Electrical Double Layer: Recent Experimental and Theoretical Developments

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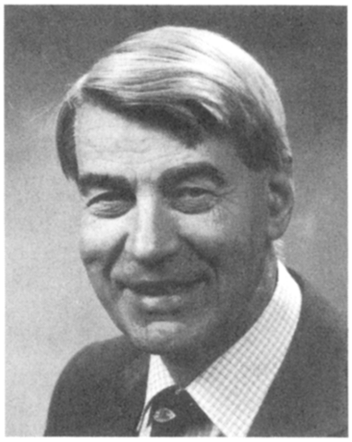

Roger Parsons began research in electrochemistry at Imperial College under the supervision of J. O'M. Bockris, receiving his Ph.D. degree there in 1948. He continued as a postdoctoral fellow at the University of St. Andrews and then was appointed to the faculty of the University of Bristol. In 1966–1967 he held an NSF Senior Visiting Fellowship at the California Institute of Technology. From 1977 to 1984 he was Directeur of the Laboratoire d'Electrochimie Interfaciale du CNRS at Meudon. Since 1985 he has been Professor of Chemistry at Southampton. He has been Editor in Chief of the *Journal of Electroanalytical Chemistry* since 1963. A palladium medallist of the Electrochemical Society in 1979, he was elected a Fellow of the Royal Society in 1980 and was President of the International Society of Electrochemistry in 1981–1982. He received the Chemical Society award for work in Electrochemistry and Thermodynamics in 1974, the Bruno Breyer Medal in 1980, the Prix Paul Pascal in 1983, and the Galvani Medal in 1986. His interests center on the properties of electrified interfaces and the kinetics of electrode reactions.

1. Introduction

The concept of an electrical double layer at the interface between conducting phases was developed early last century. The first quantitative studies concerned the electrokinetic effects[1,2] and the thermodynamic interpretation of electrocapillary curves.[3,4] However, the systematic experimental study of a particular interphase, that between mercury and an electrolyte, was due to Gouy who worked in Lyon during the first two decades of this century. In a series of five substantial papers[5-9] he used the electrocapillary technique to examine an enormous range of systems that he analyzed by thermodynamic methods to develop a plausible molecular model. The subsequent work of Stern[10] did much to unite the work on metal/electrolyte interfaces and that on colloidal systems, providing a model that has dominated thinking in this field until recently. Frumkin[11] was also able to show how direct measurements of electrical capacity could be brought into agreement with electrocapillary measurements and so led on to the systematic use of this precise technique by Grahame[12] and many others. Frumkin also pioneered the study of the solid metal/electrolyte interface with his work on platinum[13] as well as the study of the free surface of electrolytes,[14] which links with the study of insoluble surface films originated by Langmuir, Harkins, and Adam.

This vast body of work depending on classical experimental techniques of measuring potential, charge, current, capacity, interfacial tension, etc., and using classical physicochemical concepts, particularly of thermodynamics, has been summarized in many excellent reviews.[15-30] A substantial collection of data for mercury electrodes is also available.[31]

In the last two decades there has been a substantial change in the character of the study of electrical double layers. Although many of the new aspects of this work have developed out of older work, there does seem to have been a qualitative as well as a quantitative change. Particular features may be noted: The widespread use of digital recording methods with microcomputers has replaced point by point measurement, e.g., use of ac

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bridges, analog instrumentation, etc. Direct spectroscopic investigations have become possible. This may be dated from the Faraday Symposium in 1970,[32] but the significant breakthrough occurred later with the discovery of the surface-enhanced Raman effect (leading to the spectroscopy known as SERS)[33] and the demonstration that good IR spectra of adsorbed species could be obtained by external reflection and modulation.[34] During a similar period the use of well-defined solid metal electrodes characterized by LEED and electron spectroscopy was pioneered, notably by Hubbard.[35] These experimental advances stimulated the interest of theoreticians in the problems of electrified interfaces and led to the development of new models whose features are in many cases still awaiting experimental test. This aspect was particularly stimulated by the first[36] of a series of conferences[37-40] bringing together electrochemists, spectroscopists, physicists, and theorists.

This review is focused on these recent developments although previous work will be considered when necessary. In particular, the traditional model for electrified interfaces will be described briefly as a starting point. In this highly active area, it would be difficult to include every aspect. The aim here is to provide enough information and references to enable the reader to find a way into the subject. To limit the field to some extent, the systems where the surface bonding may be described as chemisorption, as in H or O adsorption on the platinum metals or the so-called underpotential deposition of metals, have been excluded. This is an essentially arbitrary exclusion.

2. Traditional Model of the Electrical Double Layer

(I) Metal/Electrolytic Solution Interface

For many years experimental results obtained largely on mercury by the thermodynamic route have been interpreted with use of a model introduced by Stern[10] though largely anticipated by Gouy.[9] It was then modified to some extent by Frumkin[41] and by Grahame.[21] The first body of results (largely due to Gouy[5-9]) was obtained with use of a capillary electrometer, i.e., from the measurement of interfacial tension as a function of electrode potential and composition of the two adjoining phases. Application of the Gibbs adsorption equation to an interface across which no charge transfer is possible leads to the fundamental electrocapillary equation for a plane interface[21,27,42]

$$-\mathrm{d}\gamma = \upsilon \mathrm{d}p - s\mathrm{d}T + \sigma \mathrm{d}E_{\pm} + \sum_{i,j}\Gamma_i\,\mathrm{d}\mu_{ij} \qquad (1)$$

where γ is the interfacial tension, υ the excess volume of unit area of the interphase, s the excess entropy per unit area, σ the charge per unit area on the metal side of the interface, and $E_{\pm}$ the potential of the metal with respect to a reference electrode in equilibrium with a cation or anion in the electrolyte. Γ_i is the surface excess of species i per unit area, and μ_{ij} is the chemical potential of a salt of i in the electrolyte. The charge on the metal (and the equal and opposite charge on the electrolyte) can be obtained from the variation of γ with potential at constant T,p and composition. This is the Lippmann equation.

$$-(\mathrm{d}\gamma/\mathrm{d}E_{\pm})_{T,p,\mu_{ij}} = \sigma \qquad (2)$$

A differential capacity of the interface can then be defined

$$(\mathrm{d}\sigma/\mathrm{d}E_{\pm})_{T,p,\mu_{ij}} = C \qquad (3)$$

and can be measured directly, for example with an ac bridge with small-amplitude potential signal

$$(\mathrm{d}^2\gamma/\mathrm{d}E_{\pm}^2)_{T,p,\mu_{ij}} = -C \qquad (4)$$

which shows that measurement of the capacity provides an alternative route to the interfacial properties.

