3 P. T. Taylor, *J. Phys. Chem., 31,* 1478 (1927).
4 J. Bagg and G. A. Rechnitz, *Anal. Chem., 45,* 271 (1973).
5 G. Milazzo, N. Bonciocat and M. Borda, *Electrochim. Acta, 21,* 349 (1976).
6 V. A. Rabinovich, A. E. Nikerov and V. P. Rotshtein, *Electrochim. Acta, 12,* 155 (1967).
7 R. G. Bates, B. R. Staples and R. A. Robinson, *Anal. Chem., 42,* 867 (1970).
8 H. S. Frank, *J. Phys. Chem., 67,* 1554 (1963).
9 D. C. Grahame, *Chem. Rev., 47,* 441 (1947).
10 D. C. Grahame, *J. Am. Chem. Soc., 76,* 4819 (1954).
11 M. Stastny and F. Strafelda, *Coll. Czech. Chem. Commun., 37,* 37 (1972).
12 A. De Battisti and S. Trasatti, *J. Chim. Phys., 70,* 395 (1973).
13 R. Parsons, 'Handbook of Electrochemical Constants', Butterworths, London (1959).

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.

References

1 A. de Battisti and S. Trasatii, *J. Electronal. Chem., 54,* 1 (1974).
2 H. Nakadomari, D. A. Mohilner and P. Mohilner, *J. Phys. Chem., 80,* 176 (1976).
3 R. Benes, this symposium.
4 D. de Visser, G. Perron and J. E. Desnoyers, *J. Am. Chem. Soc., 99,* 588 (1977).

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 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.

References

1 J. Pior, R. Bennes and E. Bou Karam, *J. Electroanal. Chem.*, *57,* 399 (1974).
2 E. Bou Karam, R. Bennes and D. Bellostas, *J. Electroanal. Chem.*, *21,* 84 (1977).
3 M. Hamdi, *thèse d'état,* in preparation.
4 G. E. Boyd, J. W. Chase and F. Vaslow, *J. Phys. Chem.*, *71,* 573 (1968).
5 S. Lindenbaum, L. Leifer, G. E. Boyd and J. W. Chase, *J. Phys. Chem.*, *74,* 761 (1970).

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.

References

1 E. Tronel-Peyroz, D. Schuhmann and D. Bellostas, *C.R. Acad. Sc.*, 289, Serie C, (1979).
2 V. V. Eletskii and Yu. V. Pleskov, *Electrokhimiya, 10,* 179 (1974).
3 B. B. Damaskin, A. O. Petrii and V. V. Batrakov, 'Adsorption of organic compounds on electrodes', Plenum Press, New-York and London, (1971).

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