the Gouy–Chapman theory. The effect due to the taking into account of different planes of closest approach for the anion and the cation is not sufficient to account for this difference and one must envisage the competitive influence of the ion-solvent interactions which is all the more important that one is dealing with mixed solutions of choline and potassium chlorides. As in the case of tetralkylammonium salts one notes an effect due to the cation on the adsorption of the anion. The adsorption of the chlorides exactly neutralizes the electrode charge even for fairly high concentrations. The adsorption of the bromide and iodide vary with the concentration in a different manner for each ion. One can interpret these results taking into account both the relative hydrophobicity of the cation and the disymmetry introduced in the choline molecule as a result of the OH group, as well as, once again, the competitive effect in the influence on the solvent between the cations and anions, an effect which varies according to the nature of the anion.

This study reveals in the case of organic cations the inadequacy of the usual differentiation between diffuse and compact layers which neglects the intrinsic solvent effect. It also shows, in this respect and with regards of all the results obtained, the fundamental importance of the solute–solvent interactions on the adsorbability.

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An Approach to Non-Specific Interactions of the Hydrophobe Type Based on the Study of the Interfacial Behaviour of Normal Aliphatic Alcohols

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The adsorption of normal aliphatic alcohols at the mercury aqueous solution interface has been studied by measuring the differential capacity at the potential of minimum capacity (*i.e.* maximum d'adsorption) as a function of the length of the aliphatic chain, the concentration of the alcohol in solution and the nature of the electrolyte [1].

C^{-1} is observed to vary linearly with the number of carbon atoms n_C in the aliphatic chain and the slope varies with the nature of the anion of the base electrolyte (F^-, Cl^-, Br^- or I^-) but not with the cation (K^+ or Na^+). The limiting value for $n_C = 0$ shows that the adsorbed layer includes at least a layer of water molecules which can be attributed to the hydration of the polar heads. These results, together with those given by Pleskov *et al.* [2], obtained by photoemission studies, suggest that the alcohol molecules are probably not adsorbed in their extended conformation.

One also notes that C is independent of the alcohol concentration in solution once saturation is reached and what ever the base electrolyte. At the interface the situation is therefore the same as in solution with the appearance at this point of a new phase and this serves to illustrate the close correlation which exists between the physico-chemical properties of the interfacial phase as compared to those of the solution.

This leads to the interesting conclusion that although the adsorption of alcohols on mercury have long been studied [3] this approach sheds a new light on the interaction between adsorbed surface active substances and the other solution constituents.

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Adsorption Isotherms of Neutral Molecules for 'Regular Interfacial Solutions'

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A new determination of the adsorption isotherm based on recent developments in interfacial thermodynamics [1, 2] has been suggested, underlining 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:

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

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

$$\ln f_i^\sigma = B^\sigma(x_i^\sigma)^2 \qquad (3)$$

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.