



# THE ADSORPTION OF ISOQUINOLINE AT THE Hg/AQUEOUS ALKALINE SOLUTION INTERFACE (1)

*A semiautomatic system to measure differential capacity-potential curves has been used to study the adsorption of isoquinoline from alkaline solutions. The results indicate that isoquinoline adsorbs on Hg in three possible orientations depending on the values of electrode potential and solute concentration. A transition between two vertical orientations is identified. The results confirm proposed orientations of adsorbed isoquinoline.*

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(1) Part of this paper was presented at the 3rd "Reunião Nacional de Electroquímica" in Coimbra-Portugal between 29th June 1981 and 1st July 1981.

## 1 — INTRODUCTION

The adsorption of organic molecules that can undergo a reorientation as the result of changes in an externally applied electrical field has recently been the subject of several researches. GIERST *et al.* [1] made some important observations about the inhibitory effects of adsorbed quinoline on electron transfer reactions. They suggested that reorientation of the adsorbed molecules occurred as the electrode potential was made more negative or as the solute concentration was increased. Later, using ellipsometry, HUMPHREYS and PARSONS [2] observed that two optically different adsorbed films could be identified which they attributed to the existence of different, potential-dependent orientation of the adsorbed molecules. The transition between the limiting orientation was suggested to be sharp in the case of isoquinoline. The adsorption of isoquinoline seemed then to provide an interesting system to be studied by measurements of the differential capacity since the only work published so far was the qualitative analysis of LOVRECEK and CIPRIS [3].

## 2 — EXPERIMENTAL

**Solutions** — a stock solution saturated with isoquinoline ( $\sim 3 \times 10^{-3}$  M) was prepared by adding an excess of solute to a previously degassed 0.25 M aqueous solution of KOH. After being shaken to form an emulsion, the solution was left overnight to equilibrate and separate. The separation was never complete and the solution was therefore filtered to remove isoquinoline in suspension.

**Differential capacity** — Differential capacities were obtained with an automatic a.c. bridge based on Phase Sensitive Detection. A logging system was used to output all information onto tape for off-line computational analysis.

Details of the complete system are given in reference 4.

## 3 — RESULTS

### 3.1 — DETERMINATION OF THE PZC

Drop time measurements were used to determine the pzc for all solutions. The use of a streaming electrode did not give reproducible results, probably because compositional equilibrium was not attained at the surface of the electrode. Similar cons-

traints presumably affect drop time measurements, especially those with the most dilute solutions, but the observed reproducibility of the measurement and of the values of the pzc was found to be better. Table 1 contains all the pzc values obtained after polynomial fitting of the results. Within the general precision ( $\pm 10$  mV) there is a shift of pzc to less

Table 1  
Potentials of zero charge over the entire range of isoquinoline concentrations

$10^2 c/c_{\text{satd}}$	$E_{\text{pzc}}(\text{SCE})$	
	V	
0.4	$0.44_1 \pm 0.01$	V
0.8	$0.44_2$	"
1.2	$0.44_0$	"
1.6	$0.43_8$	"
2.0	$0.42_5$	"
2.8	$0.41_0$	"
4.0	$0.38_5$	"
8.0	$0.36_2$	"
10.0	$0.32_6$	"

negative values as the concentration of isoquinoline increases. With the lowest concentration, the values of pzc obtained are very close to those of the base electrolyte. The positive shift of the pzc for the higher concentrations does not only indicate the occurrence of adsorption but also indicates an average orientation of the dipole of the adsorbed molecule with the positive end towards the electrode surface. The presence of adsorption at all concentration is indicated by the systematic decrease of the drop-times compared with the values for the base electrolyte but the scatter in the data did not permit a thorough analysis.

### 3.2 — DIFFERENTIAL CAPACITY

Fig. 1 shows the differential capacity-potential relationships obtained over the entire range of concentrations. The a.c. frequency throughout was 492 Hz. The presence of adsorbed isoquinoline is indicated by the decrease in capacity with concentration. As is evident in fig. 1 the range of potentials over which the adsorption occurs depends on the concentration of the isoquinoline. For low concentration, i.e. 0.4 to 1.6 % of the saturation value, the dependence of the differential capacity on potential and on concentration is similar to that with other

organic compounds [5]. When the concentration was increased above 1.6 % of saturation a marked change in the capacity occurred at negative potentials. At a concentration of 2 % of saturation a "pit" is observed which is followed by a sharp process resembling desorption. With further increase in concentration the capacity drops to very low values where it remains constant until a sharp transition occurs. The potential at which this process occurs is displaced to more negative values as the concentration is further increased. With further increase in the concentration, another significant change in the capacity occurs. In the anodic region an adsorption-desorption type peak develops and in the cathodic region an abrupt decrease in capacity, which remains constant and independent of E and concentration.