This type of measurement and analysis has largely been fitted to the Stern–Frumkin–Grahame (SFG) model in which the metal charge resides on the surface of the metal regarded as a plane. In the simplest case the charge on the solution is separated from the metal by a monolayer of solvent and is distributed in space according to the Gouy–Chapman (GC) model,[43,44] which was a predecessor of the Debye–Hückel theory of electrolytes and uses equivalent equations. The presence of this so-called "diffuse" layer is manifest on the capacity–potential curves in dilute electrolyte as a marked minimum occurring when the charge σ is zero.

For the majority of systems, however, the model described briefly above is oversimplified because it takes no account of the specific nature of the ions other than the magnitude of their charge. In most systems the chemical nature of the metal and of the ions in the electrolyte has a pronounced effect on the observed properties. The SFG model accounts for this by assuming that ions close to the metal surface interact specifically with the metal, e.g., by forming a chemical bond, and/or indirectly by loss of some or all of the solvation sheath. Since these effects are short range in comparison with the coulomb interactions of the GC theory, these ions are assumed to occupy the monolayer next to the metal surface while the behavior in regions further from the metal can be described by the GC model. The short-range interaction of ions with the metal is described as specific adsorption and is usually treated in terms of an adsorption isotherm for monolayer adsorption, e.g., that introduced by Frumkin.[45] The adsorption of nonionic species is treated in a similar way.[46]

Adsorption in condensed systems is always a replacement process in which one species, usually the solvent, is replaced by the adsorbing species.[47] A substantial amount of work has been done in the examination of solvent effects, and this has been reviewed several times.[48-51] It has demonstrated the strong influence of the nature of the solvent on the behavior of the interface, both with and without specific adsorption.

The specific adsorption of ions with the formation of a chemical bond introduced the problem of charge transfer to or from the adsorbed species. This means that the physical location of the charge within the interphase becomes uncertain although the amount of species present in the interphase may still be found by the classical routes.[42,52] In the limit, when charge may be transferred freely between the two phases as in an amalgam/ion electrode, the uncertainty of the location of charge becomes even greater, though the interfacial composition can still be obtained. Models of the interface have been constructed for these cases by analogy with those described above by using chemical knowledge to infer the probable location of the charge.

(ii) Metal/Electrolyte (No Solvent) Interface

The metal/molten salt interface might be expected to provide a simpler system to study than one with a solvent present in addition. The earlier experimental work[53,54] was largely in "simple" melts that melt at high temperature. This results in severe experimental difficulties that were nevertheless overcome by several groups. The resulting capacity–potential curves showed rather simple U-shaped behavior, but with a marked temperature dependence. This could be accounted for qualitatively by a statistical model based on the binary distribution function derived for the bulk melt,[55] which led to a layered structure for the charge in solution, the local charge excess oscillating but damped as the distance from the metal increases. This is closely similar to the prediction of diffuse layer structure in concentrated solutions based on hard-sphere ions in a dielectric continuum.[56] An alternative model[57] is derived from the view of a solid electrolyte with mobile vacancies (see below). On the other hand, it was proposed[54] that the steeply rising capacity curves were due to the onset of a charge-transfer reaction and the departure of the system from the ideally polarizable condition. As yet there has been no convincing demonstration of the correctness of either model.

(iii) Semiconductor/Electrolyte Interface

While it was reasonable to assume for a metal that the electric field at the interface could penetrate into the interior only for a distance of the order of an atomic diameter, the field penetration for a semiconductor is over much greater distances. This is due to the normally much lower density of mobile charges in a semiconductor than in a metal. The result is a space charge layer very similar to the diffuse layer in an electrolyte. The description of this is then closely similar to that given in the Gouy–Chapman theory. In fact, in the simplest case of an intrinsic semiconductor, it is identical with that of a 1:1 electrolyte, the holes being equivalent to cations and the electrons to anions. When the semiconductor is doped, it is necessary to take into account the immobile charges of the donors and/or acceptors.[58,59]

The interphase as a whole thus behaves as a series combination of three capacitors, in the simplest case space charge layer, inner layer, and diffuse layer. Just as this circuit is complicated by specific adsorption from the solution side, it is complicated by the presence of surface states from the semiconductor side.[60]

(iv) Metal/Ionic Solid and Ionic Solid/Electrolyte Interfaces

This interface shows similarities to the one just discussed as well as to the behavior of the molten salt side of the previous one. The charge carriers in the solid are ions and may be distributed in a way similar to those in a molten salt if the mobility is high.[61–63] However, mobility in an ionic solid is often very low especially at room temperature, and in the limit the solid may behave more like an insulator.[64,65]

(v) Insulator/Electrolyte Interface

In the ideal limit no charge can be supported by the insulator. This limit is reached for example by air (and other dilute gases)[66,67] or highly purified hydrocarbon oils. The double layer is then entirely within the electrolyte phase and results from the different interfacial characteristics of the ionic constituents such as different ionic sizes or different interaction with the solvent structure at the surface. This can often be treated like a specifically adsorbed ionic layer with the resulting diffuse layer associated with it.

(vi) Interface between Two Immiscible Electrolytes

To a first approximation, such interfaces can be treated as two-electrolyte double layers back to back,[68] i.e., an inner layer flanked by two diffuse layers.[69] However, no pair of solvents is totally immiscible, and the presence of electrolytes may increase the miscibility. Consequently, the interphase is probably one in which the solvent properties change less abruptly, and this will modify the idealized model.[70]

3. Experimental Studies on Solid Metal Electrodes in Contact with Electrolytes

The primary experimental problem in making measurements on solid electrodes is that of avoiding contamination. This is most likely to arise from the electrolyte by diffusion to the interface. It may be substantially reduced by careful purification of solvent and solute. Since water is relatively easily purified by careful distillation, pyrolytic distillation,[71] or ultrafiltration, most work has been done in aqueous solutions (but see refs 72–74). Electrolytes can often be obtained in a very high purity, and remaining traces of surfactants can be removed by baking and adsorption as well as other standard techniques. Contamination from the metal should not be ignored, particularly if high-temperature preparation is involved. Surface segregation of impurities is often substantial and may be detectable by Auger spectroscopy or XPS although electrochemical detection can be more sensitive. A useful method for verifying the state of the interface is that of forming it at a controlled potential and recording its electrochemical behavior from the first contact, through all subsequent operations.

The earliest work on solid electrodes under clean conditions was probably that on low-melting metals Pb,[75] Tl,[76] Bi,[77] and Cd.[78] These gave capacity–potential curves of character quite similar to those of mercury probably because the surface is sufficiently mobile at room temperature, and then any crystallographic specificity is smeared out. The crystallographic structure of the surface becomes important when the melting point is higher, and a substantial amount of work has been done in the last two decades on Ag and Au in particular. Much of this is well reviewed by Hamelin et al.[79,80] Although there is still some disagreement in detail between work in different laboratories, a good consensus exists on the main character of the results.

