochemistry*, Vol. 3, ed. J. O'M. BOCKRIS and B. E. CONWAY, Butterworths, 1964, Chapter 3.
- 39) J. A. V. BUTLER, *Proc. Roy. Soc. (London)*, **A 122**, 399 (1929); *Electrical phenomena at interfaces in chemistry, physics and biology*, Methuen, London 1951, Chapter 2.
- 40) R. PARSONS, *J. Electroanal. Chem.*, **7**, 136 (1964), **8**, 93 (1964).
- 41) J. O'M. BOCKRIS, K. MÜLLER, H. WROBLOWA and Z. KCVAC, *J. Electroanal. Chem.*, **10**, 416 (1965).
- 42) K. MÜLLER, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **14**, 113 (1966).
- 43) K. MÜLLER, *Dissertation*, University of Pennsylvania, Philadelphia, Pa., 1965.
- 44) M. A. V. DEVANATHAN, *Trans. Faraday Soc.*, **50**, 373 (1954).
- 45) E. H. BOULT and H. R. THIRSK, *Trans. Faraday Soc.* **50**, 404 (1954). See also A. BEWICK, M. FLEISCHMANN and H. R. THIRSK, *Trans. Faraday Soc.*, **58**, 2200 (1962); M. FLEISCHMANN and H. R. THIRSK, *Electrochim. Acta*, **9**, 757 (1964).
- 46) J. O'M. BOCKRIS, M. A. V. DEVANATHAN and A. K. N. REDDY, *Proc. Roy. Soc. (London)*, **A 279**, 327 (1964).
- 47) K. SCHWABE and CHAU DIEU-AI, *Electrochim. Acta*, **7**, 1 (1962).
- 48) K. SCHWABE and C. WEISSMANTEL, *Electrochim. Acta*, **9**, 991 (1964).