### 4 — DISCUSSION

The classic way to study adsorption is to establish a model by the assignment of an isotherm. This usually requires the determination of the interfacial tension or the Parsons auxiliary quantity,  $\xi$ , as a function of either the electrode potential or charge and of the solute activity. Given the difficulty in obtaining accurate and reproducible drop times, the adsorption of isoquinoline will be discussed on the basis of the dependence of the differential capacity on the solution composition and electrode potential.

Aromatic compounds usually adsorb on charged mercury electrodes with the rings parallel (co-planar) to the metal interface. It has been proposed [5] that such orientation is due to electrostatic interactions between the ring  $\pi$  electrons and the charged electrode surface. It would follow that with increase in anodic charge these attractive interactions would get stronger thus increasing the degree of adsorption. Correspondingly, increasing negative charge on the electrode will tend to reduce the degree of adsorption and at sufficiently high negative charges desorption will be complete. For solutions of isoquinoline at concentration  $< 2\%$  of saturation, the dependence of the capacity on potential and concentration indicates that the adsorption of isoquinoline is, in general, similar to that of other aromatic compounds, the molecules being adsorbed in a flat orientation as proposed by GIERST *et al.* [1,6]. The results of HUMPHREYS and PARSONS [2] also con-

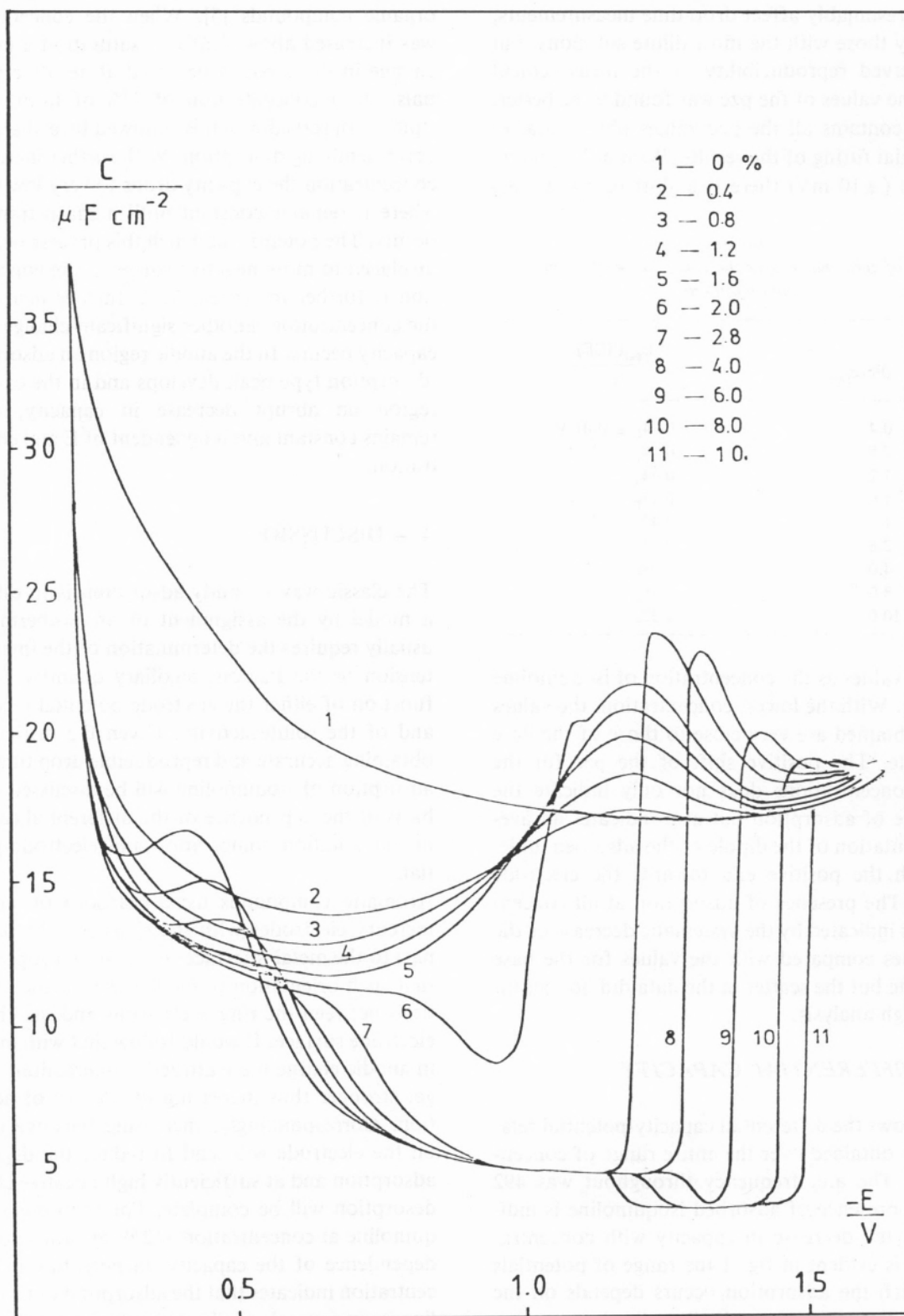


Fig. 1  
Differential capacity curves for the systems Hg/isoquinoline  
0.25 KOH

firm that to be the likely orientation of the molecules at low bulk concentration. Further support for this orientation is indicated by the virtual independence of the pzc on concentration in the range 0 to 2% of saturation. The dipole moment of isoquinoline is  $8.67 \times 10^{-30}$  Cm and the virtual independence of the pzc on concentration is evidence that such dipoles have a very small component in the direction perpendicular to the