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The Electrical Double Layer at the Solid-liquid Interface

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A review is given on the progress in the study of solid surfaces in condensed systems. Recent results are discussed of studies on the cleanliness of solid/liquid interfaces, on the definition of surface structure, on the studies of single crystal surfaces in the absence and in the case of specific adsorption. It is concluded that the present experimental evidence is limited and patchy, but at present theory is unable to explain different strengths of adsorption on different crystal planes.

1. INTRODUCTION

Current ideas about the structure of the electrical double layer between a metal and an electrolyte are largely based on studies using mercury electrodes. These are important theoretically because this system corresponds to a good approximation to the idealization of a uniform interface and the simplified one-dimensional treatment. It is also important practically because the use of a dropping mercury electrode allows reliable results for a clean surface to be obtained without too much difficulty. Nevertheless the experimental study of solid surfaces is essential because the effect of surface structure on the properties of the electrical double layer must be known if these ideas are to be applied to more practical systems.

2. THE CLEANLINESS OF SOLID-ELECTROLYTE INTERPHASES

Progress in the study of solid surfaces has been slow in condensed systems as it has in systems where the solid is in contact with a vacuum. Nevertheless in recent years it seems that it is possible to say with reasonable certainty that clean and well-defined solid surfaces can be prepared in contact with electrolytes. For some years it has been clear that electrochemical techniques are capable of considerable sensitivity and the work of Conway et al.[1] has shown empirically that the detailed shape of the cyclic voltammogram of platinum electrodes is a good indication of the cleanliness of the system. More recently the combination of electrochemical and ultra-high vacuum techniques[2–5] has enabled this type of evidence to be put on a firmer basis. In particular, rather simple transfer techniques developed by Clavilier and Chauvi-

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neau[5-6] and applied to parallel electrochemical and Auger experiments have demonstrated clearly the power and efficacy of electrochemical methods.

As an example figure 1 shows the cyclic voltammogram for clean polycrystalline gold in contact with dilute aqueous perchloric acid. Three regions can readily be distinguished:

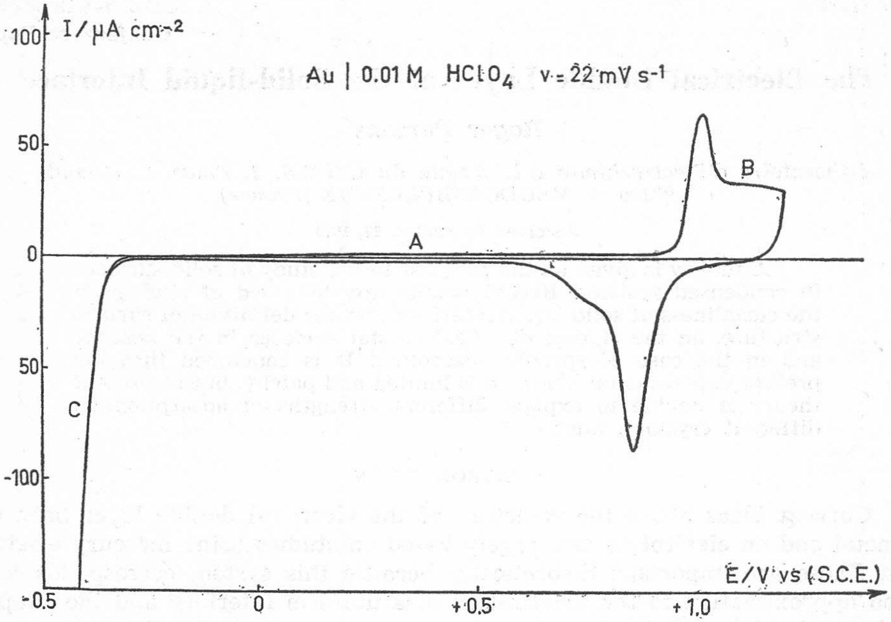

Figure 1. Cyclic voltammogram for a polycrystalline gold electrode in contact with aqueous 0.01 M $HClO_4$ at 25 °C. The electrode potential is swept at 22 mV s^{-1} (Data from Clavilier).

A — the double layer region in which the current is used to change the charge on the metal and the opposing charge on the solution,

B — the oxide region in which the current is used to form somewhat less than a monolayer of adsorbed oxygen species on the gold surface,

C — the region in which hydrogen is evolved.

This is a faradaic process in which there is continuous production of a bulk chemical species. These three regions are typical of the processes which occur at metal/electrolyte interfaces. However, the distinction between the three types of process is not always as clear-cut as in this example.