These results indicate that there are qualitative and quantitative differences between the behavior of Ag and

Au on one hand and of Hg on the other:

(i) The adsorption of weakly adsorbed anions differs to some extent in that F^- is not the most weakly adsorbed ion on the solid metals. This has been demonstrated most clearly for Ag[81,82] but is probably true for Au also.[83] On these metals the larger ions PF_6^-, BF_4^-, and ClO_4^- seem to be less strongly adsorbed than F^-. Hence, for studies of the double layer in its simplest form in the absence of specific adsorption, KPF_6 or $NaBF_4$ is preferred. This work shows that it is not always possible to assume comparable behavior at different interfaces. On the other hand, the behavior of small inorganic cations appears to be much the same for the solid metals as for Hg, and the sequence of adsorbability of the halides remains the same.

(ii) In the absence of specific adsorption, the properties of the double layer are strongly dependent on the crystallographic structure of the metal surface. This in itself provides some evidence for the maintenance of structure at the surface in the electrochemical environment. However, direct evidence is not so easy to obtain. Crystals can be oriented by X-rays and cut to a precision of the order of 1°. This precision can be improved by a factor of about 10 by using a laser[84] and reflections from natural facets. The structure of the annealed surface may be determined by LEED. The overall orientation of the surface must be retained on immersion, but modifications of the detailed structure of the surface layer may occur. In situ X-ray diffraction[85] or perhaps neutron diffraction[86] may eventually provide evidence for the surface structure, but so far this is limited. Some evidence is available on the surface symmetry from electromodulated reflection spectroscopy,[87-89] which, because of the limited field penetration into the metal, probes only the first layer of atoms. More information about surface symmetry is available from second-harmonic generation, and this has begun to yield information.[90] The in situ scanning tunneling microscope has been shown to be capable of atomic resolution,[91] and this will undoubtedly yield important results in the near future.

An alternative technique for the preparation of oriented single crystals is that of growing them electrochemically. This can be done with Ag[92,93] and has recently been extended to Cd.[94] With Ag, only the (111) and (100) faces may be obtained this way, but when the growth is observed microscopically, it is possible to prepare surfaces free of screw-dislocations in a glass or Teflon capillary.

The primary effect of crystallographic structure on the double-layer properties is related to the position of the potential of zero charge (pzc). The pzc of a metal is closely related to the electronic work function of the same metal.[95-97] Since the electronic work function is well-known to depend on the orientation of the crystal (as seen in the field emission microscope), this leads immediately to the idea that the pzc depends on crystal orientation.[98] This can be observed experimentally by locating the pzc at the sharp minimum appearing on the capacity–potential curves in dilute solutions. This is due to the diffuse layer capacity, which has a low minimum in dilute solutions coinciding with the pzc if the electrolyte is symmetrical and not specifically adsorbed. The planes of higher work function are found to have higher (more positive) potentials of zero charge. Differences of several hundred millivolts have been found: Ag(111), $E_{\sigma=0} = -0.69$ V; Ag(110), $E_{\sigma=0} = -0.98$ V (SCE).

The fact that the pzc depends on the nature of the crystal plane exposed to the electrolyte leads immediately to an idea of the difficulty of dealing with a polycrystalline electrode, which can be considered as made up of small patches of the various possible orientations. An electrode maintained at a given potential will then have patches carrying different charges. For example, on a polycrystalline Ag electrode held at 0.8 V (SCE), the (111) patches would carry a negative charge while the (110) patches would carry a positive charge. This example shows how the double-layer structure becomes complex and necessarily three-dimensional for a polycrystalline electrode, even in the simplest case when there is no specific adsorption. Valette and Hamelin[99] discussed this problem in detail and were able to produce a capacity curve approximating that of a polycrystalline electrode by combining the data for the three low-index planes in the proportion that these were observed on the etched polycrystal. Clearly this is a simplification, and this example shows the impossibility of disentangling the true behavior of homogeneous parts of an electrode from the average results obtained with a polycrystal, even with this very simple double-layer structure. Even the concept of a pzc for a polycrystal may be undefined. The effect of the patch size in relation to the double-layer dimensions has been discussed.[100-102]

(iii) The double-layer capacity of Ag and Au in aqueous solutions, in the absence of specific adsorption and at high electrolyte concentration, in contrast to that on Hg, is approximately symmetrical about the pzc where there is a high peak at about 100 $\mu F\ cm^{-2}$ for most faces so far studied. The capacity per unit area is subject to some uncertainty because of the difficulty of determining the precise area of the interface. Although polished and annealed crystal faces are close to being atomically flat, they can never be perfect and any defects give rise to a local modification of double-layer properties. For a surface close to perfection, the area is probably best determined by using the theory of the diffuse layer. This is usually done by using the so-called "Parsons–Zobel" plot,[81,82,103] which assumes the Gouy–Chapman theory of the diffuse layer. Although this is likely to be valid in the more dilute solutions, the possible crystalline heterogeneity will affect the slope of the plot. This aspect has been discussed in detail by using a plausible model for the heterogeneity effect,[82,83] but there is some doubt as to whether the experimental accuracy is sufficient to implement this analysis.[104]

(iv) At high concentrations of a nonspecifically adsorbed electrolyte the observed capacity is generally supposed to depend on the properties of the first atomic layer of the metal and the adjacent monolayer of solvent. Attempts have been made to study this region more directly with spectroscopic methods. Modulated electroreflectance in the UV–visible region has been analyzed in terms of the change in the refractive index of the water layer.[105-107] It was suggested that this arises from a small increase (~3%) in the density of water molecules as the charge on the metal increases. The electroreflectance spectrum in this region has also been interpreted in terms of a surface band model in which the presence of surface states at different energies leads to the spectra characteristic of each low-index face.[108-111] One problem with this model is that the potential dependence observed is much greater than that expected on the basis of the average field in the inner part of the double layer. This may indicate a strong dependence of the local field on position in the directions parallel to the interface, due perhaps to the presence of solvent molecules. The importance of solvent interaction with the metal was made clear in similar measurements in propylene carbonate,[73] which interacts much more strongly with Au than does water, the order of strength being (100) > (111) > (110) for the low-index planes.

