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Conference Abstract

Dipoles and Double Layers at Liquid Interfaces*

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The work described concerns principally the properties of insoluble spread monolayers of ionised amphipathic long chain molecules at liquid interfaces. As a model system for understanding the behaviour of dipoles and ions at interfaces, insoluble spread monolayers have many advantages. The superficial molecular and charge densities can be readily defined by volumetric methods (provided that spreading is well controlled) and the measurement of the thermodynamic parameters surface pressure and surface potential is now reliable at air and oil/water interfaces as a result of recent experimental advances. As compared to adsorbed films, the difficult and inaccurate procedure of using the Gibbs Adsorption Isotherm is not necessary. A disadvantage — as compared to the perfectly polarisable metal interfaces, such as mercury/electrolyte solution systems, is that the interfacial capacity is not available experimentally. For the insoluble monolayers, the results provide new insights into ionic double layer structure, the orientation of water molecules at liquid aqueous interfaces, the polarisability of surface dipoles under applied normal fields, and the long and short range interaction forces between monolayer molecules.

The experiments reported use monolayer spreading and measuring techniques developed in recent years in this laboratory[1-4]. These techniques allow study of spread films at air/water and a variety of oil/water interfaces to give absolute surface pressure and surface potential measurements as a function of surface density over a range of temperatures for various compositions of the bulk phases, and provide criteria for judging the reliability of spreading techniques and the purity of the materials used. In particular, the common problem of solvent retention on spreading a monolayer has been examined in parallel studies of spreading from crystals or from aqueous solutions[1].

One group of experiments gives the surface potential of sodium octadecyl sulphate monolayears at the air/water over a very wide range of surface areas/molecule for several NaCl concentrations at four temperatures. This work[5] has shown clearly the general inability of Gouy theory to describe the properties of the ionic double layer. The Stern theory can be made to fit the data, provided the surface density is not too low. The finding that the Esin-Markow coefficient may be larger than predicted by Gouy theory at very high molecular areas is a severe difficulty both for the Gouy and classical Stern models of the double layer, and suggests that at very low monolayer charge densities, the double layer will be dominated by forces which lead to negative ionic adsorption in the absence of a film. Another striking feature of these results is that for a given molecular area and solution composition, the magnitude of the surface potential increases with temperature. Although this does not prove absolutely that the χ potential of the clean surface of water is positive (in the convention used by Parsons and others), it does suggest very strongly that the net orientation of the surface water molecules is with the oxygen atoms towards the vapour phase. Much of this work is in the press.

In another series of incomplete experiments, an investigation is being made of the thermodynamics of the Volta effect, using spread monolayers as a useful system. In this study, the outer potential difference between an aqueous phase (with or

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without a spread monolayer at its surface) and an unchanging reference vibrating electrode connected *via* a potentiometer and an appropriate electrochemical half cell has been measured as a function of applied potential. These measurements are intended to test the assumptions of Kelvin, Lorentz and Bridgman which require the x potential at a surface to be independent of surface charge[6]. It has been shown that these assumptions hold within experimental error for many monolayers systems, but definitely break down for certain highly polarisable films such as zwitterionic phospholipids. The magnitude of the effects so far found with these films is surprisingly large, and we are in the process of examining the situation more completely.

In the last set of experiments to be described, the contribution of chain-chain interactions to the equation of state for spread or adsorbed long chain molecules is under study. Guastalla[7] showed that for uncharged monolayers at the air/water interface, that the equation of state included a term giving a negative pressure varying as $\pi_{\mathrm{coh}} = -KA^{-3/2}$ where K is a constant for a given chain length, and A is the area/molecule. Davies[8] showed that the hydrocarbon chains were responsible for this cohesion-term. Since the pressure-area isotherms for long chain charged films at the oil/water interface is independent of chain length for a given head group at high areas, one can assume that 'chain-cohesion' is absent, and that the difference between the surface pressures of a given film at the air/water and oil/water interfaces gives the cohesion contribution at the air/water interface direct. We have measured these differences for long chain sulphate and quaternary ammonium monolayers, and confirm Guastalla's findings, except that we find the coefficient to vary with values near to $-3/2$. The small variations of the Guastalla coefficient with temperature head group, salt concentration chain length are under study. The magnitude of this coefficient makes it quite clear that the chain-chain interactions are not of the simple Van der Waal's type, and a theory to explain them is currently not available.

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