Section 4. Thermodynamics and Kinetics of Micellization, including Solubilization

KINETIC AND EQUILIBRIUM STUDIES ASSOCIATED WITH THE FORMATION OF MICELLES IN AQUEOUS AND NONAQUEOUS POLAR SOLVENTS

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Recent measurements carried out using surfactant selective electrodes constructed in this laboratory have shown that for aqueous solutions of anionic and cationic surfactants with a small amount of added salt (~ 10^{-4} mol dm^{-3}) there is a significant decrease of the monomer surfactant concentration as the total concentration of the surfactant is increased in the micellar region. By carrying out simultaneous measurements using an electrode selective to the counterion it is also possible to evaluate the degree of micellar dissociation. We have considered the implications of these new data in relation to kinetic studies of monomer/micelle equilibria carried out using different relaxation techniques. As a result it has been shown that micellar parameters, which can be derived from kinetic studies, are extremely sensitive to changes in monomer surfactant concentration in the micellar region and also, to a lesser extent, to the degree of micellar dissociation. Kinetic and equilibrium measurements have also been extended to the investigation of cationic surfactants in formamide solutions. The authors gratefully acknowledge support of the SERC and Unilever Ltd.

INTERFACIAL SOLUBILIZATION OF AMINO ACIDS IN AOT W/O MICROEMULSIONS

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The interfacial partitioning of amino acids in AOT reversed micelles has been investigated using simple phase-equilibrium methods. The interfacial partition coefficient is a strong function of the electrolyte concentration and type in the conjugate two-phase system, a result of a "squeezing out" of the amino acids with increasing interfacial curvature. The importance of steric effects is emphasized by the effect of various substituents on the squeezing-out behaviour of substituted phenylalanines and tryptophans. Electrostatic factors have been assessed in terms of a structural model for the double layer inside the reversed micellar water pools. The cosurfactant effect of amino acids gives further evidence of their expulsion from the interface as it becomes more rigid and solid-like with changing salinity.
SOLUBILIZATION OF ALCOHOLS AND DIOLS IN AQUEOUS SOLUTIONS OF SODIUM DODECYL SULFATE

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The aqueous solubility of otherwise sparingly soluble substances may be significantly increased by adding surfactant, i.e. they become solubilized. The amount that can be solubilized depends, amongst other things, on the amount of surfactant added. At low concentrations of surfactant, there is a linear relationship between the amount solubilized and the surfactant concentration. However, for primary alcohols linearity only extends to a surfactant concentration of about 0.05 m. At this point the amount that can be solubilized reaches a maximum. Viscosity and light scattering data suggest that this coincides with an increase in the micellar size, from spherical to rod-or disc-like micelles. Closer inspection of the separating phase shows that this also undergoes a change around this point, from an alcohol-rich L2 phase to a lamellar D-phase. The phase diagram shows that this cannot occur for benzyl alcohol. For the linear part, i.e. at low surfactant concentrations, a simple model for calculating distribution coefficients for the solubilizate between the micelles and the aqueous surroundings has been derived. It shows that the distribution coefficients largely depend on the aqueous solubility of the solubilizate.

THE ROLE OF THE INTERFACIAL TENSION IN THE TWO-PHASE KINETICS OF SOLUBILIZATION IN REVERSE MICELLES

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The effect of the interfacial tension on the kinetics of solubilization in reverse micelles was studied in two-phase systems using a standard stirred cell. In the case of a transport (convection) controlled solubilization one may distinguish between two different states of the interface: fluid and rigid. The values of the mass transfer coefficients in systems with a low interfacial tension ($\gamma \leq 0.25$ mN/m) corresponded to those found earlier for a fluid interface; while higher interfacial tension ($\gamma > 1$ mN/m) changed the hydrodynamics so that the resulting mass transfer coefficients agreed with values found for a rigid interface. In the case of reaction controlled solubilization (interfacial process of metal ion solubilization) a decrease of the interfacial tension caused an increase of the solubilization rate. For the solubilization of a mixture of cations (high interfacial tension, Ca$^{2+}$/K$^+$) the ratio of solubilization rates was equal to the concentration ratio in a feed solution. For a mixture with low $\gamma$(Zn$^{2+}$/Ca$^{2+}$) the ratio of the solubilization rates corresponded to the equilibrium concentration ratio of the two cations in the organic phase. Based on these experimental results possible mechanisms of the solubilization are discussed.