surface which is consistent with a flat orientation of the molecule. The capacity curves obtained are very similar to those obtained with naphthalene [7] which is generally agreed to adsorb with the aromatic rings co-planar with electrode surfaces. The decrease in capacity with increasing concentration is attributed to a decrease in the local permittivity as the result of increasing coverage of adsorbate.

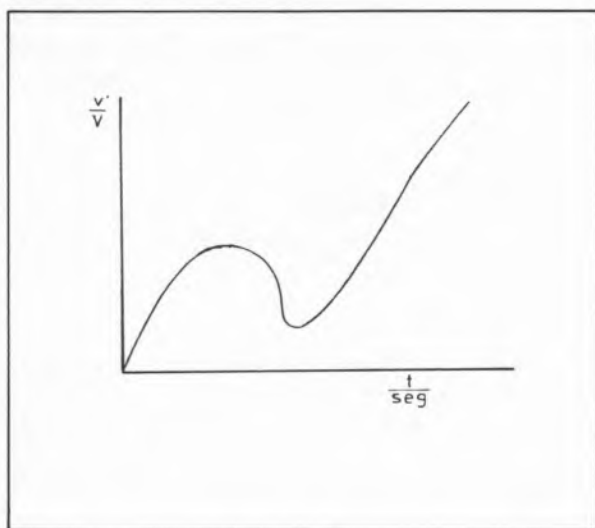


Fig. 2

Out of phase component of the a.c. current

As the bulk concentration of isoquinoline is raised above a threshold value, which for the present condition is between 2.5 and 3% of saturation, and at sufficiently negative potentials, a significant decrease in capacity occurs reaching an almost constant value of  $4.5 \mu\text{F cm}^{-2}$ . At these concentrations the pzc shifts to more positive values, indicating that some of the adsorbed molecules have assumed a different orientation at least at the uncharged electrode. This new orientation has to be such that the dipole moment of the molecule has a component in a direction perpendicular to the electrode surface. This can be achieved with several different orientations of the molecule. However, the fact that the

capacity reaches a constant value independent of the bulk concentration and electrode potential suggests that the interphase has reached an invariant composition. This is consistent with the formation of a monolayer of adsorbed molecules as has been proposed for the case of quinoline by BORDI and PAPESCHI [6] and for isoquinoline by GIERST [1]. The capacity indicates that the transition between the flat and upright orientations is gradual which is confirmed by ellipsometry [2,7]. It has been proposed [1,2,6] that the orientation of the molecules in the monolayer is with carbons 4 and 5 nearest to the surface (fig. 3) which corresponds to a thickness of 0.6 nm, cf 0.14 nm for the flat orientation. This variation in thickness could also explain the significant drop in the differential capacity. Estimating the permittivity of the adsorbed monolayer as the