More detailed information about the water structure in the monolayer would be expected from vibrational spectroscopy. So far, Raman spectroscopy has not yielded a signal from these simple surfaces. On the other hand some information from infrared spectroscopy has been obtained but as yet only for polycrystalline Pt and Rh surfaces. The use of a dispersive technique in electromodulated infrared spectroscopy (EMIRS) showed that water bands could be detected, and in the initial work on Pt and Au it was suggested that the water at the interface was bulklike at the pzc[112] while the structure broke up into clusters as the field was applied. On Pt, water bands were detected when the so-called weakly bound hydrogen was present on the surface.[113-117] This suggests a hydrogen-bonded structure linked to the surface via chemisorbed hydrogen. Later work using the Fourier transform technique, subtractively normalized Fourier transform infrared spectroscopy (SNIFTIRS), has obtained spectra from water over a range of nearly 1 V positive from 0.2 V (SHE) on Pt.[118] The increase of intensity as the potential was made more positive was interpreted as a progressive increase in the orientation of the molecules perpendicular to the electrode surface. This is indirect evidence for the contribution of water orientation to the capacity curve although, as yet, there is no example of the two types of measurement being made on the same interface.

(v) In the presence of specifically adsorbed ions, notably the higher halides and SO_4^{2-}, the capacity can rise to very high values on Ag[119,120] and Au.[121-123] This is partly because the potential range on these metals extends further from the pzc than on Hg before a faradaic reaction predominates. Hence, measurements can be made up to full monolayer coverage of the anion.′ The amount of adsorption can be obtained from the concentration dependence of the capacity by the classical thermodynamic route if sufficiently precise measurements are available. This has been done for Cl^- and Br^- on Ag[119,124,125] and for I^- on Bi.[126] The results for specifically adsorbed amounts are of decreasing accuracy as the amount adsorbed increases. The more significant results at low coverages are qualitatively similar to results for mercury and have been discussed in similar terms. Capacity measurements do not seem to be sufficiently accurate on Au for this type of analysis, but Br^- on Au has been studied chronoamperometrically.[127] Since adsorbed anions modify the electroreflectance spectrum substantially, this would appear to be an attractive route to the study of specific adsorption. For Br^- on polycrystalline Au[128] it was shown that the reflectivity change at 500 nm was proportional to the amount of Br^- adsorbed at a given potential, the latter being obtained by studying the adsorption as a function of time under diffusion-controlled conditions. The optical method has not been widely used, perhaps because of the need for calibration, but the use of ellipsometry[129-131] does overcome this by using a plausible model for the optical constants of the surface layer.

Vibrational spectroscopy can provide information about the orientation of polyatomic ions and about solvation properties. The peak area corresponding to the P–O stretch in $H_2PO_4^-$ has been used to obtain amounts of this ion adsorbed on Pt and Au,[132] but a more detailed analysis of structure has been carried out for the adsorption of HSO_4^-/SO_4^{2-} on Pt low-index planes.[133] Raman signals were obtained also for polyatomic ions, first CN^-[134,135] and then SCN^-.[136,137] These appear to suggest the formation of a surface complex on Ag electrodes. Somewhat similar conclusions are suggested for halide ions, and it is possible that this is a result of the special treatment of the electrode by an oxidation–reduction cycle that undoubtedly roughens the electrode. However, results have been obtained on single-crystal electrodes with minimum perturbation.[138,139] Because of the absence of information on the cross-section, it is not possible to use the Raman signal for quantitative study of amounts adsorbed although a semiquantitative relation is observed,[140] but it provides valuable information about local structure. Vibrational features from water molecules can be obtained in the presence of adsorbed ions[139-141] like halides and in this case are strongly dependent on the nature of the cation present, suggesting that there is a water molecule bridging between the anion and cation.[142]

In situ X-ray studies are also beginning to produce structural information about adsorbed species. With use of position sensitive detection, long-range order was demonstrated for the adsorption of I_2 on graphite,[143] and in principle this technique could be used to investigate the more usual types of specific adsorption by using the X-ray standing wave generated by the interference between the incident and reflected beam and observing the fluorescence generated, to study the local positions of atoms.[144] A study of I adsorption on Pt as a function of coverage[145] has complemented measurement of interatomic distances by EXAFS,[146] which gave a Pt–I distance of 0.264 mm, a value that would confirm that the iodine ion loses most of its charge in this state.

Nonspectroscopic methods for studying adsorption include the long-established radiotracer method,[147] which has recently been adapted so that adsorption on well-defined surfaces can be studied[148,149] notably for the adsorption isotherm of sulphate on Pt(111). The accuracy obtainable remains rather low, and the results must be considered only semiquantitative. Thus, they are important for identifying adsorbed species more than for the detailed test of models. Surface resistivity has been shown to depend linearly on specific adsorption in the case of Cl^- adsorbed on a (111) oriented Au film.[150] Such measurements have the advantage that they are not perturbed by faradaic processes, but they are of course limited to electrodes obtainable as thin films, around 100 nm thick, and so have not been used widely to study specific adsorption.

An indirect experimental approach to the understanding of specific adsorption on well-defined electrodes has been developed by attempting to synthesize the electrical double layer on a well-defined metal surface in UHV by adsorbing solvent molecules and ionic species.[151-153] This process can be followed by surface science techniques in considerable detail. However, the correlation with the usual electrochemical interfacial experiments is open to some question because of the absence of the bulk liquid phase and the fact that the UHV experiments must be carried out at low temperatures. These problems may be seen to be linked as, for example, water monolayers on Pt metals evaporate into vacuum at 90–150 K. On the other hand, a comparison of Br (and also Cl) adsorption on Ag(110) under vacuum and in solution[154] suggests a very close parallel in the potential distribution resulting from the adsorption in the presence of water molecules; somewhat similar conclusions can be reached from the experiments on emersed electrodes,[155] which can also be combined with UHV measurements.[156] The latter have shown evidence for ordered layers of hydrogen-bonded sulfuric acid on Au(111) and of halides on Pt(111)[157] and on Ag(111).[158] Again, some uncertainty exists about the presence of such ordering in the presence of the bulk solution.

(vi) Molecular adsorption on solid electrodes follows the same pattern as on mercury electrodes[16] although the features are smeared out on polycrystalline electrodes as a result of the heterogeneous surface, and also probably due to the relatively slow adsorption/desorption process, the characteristic peaks in the capacity–potential curve appear at lower frequencies. The former problem is eliminated to a large extent by using single crystal faces[93] although there is some evidence that there is a marked effect of the number of steps on the surfaces. Heterogeneity is also less in evidence for low-melting metals,[159-162] presumably because the higher surface mobility tends to eliminate differences in surface structure. The problem of slow adsorption means that ac measurement of the capacity can lead to nonequilibrium values. In the case of the adsorption of diethyl ether on Au,[163] this was solved by using a chronocoulometric determination of charge density, which has a longer time scale than that normally used in a bridge. Diethyl ether would be expected to bond weakly with a gold surface, but its adsorption is surprisingly dependent on the surface crystal structure. This was attributed to the predominating effect of the water replaced in the adsorption process.

