EC solvent mixture. The high value of the solvation number in 100 wt.% EC may be due to the primary solvation layer together with some contribution from the secndary solvation layer.

An Estimation of the Volume of Restructured Water Shells around Hydrophobic Solutes

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Water is known to be a largely associated liquid. The presence of non-electrolytes or large organic ions, tends to strengthen the hydrogen bonds between the water molecules near the large hydrophobic solute, and a cage or ‘iceberg’ is effectively formed around them. This model of the hydrophobic hydration of alkyl groups is widely accepted but the thickness of restructured water shells around hydrophobic solutes has not been determined. In order to estimate the volume of restructured water per mole hydrophobic solute we used the differential conductometry of carefully thermostatted (0.001 °C) solutions [1, 2]. The experimental procedure consists of measuring the specific electrical conductance (χ) of a strong electrolyte solution before and after adding a small amount of hydrophobic solute. Provided the equivalent conductance of the strong electrolyte ions in the restructured water shell is zero [3] the volume of the restructured water shell is given by [2, 3].

$$V_{s,o} = \frac{\Delta\chi \cdot 10^3}{\chi \cdot c} \ [\mathrm{cm^3/mol}]$$

where $\Delta\chi$ is the change in χ, corrected for the increase in volume and c is the molar concentration of the strong electrolyte.

We have attempted to measure the $V_{s,o}$-values in aqueous solutions of perchloric acid for 16 alkylammonium ions. The results obtained can be summarized as follows:

$$V_{s,o} = n(CH_3) \cdot V(CH_3) + n(CH_2) \cdot V(CH_2) + n(NH_3^+) \cdot V(NH_3^+)$$

where n(i) is the number of groups i in the ion studied and V(i) is the specific volume of hydration shell of i-group. In 10–20% $HClO_4$(w/w), $V(CH_3) \approx V(CH_2) \approx 40 \pm 10$ [cm^3/n(i) mol] and $V(NH_3^+) \approx -48 \pm 10$ [cm^3/n(i) mol]. The negative value for $V(NH_3^+)$ reflects the negative hydration of $-NH_3^+$-group.

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Structure of Aliphatic Alcohols in Electrical Double Layer on Electrode Surface

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The structure of solvent in the field of the electrical double layer exerts significant influence on the inner layer properties on adsorption of ions and molecules. Some theoretical models considering differently the interaction of solvent dipoles in the inner layer have recently been elaborated [1–3]. On the basis of the experimental data obtained by us on bismuth electrode in alcoholic solutions, mainly in ethanol, the analysis of the validity of the cluster models [1–3] for the description of the solvent structure in the inner layer has been carried out in this paper. Cluster model was chosen since alcohols belong to the group of associated liquids. According to cluster model solvent exists on the electrode surface in the form of separate chemisorbed molecules with constant orientation and of associates of molecules (clusters) the orientation of which depends upon electrode charge q and the composition of which varies with temperature T.

By use of the equations of the cluster model [1–3] the electrode charge has been calculated for several temperatures in the interval from −15 to 50 °C. The results of the theoretical calculations were compared with the experimental data in the form of the plots of the inner layer integral capacity K_{02} against q at several T. Experimental values of K_{02} were found from the differential capacity of bismuth in alcoholic solutions of $LiClO_4$ at various temperatures.

On the basis of the calculations it was established, that at T < 25 °C the ethanol molecules exist in the inner layer mainly in the form of two-dimensional double associates due to the hydrogen bonding 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 $Pt|H_2|HCl(m)|air|HCl(m_{ref})|H_2|Pt$. 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):

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

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 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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