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.

In our investigations the interactions between solvent molecules and ions as well as the intraionic and intramolecular interactions of ions and molecules have been considered at a mercury electrolyte solution interface.

The effect was studied of geometric isomerism and intramolecular rotational isomerism of fumarate, maleate, succinate and 1,2-dihalogenoderivates of ethane on solvent structure and electric permittivity at an electrode electrolyte interface.

The molecular and intramolecular interactions in the electrical double layer region were investigated using both experimental and theoretical methods. The differential capacities measured by bridge method as a function of applied potential at presence of molecules and ions under investigation, were analysed theoretically.

Our investigations lead us to the conclusion that some experimental observations concerning some electrical properties of an interface region can be explained as specific molecular interaction.

Solute–Solvent Interactions and Double Layer Effects. Adsorption of Hexafluoropropan-2-ol on Hg

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The need to enlarge the extent of the thermodynamic analysis on the state of the solutes involved in adsorption phenomena at electrified interfaces has been already underlined [1].

Attention has been consequently given to the system hexafluoropropan-2-ol (HFIPA)–Na_2SO_4–H_2O/Hg electrode, in order to study the interfacial behaviour of fluorinated compounds, HFIPA in particular, whose unusual behaviour in aqueous solution is known (*see e.g.* [2]). The possible interactions in solution, between solutes and solvent, in the above system, which can result in a more or less marked influence on the activity of both organic and inorganic solute are analyzed: *a*) through e.m.f. measurements of galvanic cells without transport; *b*) by means of non electrochemical techniques as density and calorimetric measurements. For sake of comparison parallel measurements are performed on the totally hydrogenated isomer iPrOH. Condition are selected in order to keep Na_2SO_4 activity constant with varying HFIPA concentration. Parallel series of electrocapillary and differential capacity measurements on Hg electrode are performed on solutions of HFIPA respectively at $a_{Na_2SO_4}$ and $C_{Na_2SO_4}$ constant. The whole of the experimental results is analyzed and discussed mainly in terms of significance of the adsorption isotherm obtained in both cases, prior to entering more deeply into detailed questions as to congruence problems or to considering a detailed picture of double layer structure and composition.

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On the Inhibitory Effect of Normal Aliphatic Alcohols upon Cd^{2+}, $Pb(OH)_3^-$ and Bi^{3+} Electroreductions on Mercury at High Surface Coverages

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A detailed investigation of the inhibitory effect of normal aliphatic alcohols, from n-butanol to n-octanol, upon Cd^{2+} and Bi^{3+} reductions and Cd°(Hg) oxidation in perchloric medium, as well as upon $Pb(OH)_3^-$ reduction and Pb°(Hg) oxidation in (NaF + NaOH) mixtures, was carried out at different ionic strengths on dropping mercury and amalgam electrodes. Experiments were conducted under conditions in which the coverage θ of the electrode surface by the surface-active alcohols is almost complete ($\theta \cong 1$). The experimental values of the ratio ($k_{\theta=1}/k_{\theta=0}$) of the rate constant for the electrode reaction at high surface coverages to the corresponding rate constant in the absence of the alcohols, were compared with a theoretical expression of the form [1]

$$k_{\theta=1}/k_{\theta=0} = (c_S^*/c_W^*)^{-n_{\neq}/n_S} \exp(n_{\neq}\Delta G^{\circ}_{ads}/n_S RT) \exp(-cn_{\neq}\Delta G_{lat}/RT) \quad (1)$$

Here c_S^* and C_W^* are the bulk concentrations of the alcohol(S) and of water (W), $n_{\neq}$ and n_S are the numbers of adsorbed water molecules displaced from the electrode surface by one adsorbing particle of the activated complex for the electrode reaction ($\neq$) and by one adsorbing molecule of the surfactant S, respectively, and ΔG°_{ads} is the standard free energy