Similar measurements have been made for *tert*-amyl alcohol on Au(100)[164] and for pyridine on Au(100),[165] polycrystalline Au,[166] and Au(110).[167] The coadsorption of pyridine on Ag with Cl^- is of obvious interest as the first system studied by Raman methods, but only semiquantitative work had been attempted on this previously.[168] A later Raman analysis showed that pyridine was adsorbed flat on Ag.[169] The orientation of pyridine is found to be strongly potential-dependent but in a different way on Au and Ag; on the former the flat orientation appears at negative charges while on the latter it occurs at positive charges as on Hg.[170] More detailed and precise information can be obtained by Fourier-transformed Raman spectra,[171] and this is likely to be used extensively in the near future. At present there is no information about the effect of the anion, which, by analogy with results for similar compounds on Hg,[172] might be expected to be marked. A study of a great number of compounds on smooth polycrystalline Pt by thin-layer coulometry has shown that reorientation occurs frequently and that it is often dependent on the concentration of the adsorbing species in solution (see e.g. ref 173).

A great many organic compounds have also been studied by SERS on roughened Ag electrodes,[174] and it has been suggested that the potential dependence of the SERS signal for pyridine indicates reorientation of the type described above[175] but there seems to be no clear confirmation of the reverse behavior on Au.[176]

4. Experimental Studies of the Interface between Two Immiscible Electrolyte Solutions

This is the other principal area of double-layer studies where substantial advances in the experimental study have been made in the last two decades. Several comprehensive reviews have appeared[177-180] on this subject, which is sometimes given the acronym ITIES. Although such interfaces were studied over most of this century, new impetus was given to the study by the application of the electrochemical techniques used for the metal/electrolyte interface such as chronopotentiometry[181] and potential step.[182] This was followed quickly by the development of the analogue of the dropping mercury electrode for this system[183,184] and the use of cyclic voltammetry.[185] Studies of the double layer were begun with the measurement of interfacial tension by the drop weight method.[69] The surface excesses of tetraalkylammonium bromides were obtained by the classical thermodynamic route and interpreted (at least for the ions with shorter alkyl chains) in terms of the double diffuse layer model.[68] A calculation of the galvani potential drop across the inner part of the interface from Gibbs energies of ionic transfer (which requires a nonthermodynamic assumption[186]) suggested that an inner layer exists but that the potential difference across it is very small, i.e., a few hundredths of a volt, or even zero.[187]

The interfacial tension has also been measured by the drop time method,[188] by the maximum bubble pressure method,[189] and by recording the profile of a static drop.[190] Results obtained with the latter to determine the surface excess of water[191] at the interface between aqueous solutions and several nonaqueous solutions suggested that with the more nonpolar solvents there might be a degree of mixing at the interface, which would then consist of a region having a gradation of properties from those of one solvent to those of the other. In this situation the idea of an inner layer loses its meaning as the two ionic layers may overlap. This also leads to the suggestion that significant ion-pairing may occur, in the interphase, between ions normally in different phases.[192] An extreme example of this may result when phospholipids are adsorbed at the interface.[193]

Direct measurements of the capacity at an interface with negligible charge transfer (ideal polarized or blocked) have been made[194,195] by methods conventional in principle and yield rather featureless U-shape curves that are similar to those to be expected from the two diffuse layer model.[68] They are also quite similar in general form to the capacity of a metal in a molten salt where the effect of incipient charge transfer is believed to play a role.[54] It should also be mentioned that the use of a four-electrode potentiostat may lead to problems in extracting the capacitance, and a careful analysis of the frequency dependence must be carried out.[196-198] The pzc can be measured by the streaming electrode technique,[199] and it has been verified that the twice-integrated capacity curve agrees with the directly measured electrocapillary curve.[192]

A somewhat similar system is that of a polymer, above its melting point and glass transition temperature, in contact with an aqueous solution. Impedance measurements have been used recently to measure the capacity of this interface.[200] It appears to be dominated by the diffuse part of the double-layer capacitance inside the polymer although this is not in very good agreement with a calculation based on Gouy–Chapman theory.

5. Experimental Results on Other Types of Systems

No comparable advances have been made in the study of double layers at other types of interfaces. The double layer in solid electrolytes has been the subject of a series of investigations summarized recently.[201,202] The principle of the measurement is conventional, but the technique of working around 1000 °C is exceptional. Molten metals are used to contact an oxide electrolyte and yield U-shaped capacity curves that are strongly temperature-dependent and have a minimum at the pzc;[201] however, temperature measurements with silver ion conductors give substantially different results on Pt and Au electrodes although in both cases the capacity is markedly lowered by the addition of Cd^{2+}. The divalent ion is said to block sites near the electrode and so to prevent the movement of Ag^+. The capacity is said to arise entirely from the electrolyte phase, and the specificity of the metal electrode is ascribed to specific interactions with the metal.

Work on ionic melts has extended to room-temperature melts.[203] This allows a mercury electrode to be used (cf. ref 204). The capacities in aluminum chloride + 1-butylpyridinium chloride are fairly independent of potential at about 20 μF cm^{-2} except when there is an excess of the latter component when only a steeply rising capacity is seen. This is probably due to the adsorption of the free Cl^- appearing in these compositions.

In the last two decades there has been a great expansion in the study of semiconductor/electrolyte interfaces because of the interest for photoelectrochemical conversion. Little evidence has been acquired for the structure of the electrolyte side of this interface because the behavior of the whole interface is dominated by the space charge region. The classical theory of the latter part of the interface (equivalent to the Gouy–Chapman model) appears to be adequate, provided the crystal is uniform in this region. Deviations are discussed in terms of surface states.[205]

6. Models of the Electrical Double Layer

(I) General Discussion

The analysis of the interfacial region has been the subject of intense activity in the last two decades, and this has been reviewed from various points of view.[206-211] Most of this has been focused on the metal/liquid electrolyte interface although the results are usually of sufficient generality to be applicable, mutatis mutandis, to other interfaces. The traditional division of the problem into regions has been vigorously criticized,[212] and some of the recent models have achieved a self-consistent solution of this difficult problem. There is no question that the input of sophisticated theory into the subject is of great value, but at the present time there has been no systematic attempt to evaluate these models in terms of the vast amount of experimental material available,[31,79] especially taking account of the fact that many of the derived quantities depend on earlier models of the interphase and the difficulty of assessing the reliability of results obtained for static and solid surfaces. This must be a task for the future.