Clavilier and Chauvineau showed[6] using small gold sphere electrodes of the type used in the experiment of figure 1 that the detailed shape of the voltammogram especially in the oxide region correlated closely with the species observed in the Auger spectrum in a parallel experiment using an identically prepared gold sphere. Thus an electrode prepared in an argon glow discharge which gave on the first cycle of the voltammogram immediately the final, stable, curve was considered to be clean from an electrochemical point of view. In the Auger spectrometer, an electrode prepared in the same way shows the minimum amount of impurity species. On the other hand, electrodes which show substantial amounts of impurities in the Auger spectrum

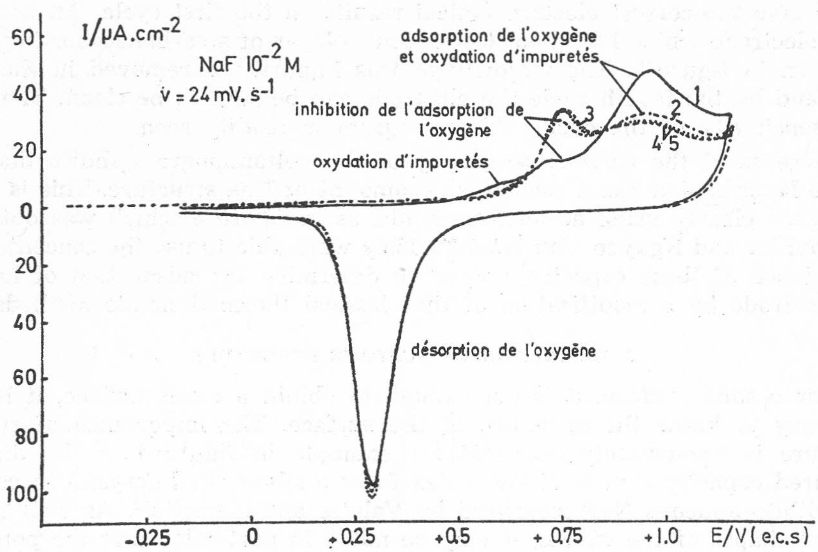

Figure 2. Cyclic voltammogram for a polycrystalline gold electrode in contact with aqueous 0.01 M NaF at 25 °C. Curve 1 shows an electrode contaminated with about 1/3 of the surface covered with a monolayer of carbonaceous matter. Curves 2, 3, 4 show successive cycles in which these impurities are removed. Curve 5 shows the cycle on a clean electrode (Data from Clavilier).

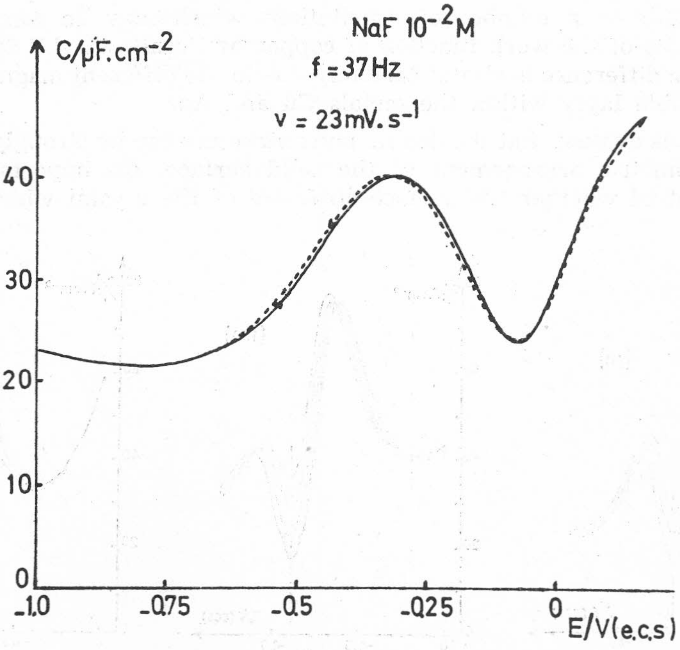

Figure 3. Differential capacity of a polycrystalline gold electrode in contact with aqueous 0.01 m NaF at 25 °C. Measurement made with a phase sensitive detector and a sweep speed of 23 mV s-1 (Data from Clavilier and Nguyen-Van-Huong[8]).

fail to give the correct electrochemical results on the first cycle. An example of an electrode which has about 0.3 of a monolayer of a carbonaceous impurity is shown in figure 2. The majority of this impurity is removed in the first cycle and by the fourth cycle the electrode can be seen to be clean. The very high sensitivity of the cyclic voltammogram is readily seen.

