the basic hypothesis which sometimes tend to be overlooked in previous publications on the problem This isotherm can be written in a form reminiscent of the law of mass action

$$-\Delta G^\circ/\mathrm{RT} = \ln(a_2^\sigma/a_2^\alpha)/(a_1^\sigma/a_1^\alpha)^n \qquad (1)$$

where $a_i^{\sigma,\alpha}$ are the activities in the interfacial (σ) or volumic (α) phases of the two constituents 1 and 2 of a binary system If one makes the symmetric choice for the activities then ΔG° depends, to all intents and purposes, only on the superficial properties of the pure substances 1 and 2 Finally n is the ratio of the partial molar areas of these two substances *i e* $n = A_2^\sigma/A_1^\sigma$ The above equation corresponds to an equilibrium

$$n(\text{moles } 1)^\sigma + 1(\text{mole } 2)^\alpha \rightleftharpoons 1(\text{mole } 2)^\sigma + n(\text{moles } 1)^\alpha \qquad (2)$$

The simplest symmetrical expression for the activity coefficients at the interface leads to

$$\ln f_1^\sigma = B^\sigma (x_1^\sigma)^2 \qquad (3)$$

and to the following expression for the isotherm

$$-\Delta G^\circ/\mathrm{RT} - \ln[(a_1^\alpha)^n/a_2^\alpha] = B^\sigma \frac{n^2(1-\theta)^2 - n\theta^2}{[\theta + n(1-\theta)]^2} + \ln\left[\frac{\theta}{n^n(1-\theta)^n}\{\theta + n(1-\theta)\}^{n-1}\right] \qquad (4)$$

which constitutes a generalized form of the Bockris and Swinkels equation For more dilute solutions one can assume

$$\ln (a_1^\alpha)^n/a_2^\alpha = -\ln \frac{C_2}{55\;5} - B^\alpha \qquad (5)$$

where the coefficient B^α is related to the solubility at infinite dilution For n = 1 one finds Frumkin's equation, the interaction coefficient then corresponds to B^σ and the apparent adsorption energy is

$$\Delta G^\circ_{\mathrm{app}} = \Delta G^\circ + \mathrm{RT}(B^\sigma - B^\alpha) \qquad (6)$$

This method of proceeding brings out the fact that the Frumkin's isotherm is only strictly applicable to the case where the solute and solvent molecules are of the same size The interaction coefficient cannot be simply reduced to 2–2 interactions, eqn (3), as is usually done but must take into account 1–1 and 1–2 interactions Equation (6) reveals the relationship between the solubility and adsorption and if one observes a variation of the adsorption in agreement with the law of Traube for an aliphatic series this may be due simply to interaction effects in solution, eqn (6) Although the parameter B^σ does not entirely represent the deviation from an ideal behaviour at this interface it is never the less related to the interactions between the constituents This explains, that for an aliphatic series, the existence of correlations between B^σ and B^α can be interpreted in terms of structure It is only the use of the isotherms which leads to the establishment of a correlation between the variation of the apparent adsorption energy and the nature of the polar head associated with the aliphatic chain and the corresponding dipole It is thus possible to use this type of approach for a comparison of the hydrophilic–lyophilic equilibria in solution and at an interface

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The Variation of the Superficial Excess of Entropy in Relation to the Structure of Water in Sodium Fluoride Solutions

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The mercury–NaF aqueous solutions interfacial tension has been measured at varying concentrations and temperatures These results, associated with those of other authors [1, 2], enable one to determine, without ambiguity, and for all accessible values of the electrode charge, the sign and the order of magnitude of the variation with the temperature of the superficial excess of entropy The curves showing the variations of the superficial excess of concentration with the charge indicate a very slight specific adsorption of the fluoride ions at low temperatures which leads to a contribution of about 0 007 erg K^{-1} cm^{-2} to the entropy These results have been compared with those forecast theoretically by Bockris and Habib [3] who schematically consider the interfacial layer of water as being composed of monomers and dimers, the latter being unaffected by the electrical field

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, constitutes 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.