1 Introduction to specialist surfactants
I.D. ROBB

1.1. Introduction

Surfactants have long been used to improve the properties of dispersions and films in many industrial products and processes, with the simpler (and hence cheaper!) ionic and nonionic surfactants mainly being used. In recent times there have emerged more unusual surfactants that initially are finding use in niche areas, that are expanding rapidly. In order to understand the behaviour of these specialist surfactants it is worth considering some of the principles that govern this behaviour.

The useful and fascinating properties of surfactants are essentially a result of combining into one molecule certain groups that as separate molecules would be incompatible. Thus, surfactants usually have polar and nonpolar components and the resolution of this ‘incompatibility’ by aggregation or adsorption at interfaces is what makes surfactants the important materials they are. The basic details of surfactant aggregation have been outlined in a number of books including the recent contribution by Clint [1].

Surfactant aggregation is complex but reasonably well understood. The type of aggregate formed is largely determined by the relative cross section areas and shapes of the polar and nonpolar groups. The relations between the geometry of a surfactant and type of mesophase preferred have been derived [2], and are shown in Table 1.1. The geometry of the surfactant molecule is described by taking \( a \) as the head group area, \( v \) the volume of

<table>
<thead>
<tr>
<th>Packing factor ( v/a l_c )</th>
<th>&lt;1/3</th>
<th>1/3–1/2</th>
<th>1/2–1</th>
<th>~1</th>
<th>&gt;1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Effective shape of surfactant molecule</td>
<td>cone</td>
<td>truncated cone</td>
<td>truncated cone</td>
<td>cylinder</td>
<td>inverted truncated cone</td>
</tr>
<tr>
<td>Preferred structure</td>
<td>spherical micelles, isotropic phase</td>
<td>cylindrical micelles, hexagonal phase</td>
<td>flexible bilayers, vesicles</td>
<td>planar, bilayers, lamellar phase</td>
<td>inverted micelles, isotropic phase</td>
</tr>
</tbody>
</table>
the hydrophobic tail and \( l_c \) the critical chain length, this being slightly less than the length of a fully extended chain.

These cross section areas are the effective areas and include not only the actual geometrical areas but also any electrical repulsion between head groups. Thus ionic surfactants, in the absence of added electrolyte, have relatively large effective head group areas. At concentrations just above the critical micelle concentration, and in the absence of electrolytes to reduce the electrical repulsion, ionic surfactants have an effective shape of an ice cream cone, the resulting micellar aggregate being spherical. In the presence of high electrolyte, ionic surfactants may form hexagonal or lamellar phases at high surfactant concentrations. These packing arguments apply to the specialist surfactants described in this book as much as to the more widely studied conventional materials.

The 'incompatibility' of the groups in a surfactant manifests itself not only by aggregation but also by adsorption at interfaces. At the air/water (A/W) interface, there is usually a positive adsorption of surfactant molecules, giving a higher concentration of surfactant in the surface layer than in the bulk. This positive adsorption lowers the free energy of the system, as observed by a decrease in the surface tension \( \gamma \). The relation between this free energy change, the adsorption and the surfactant activity \( (a_2) \) is described by the Gibbs equation:

\[
\Gamma = \left( \frac{1}{RT} \right) \frac{\partial \gamma}{\partial \ln a_2}
\]

where \( \Gamma \) is the surface excess of the surfactant. Whilst surfactants show positive adsorption, the rarely studied increase in surface tension of water in the presence of some acids is a result of the negative adsorption of ions from the interface. These principles of positive and negative adsorption altering the free energy of the system may be applied to dissolved molecules as well as at macroscopic (A/W) interfaces as discussed below.

### 1.2 Head group interactions

Since the properties of surfactants are partially controlled by those of the head group it is worth considering how different groups respond, particularly to variations in electrolyte and temperature. Surfactants are often used at variable temperature or electrolyte concentrations and it is important to understand which head groups are most susceptible to changes in these conditions. Addition of electrolyte often changes the quality of solvent for various polar groups, though these changes depend on the nature of both the polar group and the ion, showing that the effect of the ions on the structure of water is not the primary cause of the effect on solvent quality. Determining the effects of temperature and added electrolyte on the solvent quality is probably more easily done by examining the properties of