Taking into account the variation with the temperature of the various factors contributing to the interfacial entropy, as envisaged by these authors, one finds a variation of -0.04 erg K^{-1} cm^{-2} as compared with $+0.14$ erg K^{-1} cm^{-2} found experimentally. This reveals the shortcomings of the proposed model in spite of the good agreement obtained at one temperature for the variations with the charge. This model can therefore only be considered as acceptable if supplementary hypotheses are made as for example assuming interactions between the different molecular forms. One can also consider that this type of dimer or even larger aggregate such as those envisaged by Frumkin [4] and Parsons [5] for the interfacial water, consistutes a somewhat over simplified approach of the problem.

The experimental results obtained and their examination in the light of recent theories show that the important problems of the structure of the interfacial water still remains unsolved. There is therefore a need for a statistical approach to these questions based the theories suggested for the volume, and also taking into account the influence of the substratum.

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On the Interaction between Anions and Organic Surfactants in the Inner Part of the Double Layer at the Mercury–Water Interphase

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At the mercury–water interphase, synergic coadsorption is observed between organic surfactants of the azine group (quinoline, isoquinoline and some of their monomethylderivates) and bulky anions (like perchlorate and hexafluorophosphate, amongst others) which are not intrinsically very tensioactive.

The characteristics of the composite inner layer have been investigated on the basis of the following data:

a) the Gibbs individual superficial excesses,

b) the Esin–Markov potential shifts at various constant charge densities,

c) the factors determining the differential capacity of the inner layer,

d) the extent of inhibition affecting electrode reactions of various degrees of complication (single electron exchange without mass transfer through the interphase, reduction coupled with amalgamation, or with chemical steps like protonation or decomplexation).

As a rule, coadsorption leads to the formation of highly compact multilayers, with no definite stoechiometry. Structure stabilization appears to be essentially governed by the common hydrophobic behaviour shared by the anion, the surfactant and the positively charged mercury.

Recourse to potential-step techniques indicates that the anion adsorption–desorption process is controlled by a slow relaxation step giving falling i–t transients, with time constants relatively independent from the values of the initial and final potentials.

In the particular case of 3-methyl-isoquinoline, the region where coadsorption occurs is sharply limited by two potentials corresponding to phase transitions with an abrupt charge density variation. Analysis of the related current–time transients indicates that the surface reorganization proceeds from nucleation centers, in a way reasonably described by the Avrami theory.

Molecular and Intramolecular Interactions in Electrical Double Layer Region

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Molecular and intramolecular interactions are investigated very widely by applying various methods. These investigations mainly concern the bulk of a given phase.

In the case of an interface region due to significant short-range ordering molecules are in different state as compared to molecules in the bulk. Hence, different behaviour and interactions of molecules are to be expected.