Increase of the current sensitivity of the voltammogram shows that the double layer region has a considerable amount of fine structure. This is revealed more clearly using ac measurements, as in figure 3 which was obtained by Clavilier and Nguyen Van Huong[8]. They were able to use the concentration dependence of these capacity curves[9] to determine the adsorption of ions at the electrode by a modification of the classical thermodynamic methods.

3. DEFINITION OF SURFACE STRUCTURE

For a solid surface, it is not enough to obtain a clean surface, it is also necessary to know the structure of the surface. The importance of surface structure is immediately apparent for example in figure 4 in the directly measured capacity curves of low index faces a silver single crystal in contact with dilute aqueous NaF measured by Valette and Hamelin[10]. As well as the general shapes of the curves, it may be noted in particular that the potential of zero charge (indicated by the sharp minimum in the curves) is different on each surface. In view of the fact that the electronic work function is dependent on the orientation of the crystal[11] and of the well known relation between work function and the p. z. c.[12] this difference is not surprising, but it was apparently first remarked by Frumkin[13]. The close parallelism of these two properties is notable in the results of Lecoeur[14] for the p. z. c. of gold single crystals of a number of orientations which may be compared with measurements of the work function of copper by Peralta et al.[15] figure 5. The quantitative difference is almost certainly due to the different magnitude of the surface double layer within the metals Cu and Au.

Thus it is evident that the double layer structure can be strongly dependent on the geometric arrangement of the solid surface. An important problem here is that of whether the surface structure of the crystal which might be

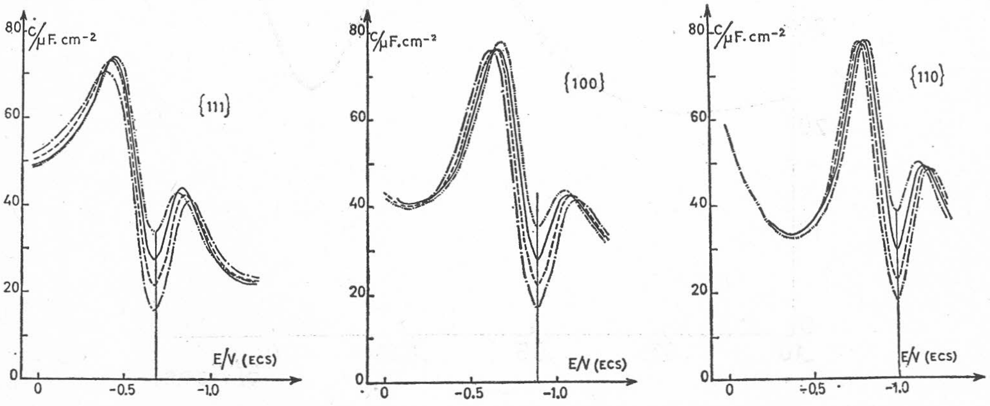

Figure 4. Capacity of a silver single crystal in aqueous NaF at 25 °C (Data from Valette and Hamelin[10]).

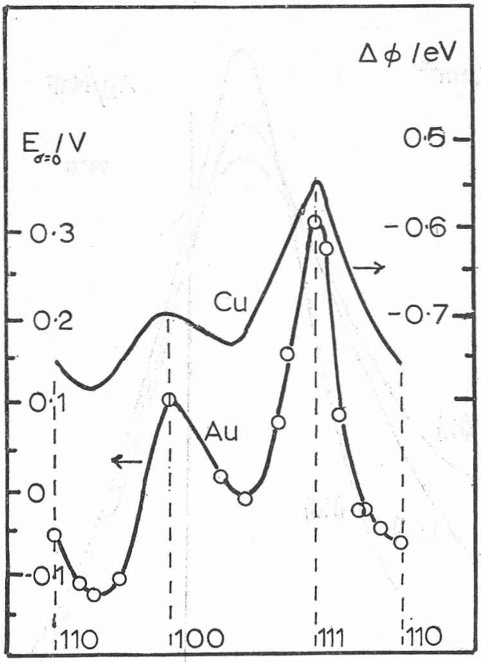

Figure 5. Potential of zero charge ($E_{\sigma=0}$) for a gold single crystal as a function of orientation (Data from Lecoeur, reference (14). Work of extraction of electrons from a copper single crystal as a function of orientation (Data from Peralta et al[15]).

determined outside the electrochemical cell by a technique such as LEED, is maintained when the crystal is immersed in the solution. At present only limited information is possible on this problem, but electroreflectance, which is sensitive to the first layer of the metal surface, shows that the symmetry properties of the crystal face are maintained in solution[16-19].

It is also probable that the more detailed structure of the surface may affect its interfacial properties. For example the adsorption of sulphate on silver seems to be very sensitive to the number of defects on the surface[20,21].

