- 3 P. T. Taylor, J. Phys. Chem., 31, 1478 (1927).
- J. Bagg and G. A. Rechnitz, Anal. Chem., 45, 271 (1973).
 G. Milazzo, N. Bonciocat and M. Borda, Electrochim.
- Acta, 21, 349 (1976).
 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.
- 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

R. BENNES, A. MAZHAR and D. SCHUHMANN*

CNRS, Physicochimie des Interfaces, B.P. 5051, Montpellier Cedex, 34033, France

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:

$$-\Delta G^{\circ}/RT = 1.4 \exp[-17(E - E_{\rm M})^2]$$
(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

M. KABA and M. PRIVAT*

CNRS, GR 28, Physicochimie des Interfaces, B.P. 5051, Montpellier Cedex, 34033 France

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