The Use of Surfactant Selective Electrodes in Non-aqueous Solvents

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Membrane electrodes selective to the surfactants cetyltrimethylammonium bromide and cetylpyridinium bromide have been constructed and used to investigate the aggregation properties of the surfactants in ethylene glycol; the data clearly reveal the existence of premicellar association prior to a critical micellar concentration.

There is currently much interest in the solution properties of surfactants in non-aqueous polar solvents.[1–4] Although surfactant association structures in non-aqueous polar solvents have been known for some time,[5] there are still many issues which remain unsolved; in particular the role of any 'solvophobic' effect, as opposed to other factors which control aggregation.[6] Moreover, there are certain controversies associated with experimental data on these systems,[4] related to the micellar structure model and the ways of estimating critical micellar concentrations. A key parameter in understanding the aggregation process is the variation of surfactant monomer concentration with total concentration.

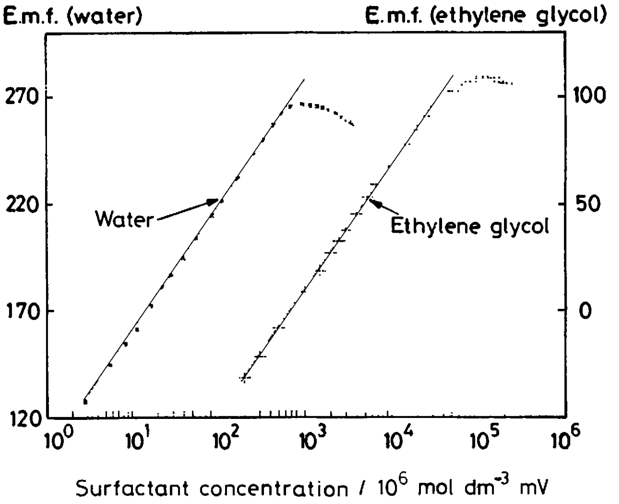

Figure 1. E.m.f. as a function of concentration for the cetylpyridinium bromide electrode in water and ethylene glycol.

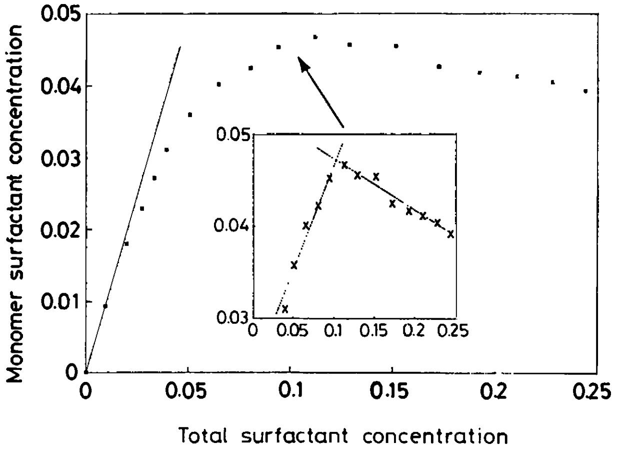

Figure 2. The monomer concentration of cetylpyridinium bromide plotted against total concentration.

Recently, we have been successful in the application of surfactant membrane selective electrodes to investigate the equilibrium properties of aqueous solutions of surfactants containing various additives.[7,8] The advantage of these electrodes is that monomer concentration of surfactant can be monitored directly in these various formulations. This technique has now been extended to monitor surfactant concentrations and micelle formation in non-aqueous polar solvents. In this communication, we present our results involving e.m.f. measurements on cetyltrimethylammonium bromide ($C_{16}TAB$) and cetylpyridinium bromide ($C_{16}PB$) in ethylene glycol.

The surfactant selective membrane electrodes were constructed using the same procedure as described in an earlier publication.[9] The membrane comprises a specially conditioned polyvinyl chloride and a commercially available polymeric plasticizer. The polyvinyl chloride used in the present work contains negatively charged groups which are neutralised by the surfactant cation before use. Monomer surfactant activities in various solutions can be obtained from e.m.f. measurements on the following cell.

Surfactant electrode	Solutions containing 10^{-4} mol dm^{-3} sodium bromide	Electrode reversible to Na^+

During these experiments we also carried out simultaneous e.m.f. measurements using a bromide ion selective electrode to obtain information about counterion binding. The e.m.f. of the electrode was measured relative to a standard sodium electrode and as a consequence all the solutions that were studied were made up in 10^{-4} mol dm^{-3} sodium bromide. The surfactants used in this work were purified by repeated crystallisation of commercial samples in acetone.

The first positive and encouraging feature to report is that the electrodes used in this work operate successfully in the ethylene glycol solvent and show very good Nernstian responses as shown in Figure 1 for $C_{16}PB$. The response of the electrode in aqueous solutions of $C_{16}PB$ is also given in Figure 1 for comparison with the results in ethylene glycol, the solid lines for both plots refer to the Nernstian slopes and the points are experimental. In water the electrode displays perfect Nernstian behaviour until the critical micelle concentration (c.m.c.) of the surfactant is reached, after which the monomer surfactant concentration decreases as more surfactant is added. In this case the c.m.c. is well defined. In ethylene glycol, the e.m.f. behaviour is qualitatively similar, but the turning point in monomer concentration occurs at much higher surfactant concentration. In addition, this turning point, as indicated in the diagram, is not as sharp as that observed in water. Another feature of the electrode data in ethylene glycol is that there is a deviation from Nernstian behaviour at a small range of concentrations immediately below this turning point. This behaviour is illustrated very clearly in Figure 2, where the monomer concentration derived from the electrode data is plotted against total surfactant concentrations on a linear scale. The solid line in this case is equivalent to Nernstian behaviour.

Furthermore, once this non-ideal behaviour starts, the deviation increases as the surfactant concentration is increased until the turning point of monomer concentration is reached. We interpret these observations in the following way. Firstly, consider micelle formation. The turning point in monomer concentration corresponds to the c.m.c. of the surfactant in ethylene glycol. The fact that this is not as well defined as in water is not surprising, since micellization occurs at a rather high concentration. Indeed, this behaviour is very similar to that shown by short chain surfactants (typical C_8 sulphate and C_8TAB) in water, where the c.m.c. is known to occur over a narrow range of concentrations. We have estimated the c.m.c. in the present work by expanding the plot in Figure 2 around this turning point as is shown in the expanded insert in this diagram. Secondly, consider pre-micellar aggregation. We attribute the non-ideal behaviour of the electrode at concentrations immediately below the c.m.c. to pre-micellar aggregation. There is no question that this is a real effect in the sense that Nernstian behaviour of the electrode occurs right up to the c.m.c. in aqueous solution but not in ethylene glycol. In this region where pre-micellar association occurs the aggregation pattern is consistent with the trimerization model. Once the c.m.c. is reached the data are then consistent with the micellisation process, as indicated by the decrease in monomer surfactant concentration with increasing surfactant concentration. In addition, we also observe an increase in the counterion concentration as the concentration of the surfactant is increased. These observations are typical[10,11] of the micellar behaviour of ionic surfactants in aqueous solutions. As far as we are aware, this is the first time that monomer concentrations have been evaluated for surfactants dissolved in nonaqueous solvent and, indeed, in ethylene glycol, contrary to other observations,[2] the present data clearly shows the formation of micelles.

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