4. THE STRUCTURE OF THE INNER LAYER ON SINGLE CRYSTAL SURFACES IN THE ABSENCE OF SPECIFIC ADSORPTION

The capacity of a single crystal silver electrode in aqueous NaF may be analysed by assuming that this electrolyte is not specifically adsorbed. The diffuse layer capacity may then be calculated from the charge and subtracted (using the model of capacities in series) from the observed capacity[22]. The result (figure 6) for the low index planes[10] is an inner capacity-charge curve which has a high maximum of 110 to 130 μF cm^{-2} and which is almost independent of the nature of the crystal plane at negative charges while showing a more marked dependence at positive charges. The latter effect is probably because the excess of electrons on the negatively charged surface tends to smooth out the structural differences whereas the electron deficiency at positive charges tends to emphasize them.

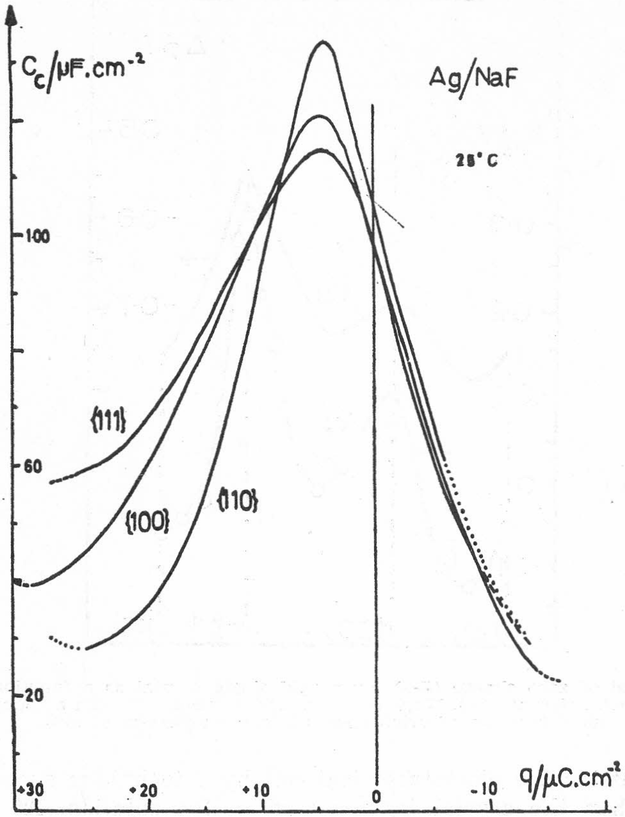

Figure 6. Capacity of the inner layer of a silver single crystal in aqueous NaF at 25 °C (Data from Valette and Hamelin[10]).

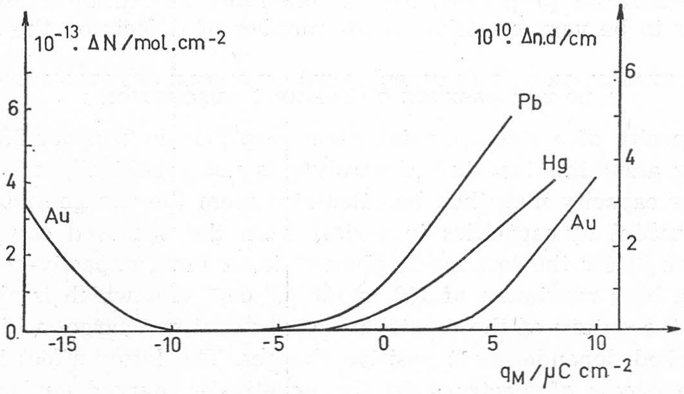

Figure 7. Change of concentration of water in the inner layer of mercury and polycrystalline lead (Data from Bewick and Robinson[28]) and also for polycrystalline gold (Data from Hinnen et al.[29]).

By analogy with the interpretation of the hump in the capacity curve on mercury[23] it seems reasonable to attribute this peaked curve to the reorientation of water in the inner layer. However a model of molecular clusters[24,25] does not seem to be able to account for a capacity peak of this magnitude. It can be approximately fitted using the BDM model[26] with a very low interaction parameter. However, a low interaction parameter in this model is probably not admissable[27]. There is also some difficulty in accounting for the particular type of asymmetry observed. In view of the structural sensitivity of the inner layer capacity, it seems probable that the neglect of specific interaction with the metal is an important deficiency of these models.

