between the molecules in an associate. At T > 25 °C the associates decompose and the number of chemisorbed molecules increase rapidly. Two-dimensional association on the electrode surface takes place also in methanol, 1-propanol and butanol. A general feature is that the association is the less pronounced the longer is the hydrocarbon radical of the alcohol molecule.

The conclusions about the association of alcoholic molecules in the inner part of the electrical double layer found confirmation by the data obtained in the study of the adsorption of some aromatic compounds and inorganic ions on bismuth in alcoholic solutions.

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Determination of Single Ion Activity by Relying on the Electrical Double Layer Model

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It is well known that on the basis of strictly thermodynamic arguments single ion activities are not amenable for direct experimental determination [1–3]. However, single ion activities are much more significant than mean activities with respect to the problem of assessing the structure of solutions. Therefore, various methods have been proposed to derive single ion activities from experimental quantities. All these methods necessarily imply some non-thermodynamic arguments and approximations. The unavoidable step to be taken to arrive at single ion activities is thus the introduction of some model assumptions.

Experimental methods have been proposed based on (a) the correction for the liquid junction potential of measured emf's of cells with constant potential reference electrodes [4], (b) the measurement of the potential difference for a non-isothermal system constituted by two equal electrodes [5], and (c) the measurement of the potential difference for an 'air gap' cell [6] of the type $\mathrm{Pt}|\mathrm{H_2}|\mathrm{HCl}(m)|\mathrm{air}|\mathrm{HCl}(m_{\mathrm{ref}})|\mathrm{H_2}|\mathrm{Pt}$. A proposed non-experimental route rests [7] on the assumption that for not very dissimilar ions the difference in activity coefficient γ_i is essentially related to the difference in ion solvation. A number of factors which may make γ_+ to differ from γ_- have been discussed by Frank [8].

The ultimate scope of a measurement to determine single ion activity coefficients is possibly to reproduce the condition of constancy in potential of one of the two electrodes in an electrochemical system. In this work we propose to adopt the electrical double layer model in the absence of specific adsorption [9] as the one best meeting the above requirement. This model has been verified independently [10] and within the validity of the usually accepted Stern–Gouy–Grahame theory, it can be used without any further justification. Work in this direction was first carried out by Stastny and Strafelda [11]. No further attempt appears to have been made.

The basic assumption is that a cell of the type (σ is the charge density on the metal):

$$\mathrm{Hg}(\sigma = \mathrm{const})|\mathrm{NaF}(m)|\mathrm{F}^-\ \text{selective electrode}, \quad (1)$$

exhibits a potential difference strictly dependent on the sole activity of F^-. Although the method is in principle valid at any value of σ, the direct measurement of E for cell (1) can be carried out only at the potential of zero charge. E at other values of charge can be obtained by integrating double layer capacity data and correcting for diffuse layer effects (concentration effects at the Hg electrode).

Capacities and potentials of zero charge have been determined for Hg in a number of NaF aqueous solutions at concentrations ranging 0.01 to 0.9 mol dm^{-3}. An Orion $\mathrm{LaF_3}$ crystal electrode has been used as the F^- sensitive electrode. From these measurements the γ_- values have been derived with the procedure described elsewhere [12]. The γ_+ values have been obtained from the known values of the $\gamma_\pm$ for NaF [13].

γ_-'s have been found to be higher than γ_+'s. This will be shown to be in disagreement with the prediction of the 'hydration' theory [7]. The values of γ_- are apparently independent of the value of σ on Hg. Ultimately, these results point to some reciprocal support of the various theories involved in the present approach. The present results will be compared with those obtained with the 'air gap' cell [6]. Merits and limits of the present method will be discussed.

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On the Interfacial Behaviour of Water–*ter*-Butanol–KCl Mixtures

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The study of the interfacial behaviour of aliphatic alcohols with branched short carbon chains can yield information on the part played by cosurfactant in detergent systems. The choice of t-butanol in this respect is particularly interesting in view of the importance of the thermodynamical data available for aqueous electrolytic solutions of this substance. It is thus possible to choose exact conditions suitable for the application of Gibbs's law [1, 2]. The isotherms show that the monolayer model is not applicable to solutions containing more than 3% t-BuOH for which the structure of the solutions changes [4]. However the results for more dilute solutions can be analysed in detail, an approach similar to that described in another communication [3] being utilized. One finds that the adsorption energy does not vary with the potential as a parabola as in the case of normal alcohols studied using the Frumkin isotherm, but that in the region of ±0.3 V round the potential of the maximum E_M it obeys rather a relation of the type:

$$-\Delta G^\circ/RT = 1.4\exp[-17(E - E_M)^2] \qquad (1)$$

The model chosen enables one to calculate the variation of the interfacial activity coefficient of the t-BuOH with the corresponding molar fraction. The function evaluated vary only very slightly with the potential. The curves obtained are somewhat slightly more apart than the corresponding one for the solutions.

The overall results for the diluted solutions can be interpreted on the basis of a competitive effect between the interfacial field and water molecules adsorbed on the interfacial structure, the effect of the co-solvent tending to predominate for weak fields. This leads one to believe that cosurfactants act essentially within a colloidal or polyelectrolyte systems by an indirect effect on the structure of the water surrounding the particle.

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The Adsorption of Choline Halides at a Mercury–Solution Interface

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Against the background of investigations undertaken on the importance of hydrophilic and lipophilic reactions, and more particularly in the case of quaternary ammonium cations [1–3] a study of the influence of a hydrophilic alcohol group has been carried out using aqueous choline halide solutions. Previous publications [4, 5] dealing with these solutions have shown that the solute–solvent interactions are complex. They reveal the existence of competitive effects between those due to the action of the cations on water which favours the formation of hydrogen bonds in the solvent around the ion (an effect which is modulated by the presence of the OH group in the choline) and that due to the anion which diminishes the number of these hydrogen bonds as its size increases. This competition leads to a change in the properties of the solutions when in a series one passes from the chloride to the bromide and iodide.

The adsorbability of the cation as related to the properties of the OH group is indeed diminished as compared to the corresponding quaternary ammonium cation. Further one notes that the adsorption in the diffuse layer is inferior to that predicted by