(II) Double Layer with Structureless Metal Wall and No Specific Interactions

This type of model may be expected to account for systems such as Hg/NaF(aq) or even $Ag(hkl)/KPF_6(aq)$ or $Au(hkl)/KBF_4(aq)$. The classical model of a Gouy–Chapman ionic distribution with a distance of closest approach (sometimes called modified Gouy–Chapman) is not self-consistent in the way it treats ion sizes. A slightly more realistic model is the so-called restricted primitive model in which the ions are represented by equal-sized charged spheres but the solvent remains a structureless medium characterized by its bulk permittivity. Even with this model a complete solution presents severe problems, so that approximations must be made. In the hypernetted chain (HNC) approximation the pair correlation functions for pairs of ions are expanded in a power series in the density, described in terms of graphs as in the Mayer cluster expansion theory.[207] If this series is truncated after the linear term, the result is the mean spherical approximation (MSA). This can be solved analytically and yields a differential capacitance of the interphase as

$$C^{-1} = \frac{L_D + d/2}{\epsilon} \tag{5}$$

when L_D is the Debye length, d is the hard-sphere diameter, and ϵ is the permittivity. This approximation becomes exact only at the pzc and in dilute solutions where $L_D \gg d/2$ reduces to the corresponding Gouy–Chapman result

$$C^{-1} = L_D/\epsilon \tag{6}$$

Although formally it provides for an inner layer, the high concentration limit

$$C^{-1} = d/\epsilon_s \tag{7}$$

is unrealistic because of the use of the bulk permittivity.

In the nonlinear region the HNC must be solved numerically, which requires considerable computing resources, and various routes have been adopted to simplify the computation (see refs 207 and 208). An alternative route is the so-called modified Poisson–Boltzmann (MPB). This introduces the ionic size into the Poisson–Boltzmann equation and yields results comparable to the HNC approach.[213] The results are no better in comparison with experiment as far as the capacity is concerned, but they have been compared extensively with Monte Carlo simulations of the same model with respect to the distribution of potential and ionic species near the interface. This is of interest because the Monte Carlo results are an exact solution for this particular model, the primitive model, and hence the validity of the various approximations can be assessed.[214-218] In general, these comparisons show that the Gouy–Chapman solution for the *diffuse* part of the layer is a good approximation for the primitive model of this part of the interphase up to about 1 mol dm^{-3} and reasonable electrode charge densities for a 1:1 electrolyte. It tends to break down seriously for unsymmetrical electrolytes at lower concentrations, whether the asymmetry is in charge or ion size. The latter produces more pronounced deviations when image forces are introduced. Under these more extreme conditions both the HNC[219,220] and the MPB[221] approximations appear to be very successful representations of the model. A modified HNC model leads to structure in the diffuse layer at high charges,[222] and this has been verified by Monte Carlo simulation.

A quite different model to allow for the effects of ionic size, which in fact also includes the effect of solvent molecule size, is the lattice–gas model.[223-228] This involves more order than actually exists in a liquid and is clearly more appropriate for treating a double layer in a crystal. However, it seems to provide a reasonable approach to liquids also and one more easily extendable to more realistic models of the particles in the system. It has been shown for example that this model can reproduce the simulated results[225] for a restricted primitive model at 1 mol dm^{-3} with the addition of a small amount of Coulomb interaction between the ions. This is claimed to compensate for the simplified Coulomb interaction implied by the use of the Poisson equation. The representation of the interface as a whole requires a modification of the lattice–gas model, which takes account of the saturation of the dielectric near the metal surface. This is done by considering a layered model with the planes between the layers parallel to the interface, which amounts to introducing an inner layer although it is a more flexible model. On the other hand it appears to have no possibility of accounting for asymmetry about the pzc for a symmetrically charged electrolyte, unless the properties of the lattice are changed. An alternative approach, which avoids the use of a lattice,[229] includes ion–ion interactions initially in a very general way but in order to obtain a workable solution makes approximations that (in the absence of adsorbed ions) amount to an inner layer together with a Gouy–Chapman diffuse layer.

In view of the difficulties in analyzing the primitive model, it is not surprising that progress in obtaining a useful account of a model with a more realistic solvent has been slow. A model of hard spheres for ions and solvent with a point dipole at the center of the solvent spheres has been solved at the MSA level.[230,231] It leads to an expression for the total interfacial capacitance at low concentrations of the form

$$C^{-1} = \frac{L_D}{\epsilon} + \frac{1}{\epsilon}\left\{\frac{d}{2} + \frac{\epsilon/\epsilon_0 - 1}{\lambda}\,\frac{d_s}{2}\right\} + \ldots \qquad (8)$$

where d is again the ionic diameter, d_s is the solvent diameter, ϵ is the permittivity of the solution, ϵ_0 is the permittivity of free space, and λ is given by

$$\lambda^2(1 + \lambda)^4 = 16(\epsilon/\epsilon_0) \qquad (9)$$

Like the MSA result for the primitive model this may be represented as a Gouy–Chapman capacity (ϵ/L_D) in series with a second capacity that plays the role of an inner-layer capacity although it arises not only from the first layer of the electrolyte side of the interphase. If ϵ/ϵ_0 is taken as 78, this capacity is very weakly dependent on the ionic size in agreement with experiment, when there is no specific adsorption.[232-234] However, the magnitude of this capacity is underestimated even for mercury electrodes.

For this model there is as yet no completely satisfactory simulation. Several simulations have been carried out for more or less realistic models of the water molecule between two nonpolar walls (see ref 209). They show that there is little evidence for dipole orientation near the walls, confirming the result of a monolayer simulation with and without image forces.[235] Optimized cluster theory has been used to go beyond the MSA,[236] and this also confirms the parallel orientation of the first layer of solvent. More recently, an attempt to simulate water structure in the presence of a field (a Gouy–Chapman distribution was assumed) suggested that this had virtually no effect on the water structure.[237,238] On the other hand, the very slight ice-like formation near the surface was emphasized by the introduction of image forces.

The lattice–gas model is readily extendable to dipolar solvent molecules, and both infinitesimal and finite dipoles have been considered.[211,239] An analytical solution is obtainable only in the linear region, but a numerical solution leads to a reasonable capacity–potential curve if the first layer of solvent is taken to have a low dipole moment while the layers toward the bulk have an enhanced dipole moment, which takes account of the hydrogen bonding in water and hence the high permittivity. This is in general agreement with the view held for many years that the water structure near the metal is strongly perturbed and has a much lower permittivity than that of bulk water.[240,241] This is one way in which the behavior of a more elaborate statistical theory can be brought into agreement with experiment. The most extreme version of this route is that of treating the monolayer of solvent separately and introducing more specific properties of the solvent molecules. This approach is the oldest[242,243] and has gone through many modifications, culminating in a model that attempts a realistic account of hydrogen bonding in the interphase as well as applying the model to a wide range of observed phenomena.[244,245] This model is able to account for the shapes of capacity curves on different metals, the temperature effect, the effect of replacing H_2O by D_2O, and the behavior of adsorbed organic molecules. Although it is open to the criticism that it maintains the division of the interphase into inner and diffuse layers, it still appears to be a model having significant features related to the real systems, which need to be incorporated eventually into the whole double-layer models. An even more detailed conformational analysis was carried out for propylene carbonate.[246]