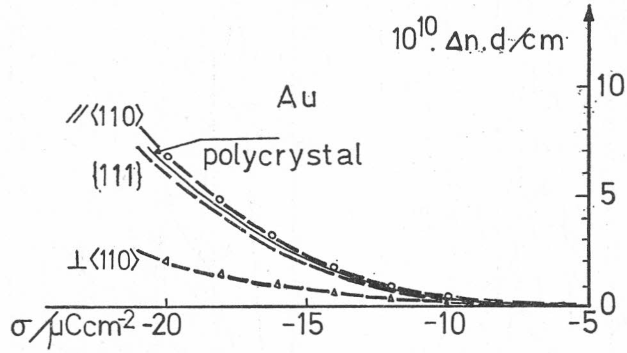

Figure 8. Change of concentration of water in the inner layer of single crystal gold (Data from Hinnen et al.[31]).

Some further information on the state of water in the inner layer can be obtained from electroreflectance measurements. Bewick and Robinson[28] used an approximate analysis of the reflectivity of mercury and lead electrodes to separate the contributions of the metal (absorbing) and the inner layer (transparent). The behaviour of the latter at the more positive charges could be interpreted if there were a small (~5%) increase in the water concentration in the inner layer (figure 7). A similar effect has been found at polycrystalline gold at both extremes of charge by Hinnen et al.[29]. On single crystal surfaces the study of positive charges is prevented at present because of the difficulty in understanding the optical effects of a »pre-oxidation step«[30], but at negative charges similar effects are found[31]. However, the most interesting result is obtained on the (110) surface which is anisotropic and may be regarded as formed of »rails« with hollows in between. When the electric vector of plane polarized light is parallel to these rails (figure 8) the change in the apparent concentration of water at negative charges is very similar to that on the (111) surface or on polycrystalline electrodes. However, when the electric vector is perpendicular to these rails the apparent change in concentration is much less. This seems to be due to the freedom of movement of water molecules along the rails but not across them. It is possible that the asymmetry of the inner layer capacity peak may be understood in terms of the different interaction of water with the different crystal planes and work is continuing on the electroreflectance of silver in the hope of understanding this problem better.

5. SPECIFIC ADSORPTION ON SINGLE CRYSTAL SURFACES

The most complete study so far is that for halide ions on silver single crystals[20,32]. A general view of the capacity curves for four of the simple surfaces is shown in figure 9. Although there is a great variety of behaviour evident in these results, some general trends may be identified. In many cases three peaks in the capacity may be seen, two broad peaks at more negative

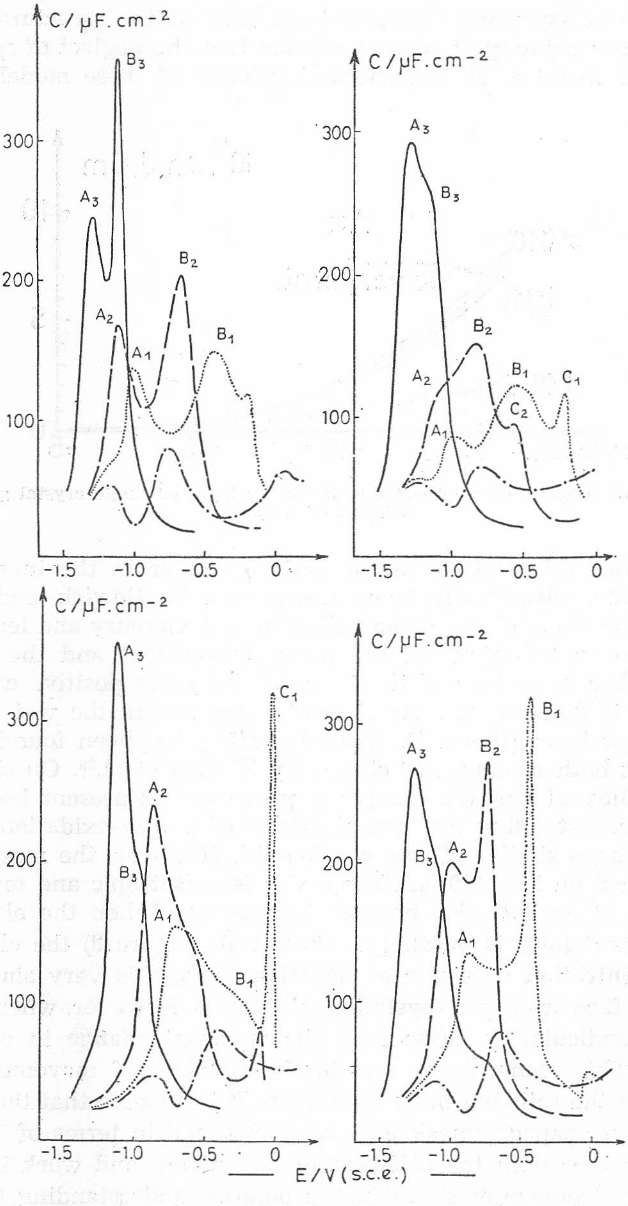

Figure 9. Capacity of silver single crystal in 0.01 M aqueous solution of sodium halides (Data from Valette et al.[32]).

potentials and a narrow one at a more positive potential. In the case of chloride a detailed thermodynamic analysis of the adsorption has been made[32] and this indicates that the first broad peak (A) occurs at quite low coverages ($< 10\%$) while the second (B) occurs in the region of half coverage. The narrow peak (C) occurs when the adsorption monolayer is approaching completion.

