Effects of Solvent and Solute Interactions on Double Layer Properties and Electrode Kinetics

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Local Order and Hydrogen Bonding in a Molecular Model for Adsorbed Solvent, with and without Adsorption of a Neutral Polymer Species

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With few exceptions [1–4], orientational models for solvent adsorption do not include consideration of solute adsorption and hence can only be compared with experimental curves of the inner-layer differential capacity for the solvent under conditions in which solute adsorption is regarded as negligible. More generally, however, any consistent orientational model for solvent adsorption, once generalized through the inclusion of solute adsorption, should also be able to account for the adsorption behaviour of solute species. The implications of the 0th (random) approximation in the statistical mechanical treatment of an adsorbed monolayer consisting of 'up' and 'down' solvent molecules, with and without the further presence of the polymer molecules of a neutral solute adsorbed in a single orientation, are briefly examined.

The different size of solute and solvent particles is accounted for *via* Flory–Huggins statistics. Certain inconsistencies in previous work on the subject are thus evidenced. It is concluded that the role played by local order in affecting the inner-layer properties cannot be disregarded. The above model of adsorbed monolayer is therefore reexamined taking local order into account *via* the quasi-chemical approximation. It is thus shown that an increase in attractive lateral interactions between adsorbed solvent molecules causes the single hump in the curve of the inner-layer capacity *versus* the charge density on the metal to split into two distinct humps. This may explain the presence of two humps in the differential capacity curves of certain highly polar organic solvents [5, 6]. Moreover, it is shown that a Frumkin isotherm behaviour over a wide range of surface coverages is to be expected, provided that solvent–solvent lateral interactions are more attractive than solvent–surfactant and surfactant–surfactant lateral interactions. Noting that the adsorption of several bulky organic molecules from aqueous solutions actually satisfies the Frumkin isotherm, appreciable hydrogen bonding between adsorbed water molecules must be inferred.

To account for the effect of hydrogen bonding both on differential capacity curves and on the adsorption isotherms of neutral surfactants, a general statistical mechanical treatment of the adsorbed monolayer is developed, in which solvent molecules are allowed to be adsorbed in an unspecified number of orientations, certain contiguous pairs of these orientations giving rise to hydrogen bonds. Local order and difference in size between solvent and solute particles are both accounted for. On the basis of quite general considerations it is shown that the maximum in the entropy of the adsorbed monolayer occurs at the same charge density at which the surface potential $\Delta\chi$ is zero, independent of any detailed model of the adsorbed monolayer. This prediction agrees with the experimental behaviour of the mercury-water interphase in the absence of solute adsorption [7, 8].

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Specificity of Hydration of Individual Ions in Relation to their Adsorption at Electrodes

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In the aqueous medium, H-bonding structural equilibria play a major role in the hydration of ions and in their adsorption behaviour at electrodes. Not only energy but entropy factors in adsorption are consequently important and lead to specificity in ion hydration interactions and ion adsorption.