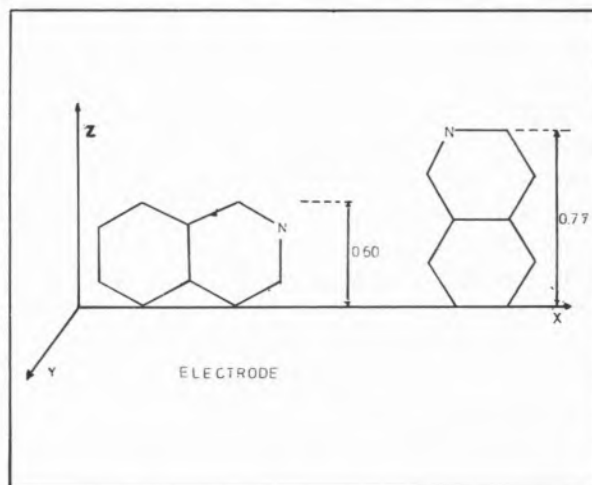


Fig. 3

Orientation of isoquinoline molecules with the corresponding thicknesses in nm

square of the refractive index of isoquinoline ( $\epsilon = n_r^2 = 2.62$ ), the capacity of a parallel plate condenser 0.6 nm thick would be  $3.9 \mu\text{F cm}^{-2}$ . This is in good agreement with the observed value of  $4.5 \mu\text{F cm}^{-2}$  and may be confirmation of the orientation proposed. According to HUMPHREYS and PARSONS [2], the monolayer organisation of the molecules in such a stacked array is stabilized by the simultaneous effect of the applied electric field and by short range attractive lateral forces between the adsorbed molecules. The capacity confirms that the potential range of stability of the monolayer is between  $-0.8$  and  $-1.3$  V (SCE), depending on the concentration as was found by HUMPHREYS and



PARSONS [2]. Thus, along the capacity curve in the anodic region, there will be a displacement of the surface equilibrium from molecules adsorbed with the rings co-planar to the surface towards others with a vertical 4-5 orientation. This displacement of the equilibrium is brought about by the combined effect of the increase in chemical potential in solution and the repulsive interactions between the electrode charge and  $\pi$  electrons of the adsorbate eventually producing complete coverage in the stacked form. The abrupt decrease in the capacity of this monolayer of adsorbed molecules observed at higher concentrations and its independence on further variation of concentration or potential are evidence that the adsorbed monolayer has assumed a different structure. HUMPHREYS and PARSONS [2] found that the transition was very sharp which is attributed to a total lock of attractive interactions between both orientations. The drop in capacity is not so sharp and DC polarography confirms that the transition on an expanding trop is not a step function of potential. The destruction of the second structure occurs at more negative potentials with the extremely sharp "desorption". Similar types of abrupt transitions in the capacity have been observed for other systems, such as uracil [8], camphor [9] and tribenzylamine [10] and attributed to a surface condensation process. According to DAMASKIN [11], the occurrence of an abrupt transition in the capacity followed by sharp desorption with the desorption potential moving towards more cathodic values as the concentration is increased is evidence for a "condensation" process possibly associated with reorientation of the adsorbed molecules. Reorientation of the isoquinoline molecule has been proposed by GIERST [1] to explain the inhibitory properties of the adsorbed layers and assumed by HUMPHREYS and PARSONS [2] to explain the abrupt variation of the optical parameters. The third orientation requires the dipole moment to be almost fully aligned with the electric field and with carbons 6 and 7 the nearest atoms to the surface. This corresponds to a different thickness (fig. 3) of the monolayer (0.77 nm according to HUMPHREYS and PARSONS [2]) and to a capacity of  $3.0 \mu\text{F cm}^{-2}$  which when compared with the experimental value of  $3.5 \mu\text{F cm}^{-2}$  is striking support for the proposed orientation. The alignment of the dipoles with the field may introduce some repulsive interactions between the molecules but the new stacking array may be stabilised

by the favourable interaction of the nitrogen end of the molecule with the solvent and by other short-range dispersive forces. The sudden drop in capacity is not observed with quinoline [6,12] because the orientation with carbon atoms 4-5 nearest to the surface also corresponds to an alignment of the dipole with the field. The behaviour of isoquinoline molecules is a good example of the importance of electrostatic interactions either with or induced by the electric field. The projected areas of the isoquinoline molecule in both upright orientations are different, thus leading to different saturation coverages. According to GIERST [12], those amounts are respectively  $6.3 \times 10^{-10} \text{ mol cm}^{-2}$  and  $8.4 \times 10^{-10} \text{ mol cm}^{-2}$  for the 4-5 and 6-7 orientations. It follows, therefore, that the transition from one to the other must occur with concomitant adsorption. The kinetics of the transition has been extensively studied by GIERST and collaborators [13,14] on the bases on of orientations here proposed to explain the behaviour of the differential capacity.

Recebido 27.Outubro.1983

## ACKNOWLEDGMENTS

One of us F.S. acknowledges the financial support of Gulbenkian Foundation (Lisbon) and INIC (Lisbon).

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