Simple ionic adsorption which follows an adsorption isotherm having a term accounting for the repulsive interaction between the ions leads to a capacity curve having a peak in the region of half coverage[33]. It is therefore reasonable to interpret the peak B as due to the usual type of adsorption effect. That is, it arises from an inner layer capacity (C^i) which may be represented as[33]

$$(C^i)^{-1} = ({}_{\sigma}C^i)^{-1} + ({}_{\sigma_{-1}}C^i)^{-1}\,(\partial\sigma_{-1}/\partial\sigma)_{\mu} \qquad (1)$$

where ${}_{\sigma}C^i$ is the differential capacity of the inner layer at constant amount adsorbed and ${}_{\sigma_{-1}}C^i$ is that at constant charge on the metal. The peak in the capacity arises from the term $(\partial\sigma_{-1}/\partial\sigma)_{\mu}$ which is closely related to the slope of the adsorption isotherm and has a maximum at the inflection point of the latter.

The first peak (A) occurs at such a low coverage that the second term on the right-hand side in equation (1) makes a relatively small contribution to the capacity, which in any case has no maximum in this region. It seems more likely that the peak observed in the capacity is due to the first term on the righthand side of equation (1) which expresses the capacity at constant amount adsorbed and which has a large peak at zero amount adsorbed, ascribed above to water orientation. As in the analysis of halide adsorption on mercury[34-36], analysis of chloride adsorption on the (110) plane of silver suggests that this capacity is to a first approximation independent of the amount of halide adsorbed. However the experimental capacity shows that the height of peak A increases with concentration. This appears to be due to the effect of the specifically adsorbed charge on the diffuse layer capacity. The experimental capacity C may be expressed as[37]:

$$C^{-1} = (C^i)^{-1} + (C^d)^{-1}\ \{1 + \partial\sigma_{-1}/\partial\sigma\} \qquad (2)$$

where C^d is the diffuse layer capacity.

In the absence of specific adsorption the term $(\partial\sigma_{-1}/\partial\sigma)$ is of course zero and equation 2 represents a simple series connection of the diffuse and inner layer capacities. In the region of the p. z. c. the effect of the diffuse layer is to lower C below the value of C^i, and in dilute solutions to produce the well-known minimum. As the amount of specific adsorption increases the term $\partial\sigma_{-1}/\partial\sigma$ decreases, attaining a value in the region of -1.3 as the coverage becomes appreciable. Thus the factor $\{1 + \partial\sigma_{-1}/\partial\sigma\}$ decreases and the effect of the diffuse layer on the measured capacity similarly decreases. In this way the measured capacity can increase towards and even a little beyond the inner layer capacity C^i. This appears to be the principal cause of the increase of peak A with concentration.

The very small width of peak C suggests that there are no longer strong repulsive forces between the adsorbing particles and this is consistent with the suggestion[39] that chloride ions are completely discharged in monolayer adsorption on silver. It therefore seems probable that at the beginning of peak C there is a quite sharp transition from the adsorption of chloride ions which retain their full charge to the adsorption of chloride ions with transfer of charge to the electrode. The appearance of a resistive component in the impedance in this region could be connected directly with this effect but a more likely explanation is that it is related to the mass transfer effects when there is a large change in amount adsorbed over a narrow potential range.

A more direct indication of the change in adsorption character seems to be indicated by the electroreflection spectrum. Figure 10 shows this for a closely similar system — bromide adsorption on a gold electrode. Then the differential electroreflectance is compared with the capacity curve and a very marked peak with reversal of sign can be seen to occur at the sharp capacitance peak. It must be noted, of course, that the electroreflectance coefficient