The MSA approximation for a binary hard-sphere fluid, appropriate to a molten salt, has been used to calculate the capacitance of a hard wall.[247] This gave reasonable agreement with the experimental results for a liquid-Pb electrode in alkali halides but was not able to account for the temperature dependence correctly. While an empirical representation of a soft wall improved matters, this has not yet been put on a sound basis.[248]

(iii) Introduction of Specific Properties of the Metal

One feature that has been ignored in the above discussion is the nature of the metal surface, which has implicitly been assumed to be a structureless plane with ideal polarizability. The existence of a charge distribution on the metal side of the double layer was considered soon after the pioneer experimental work of Gouy, by Rice,[249] and has been revived recently, with the jellium model of the metal. This model has been remarkably successful in describing the free surface of a metal, in particular in the calculation of the electronic work function.[250,251] The positive cores of the metal atoms are replaced by a uniform background of positive charge in which the valence-electron gas is free to move. At the surface there is a sharp boundary to this positive background charge, but the electrons can penetrate outside it to a limited extent. Thus, while the bulk of the metal is electrically neutral, the surface has a dipolar layer, the electrons giving rise to a negative outermost layer and the deficiency of electrons in the adjacent region of the positive background to the compensating positive layer. The combination of this with a model of the solution leads to a higher capacity both because the charge in the metal is closer to the solution and because the mean position of this charge can vary with the excess charge applied to either side of the interphase in the double-layer experiment.[252-255] In this form the metal remains structureless so that the result should be most closely applicable to Hg. In a further development, the structure of a solid metal can be modeled by introducing pseudopotentials.[251,256-258] This enables the model to deal with the specific behavior of different metals and of different crystal faces for which it is known that the capacity differs (see e.g. ref 258). However, the comparison has so far been made simply with the capacity at the pzc and not the whole form of the capacity–potential curve. An alternative approach is to relate the capacity behavior to the "chemical" interaction between the metal and the water molecule,[259] but this has reached only the stage of correlation. Another parameter used for the test of model is the potential due to oriented water molecules at the uncharged surface,[260] but there is no unambiguous way of evaluating this quantity, although plausible values can be obtained, for example from the temperature dependence of the pzc.[51]

The "chemical" approach has to some extent been incorporated in recent work on the hard-sphere ion and dipole model. Following the MSA solution,[261] a mean field approximation capable of a solution to the nonlinear problem has been developed.[262] This also permits use of different hard-sphere diameters and different adsorption potentials for the ions and the dipoles.[263] This gives the possibility of asymmetric capacity–potential curves but as yet can cope only with low-permittivity solvents.

Finally in this section, it should be noted that all of the models and theories considered here are one-dimensional in that averaging is carried out in planes parallel to the interface.

(iv) Specific Ionic Adsorption

The first problem is that the analysis of experimental results given in the literature up to the present depends on the assumption that there is a diffuse part of the double layer represented by Gouy–Chapman theory. With the solution of a single electrolyte, this implies the assumption that one ion (usually the cation) is adsorbed only in the diffuse layer and that the concentration of the other ion in the diffuse layer may be obtained via GC theory. The alternative is to use a mixed electrolyte of constant ionic strength in which the adsorbing ion replaces progressively an ion of the same charge type that is not specifically adsorbed. There is some evidence that both of these procedures give reasonably reliable results when 1:1 electrolytes are in question[214,264,265] and perhaps with unsymmetrical electrolytes at not too high concentrations. The general analysis for any composition of mixed electrolytes is given in ref 265, and the role of solution nonideality (which may be important even for 1:1 electrolytes) is emphasized in ref 266. Nevertheless, it must be recognized that the "experimental" results for specifically adsorbed quantities of ions obtained by the classical route do depend on model assumptions of this kind. The results obtained by optical techniques (e.g., refs 128–131) depend on different model assumptions and could, in principle, be used to verify the models.

The results obtained in this way have usually been represented by an essentially empirical adsorption isotherm such as that proposed by Frumkin[45] with the aim of separating the adsorption energy into a part representing the adsorption of a single ion and a part representing the change of this energy resulting from the presence of other ions, i.e., ion–interface and ion–ion interactions. This is complicated for electrochemical interfaces by the fact that the amount adsorbed depends not only on the bulk concentration but also on the electrical state of the interface. For specific ionic adsorption this has usually been handled by considering adsorption isotherms at constant charge on the metal, with due allowance for the energy required to cross the diffuse part of the ionic double layer. This has the advantage that it corresponds to clearly defined experimental conditions. Provided that the adsorbing ion retains its charge, it also corresponds to a simple model of the interphase.

The interpretation of the parameters of such isotherms is questionable because of the lack of proper theoretical backing, even for a uniform surface like mercury. For solid electrodes there is an additional factor to take into account in that the adsorption may modify the structure of the surface. In the past, for mercury electrodes a rather simple electrostatic model has been found adequate to account for the parameters (e.g., refs 267–270) although the polarization of the metal and of the diffuse layer has been treated by multiple imaging.[271-273] Greater sophistication in the modeling leads to the problem that the accuracy available for the experimental results of a rather featureless curve does not allow a critical test of the model.

A further problem in the interpretation of adsorption arises from that fact that a chemisorbed ion by definition forms a chemical bond with the metal surface and this involves an interchange of electrons. Thus, the charge on the adsorbed ion may not be the same at that on the ion in solution. This concept of "partial charge transfer" was introduced in 1961[274] and has slowly gained acceptance (see, e.g., ref 52 for a review of the earlier work). The experimental quantity is the thermodynamic coefficient

$$l = -F^{-1}(\partial\sigma/\partial\Gamma)_E = (\partial\mu/\partial E)_\Gamma \qquad (10)$$

which represents the average number of unit charges supplied to the electrode from the external circuit when one molecule of a species is adsorbed at constant potential.[275,276] A comprehensive review of experimental methods discusses the determination of l as well as its interpretation, leading to a partial charge-transfer coefficient.[277] An alternative approach[278] sets out clearly the components of the apparent charge-transfer coefficient l:

$$l = gz - \lambda(1 - g) + \kappa_{ad} - \nu\kappa_w \qquad (11)$$

Here λ is the fraction of the charge lost by the ion of charge originally ze, g is a geometric factor expressing the fraction of the double-layer potential drop crossed by the ion, κ_{ad} is the contribution of the dipole of the adsorbing species, and κ_w is that of each of the ν water molecules it displaces. There is a further contribution to l if the thickness of the double layer changes. At present there is no unambiguous method of disentangling the various contributions to l. In the absence of charge transfer (as assumed in refs 267–270 for example), $\lambda = 0$ and l is interpreted as the geometric coefficient g depending on the potential distribution in the inner layer, although the dipolar contributions have also been considered.[279] However, a systematic attempt to correlate l with the electronegativity difference between the adsorbing ion and the metal[280] has led to a plausible interpretation for most systems studied in both aqueous and nonaqueous solution in terms of the molecular structure of the interphase.

More recently, a simpler approach to the same experimental results[154] has enabled a direct comparison between the metal/electrolyte and the metal/vacuum interface. The potential drop across the former is considered as a function of the amount adsorbed under conditions (interpolated) such that the charge on the adsorbed layer is equal and opposite to the charge on the electrode; i.e., the diffuse layer vanishes. This relationship can then be compared directly with the work function change due to the adsorption of the same amount from the gas phase. These two curves are close together when Br adsorption on Ag(110) is compared with the aqueous analogue, but even closer if the gas-phase system is considered in which a monolayer of H_2O is progressively replaced by Br. The essential conclusion is that the charge distribution around Br^- adsorbed from solution is closely similar to that round Br adsorbed in vacuum. The latter is clearly more amenable to a theoretical analysis.

The slope of the linear relation between work function and amount adsorbed in vacuum, as well as that of the corresponding plot for many electrode systems, yields an effective perpendicular component of the surface dipole that is much smaller than that corresponding to a charged sphere close to a plane perfectly polarizable metal surface. At first sight this suggests that substantial charge transfer must be occurring. However, this is not necessarily supported by a more realistic model of the metal surface. Calculations based on the jellium model[281,282] show that the screening due to the polarization of the electron tail projecting from the jellium surface leads to a closely similar result without electron transfer. An extension of this model to the interface with a hard-sphere ion and dipole mixture leads to the same conclusion[283] and at the same time to a prediction of the effect of the solvent.

An alternative quantum mechanical approach to the charge distribution is based on the Anderson–Newns model[284] in which the energy levels of the ion are broadened by interaction with the metal surface and a one-electron model is used. The extension to the metal/electrolyte interphase yields[285,286] numerical values of the coefficient λ, which depends to some extent on the assumptions made about the broadening of the energy levels of the ion and about its interaction with the solvent. This model is also capable of dealing with the variation of λ as the occupation of the adlayer increases. It suggests that the charge on the ion decreases. The limited evidence on the behavior of the potential drop suggests that the effective dipole moment remains constant, at least up to moderate coverages.[154]

Ab initio calculations have been attempted for small clusters of metal atoms with a halogen atom.[287] These also suggest a reduced charge on the halogen and provide additional information on the vibrational frequencies; they yield an interaction energy that decreases from Cl to I for adsorption on a small Ag cluster (Ag_5) simulating the (100) surface, in agreement with the expectation for gas-phase adsorption.[288] The reverse order in solution arises from the contribution of the solvation energy. The sequence is not as clear for the much larger clusters treated by the extended Hückel method.[289,290]

A CNDO study of adsorption of halides on Hg has been carried out with use of a close-packed hexagonal array of Hg atoms.[291,292] The interaction of the Hg with H_2O and with halide ions was first considered separately. The adsorption energy and the charge transfer were greater for the halides when the ion was in the threefold hollow site of a six-atom triangular cluster then when it was in an on-top site on the central atom of a seven-atom hexagonal cluster.[291] Monohydrated[291] and then hexahydrated ions[292] were considered. In the latter, the progress of a weakly adsorbed fully hydrated ion to a more strongly chemisorbed ion with a deformed hydration shell is examined. The passage between these two states has an energy barrier for Cl^- and Br^- but not for I^-, and the magnitude of the chemisorption energies is in the right order, but too large. The transfer of charge is remarkably close to the experimental value of 1, which would imply that $g = 0$ in the simplest interpretation of eq 11. The extended Hückel[293] and ab initio methods[294] have also been used for halides on Hg, in both cases with use of a hexagonal cluster of seven Hg atoms and the on-top position. The qualitative conclusion about partial charge transfer is similar in that the greater charge transfer from the ion occurs with the larger ion.

It is clear that at present the simultaneous effects of increasing coverage and of electrode charge or potential cannot be modeled.

(v) Adsorption of Nonelectrolytes

The most precise measurements of nonelectrolyte adsorption obtained for mercury electrodes with a computer-controlled maximum bubble pressure method[295] have been analyzed[296] with a simple model of the interfacial layer[297] and then treating this layer as a nonideal solution. The nonideality was expressed in terms of a power series taken to seven terms. This enables the interfacial solution of water + 2-butanol to be compared with the bulk solution of the same two components. Despite the remarkable accuracy of the measurements, they have not so far led to progress in the understanding of this type of interphase at the molecular level. Probably the most important result comes from the study of the temperature dependence,[298] which shows that the entropy of mixing is far from the ideal random mixing result and hence undermines the basis of the Frumkin isotherm. The high precision of the work also shows that the shape of the adsorption isotherm is dependent on the electrical state of the interphase and that the concept of "congruent" isotherms[299] is only a first approximation.[300] In this work it was stressed that nonideality in the bulk ternary system of nonelectrolyte + electrolyte + solvent may have a strong effect on the thermodynamic analysis. This seems to be dependent very much on the system being studied, and the problem has been discussed further.[301,302]

A thorough statistical analysis of a simple model of the adsorbed layer similar to that used in the rather simplified derivations of Frumkin's isotherm has shown[303,304] that, not only this isotherm, but most of its competitors, including the power series isotherm mentioned above, are in fact approximations. It was concluded that most of the deductions about surface layer structure from the form of the adsorption isotherm and a fortiori from the values of its constants are unjustified and probably misleading.

A more detailed molecular approach allowing for the replacement of hydrogen-bonded water molecules by an organic molecule[245] has been applied to the adsorption of *n*-hexylamine at Hg. The dependence of the detailed structure on the electrical state of the interphase reinforces the point made above about the lack of congruence in the shape of isotherms.

Measurements on solid electrodes are less accurate and cannot provide material to test this essentially classical approach to the adsorption of uncharged molecules. To the present time there seems to have been no attempt to compare models of this general type with structural or spectroscopic experiments.

7. Conclusion

Despite the very great activity in this fascinating area of electrochemistry as shown by this incomplete survey, there is still much to be done in understanding the behavior of the electrical double layer. The theoretical approach has tended to be focused on simpler systems, with good reason. The range of phenomena is very large, and it is likely that it will be some time before subtleties like the difference of adsorbability of optical isomers[305,306] can be accounted for theoretically. It is hoped that this review will indicate some of the problems to be solved and stimulate others to search for the solutions.

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