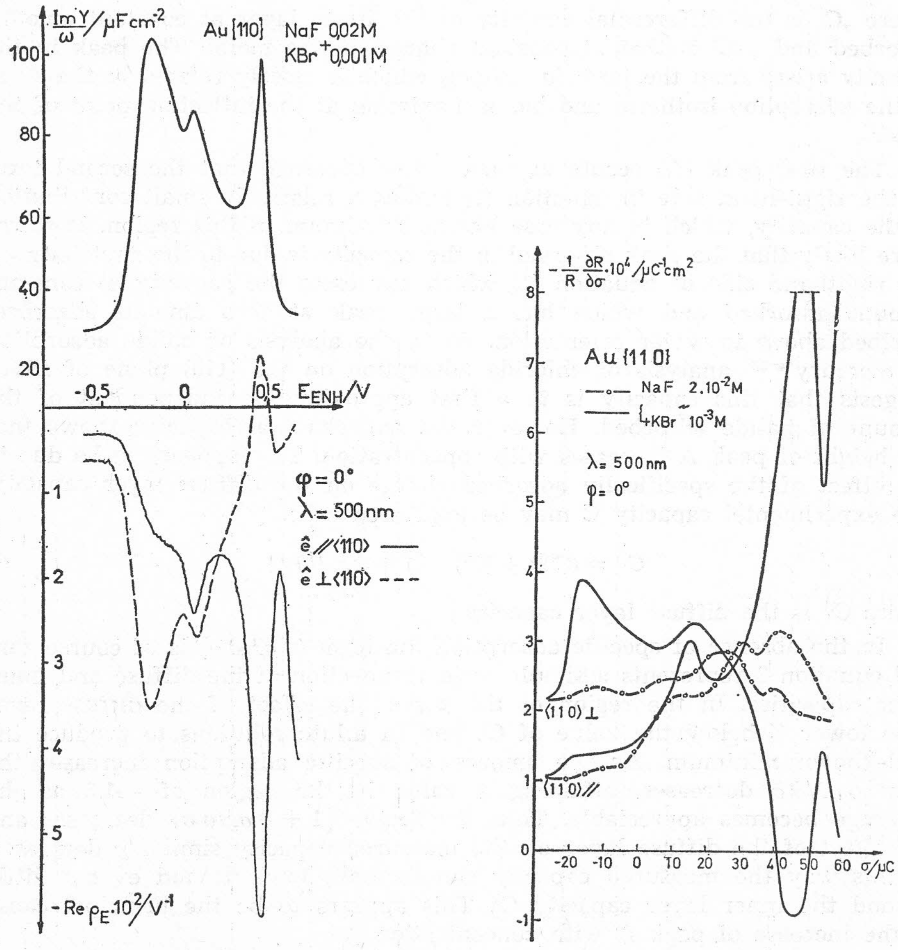

Figure 10. **A. Measured electroreflectance for (110) face of gold in contact with dilute aqueous solutions of KBr compared with the capacity curve.**
B. Differential electroreflectance coefficient with respect to charge for the same (Data from Hinnen et al.).

$R^{-1}\,\partial R/\partial E$ contains the capacity as a factor, but the removal of this in the calculation of the more significant coefficient $R^{-1}\,\partial R/\partial\sigma$ leads to the same result (figure 10 B). The detailed interpretation of the change in electroreflectance in terms of a charge transfer process is not possible at present. However, other evidence exists for this connection. Gottesfeld and Conway[40] have noted sharp changes in reflectance on mercury surfaces. In figures 11 and 12 their optical results are compared with capacity and specifically adsorbed charge curves for closely similar systems. It is evident that the sudden change in reflectivity characteristics occurs when the surface coverage is high and approaching a completed monolayer and also when the observed double layer capacity increases rapidly. It does not seem possible to see a narrow peak in these systems probably because of the superposition of the faradaïc process in this region.

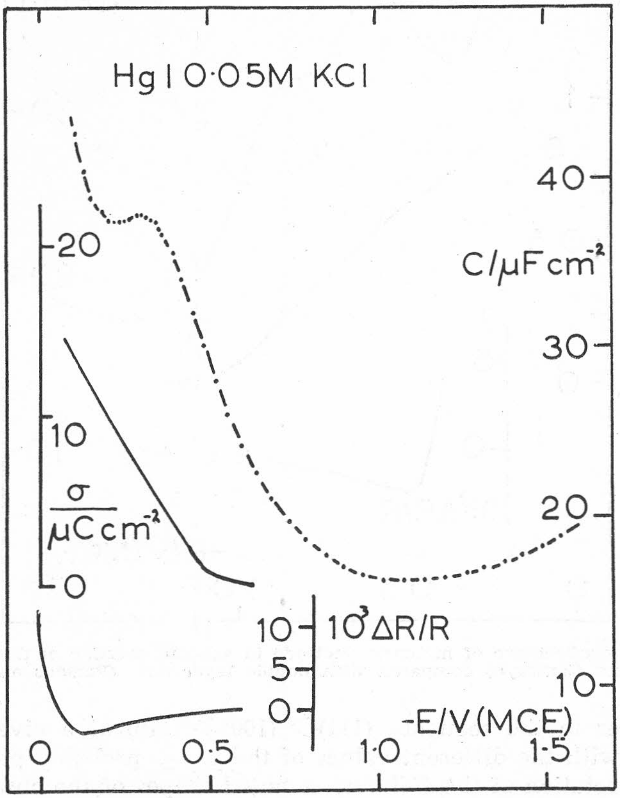

Figure 11. Electroreflectance of mercury electrode in 0.05 M chloride solution (Data from Gottesfeld and Conway[40]) compared with double layer data (Payne[41]).

In this way the general characteristics of the adsorption of chloride on silver can be understood and these ideas can probably be generalized to the higher halides on silver and also on gold electrodes. Up to the present the understanding of the differences between the surfaces of different geometry has not appreciably progressed. The strength of adsorption of chloride on

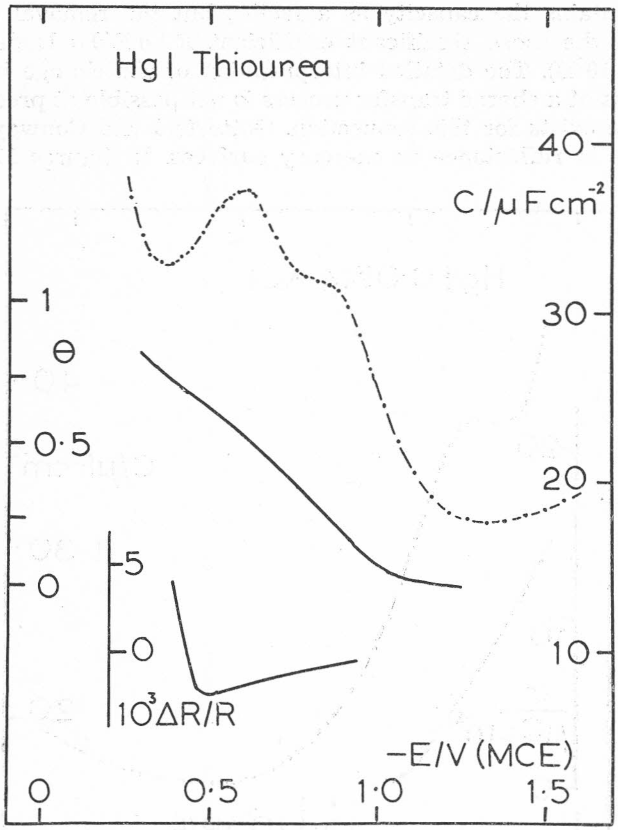

Figure 12. Electroreflectance of mercury electrode in aqueous solution of thiourea (Data from Gottesfeld and Conway[40]) compared with double layer data (Parsons and Symons[42]).

silver increases in the sequence (111) > (100) > (110) at a given charge and this together with the different values of the p. z. c. probably provides a basis for the interpretation of the different detailed shapes of the observed capacity curves, but this has not yet been verified.

The above discussion has assumed that the surfaces are ideal crystal planes. This is never exactly true although small almost ideal crystals have been used[20]. There are certainly effects which may be attributed to defects in the crystal surfaces and these seem to be particularly evident when adsorption is weak[20,21]. In the case of strong adsorption the deviations from ideal crystal structure seem less important and it is possible to neglect them to a first approximation.

6. CONCLUSION

It has not been possible to present here a very complete account of the electrical double layer at the solid metal — electrolyte interface first because the experimental information available at present is limited and patchy. Second the theory remains at a stage at which it is not able to explain the different strengths of adsorption on diferent crystal planes, for example. Similarly, the theoretical accounts of electroreflection remain inadequate to deal with the effects of solid surface structure. However progress is rapid at present and it seems likely that in the near future this method will be fully available for the study and understanding of many of these problems.

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SAŽETAK

Električki dvosloj na granici faza čvrsto/tekuće

R. Parsons

Opisan je napredak u proučavanju čvrstih površina u kontaktu s kondenziranim medijima. Prikazani su rezultati istraživanja kemijski čistih granica faza čvrsto/tekuće, definiranja površinskih struktura, kao i istraživanja monokristalnih površina uz specifičnu adsorpciju iona i bez nje. Nameće se zaključak da je raspoloživ eksperimentalni materijal još uvijek vrlo ograničen i manjkav, ali ni teorija nije uznapredovala do stupnja gdje bi mogla objasniti različite energije adsorpcije na različitim kristalnim plohama.

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Prispjelo 17. prosinca 1979.