dilational elasticity and viscosity (see Section 5.5.3, Eq. 5.6). A phase difference between the area change and the change in surface tension indicates a relaxation process which could arise from:

- movement of solute to and from the bulk liquid phase to the subsurface region;
- movement to and from the subsurface region to the surface (adsorption-desorption);
- rearrangement of the material of the adsorbed film towards its instantaneous equilibrium state.

For small molecules the rearrangement process is very fast compared to the oscillation frequency and so does not affect the measured viscosity. Similarly, it is often assumed that the establishment of equilibrium between the surface film and the subsurface region is rapid, leaving only the movement of solute between bulk liquid and the subsurface as the source of visco-elastic behaviour. Such behaviour has been treated by Lucassen and van den Tempel (1972).

For longitudinal waves of higher frequency the situation is more complex. At frequencies above about 10 Hz, the compression waves are damped out before they reach the end of the trough so reflection and interference are negligible. A time delay and a decay in amplitude between barrier movement and the consequent change in surface tension at the point of measurement must be factored into the analysis. For intermediate frequencies the changes in surface tension vary in a complex pattern along the trough, but in most cases this problem can be circumvented if measurements are taken a small distance before the mid-length of the trough where the amplitude and phase have been shown to be independent of frequency (Lucassen and Barnes, 1972).

4.4 Adsorption of non-electrolyte solutes

4.4.1 Effects of solute concentration on the surface tension

A graph of surface tension against solute concentration often has the form shown in Figure 4.3, the surface tension and the negative slope both decreasing as the concentration increases.

The slope, $\mathrm{d}\gamma/\mathrm{d}c_B$, can be determined from such curves, particularly if, as in Figure 4.3, the data can be fitted by a function that can be readily differentiated. Sometimes the plot of surface tension against $\ln c_B$ is nearly linear enabling a more accurate determination of the slope to be made. This is no the case for the data in Figure 4.3.

Once the slope, $\mathrm{d}\gamma/\mathrm{d}c$ or $\mathrm{d}\gamma/\mathrm{d}\ln c$, has been determined the adsorption can be calculated from the Gibbs equation (3.32) as shown in Figure 4.4.

This adsorption isotherm may be described as a *composite* adsorption isotherm. The theory behind this concept is discussed in detail in Section 9.4.1. The decrease in the adsorption of butanol after the peak i due to the increasing amount of non-adsorbed butanol at the surface (i.e. th

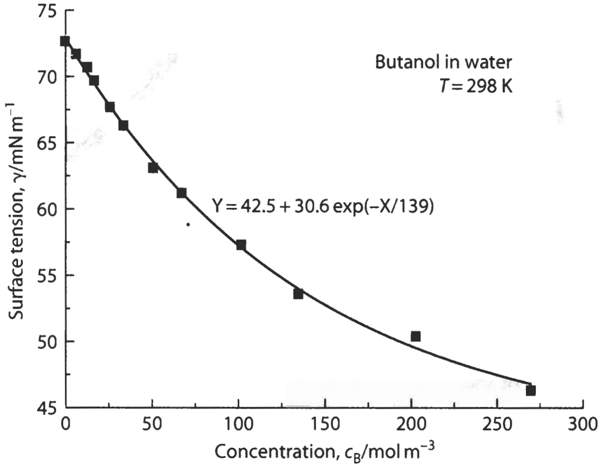

Figure 4.3. Effect of butanol concentration on the surface tension of an aqueous solution (data from Posner *et al.*, 1952).

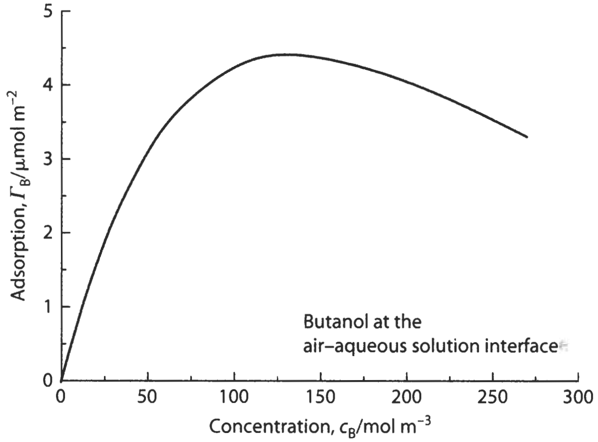

Figure 4.4. Adsorption of butanol at the surface of butanol + water solutions. Adsorption values are calculated from the data in Figure 4.3 using the Gibbs equation.

amount that would be at the surface if there were no adsorption) and competition for the remaining sites from the water. Note that as we approach pure butanol the *adsorption* falls to zero even though the surface layer is pure butanol.

4.4.2 Szyszkowski–Langmuir adsorption

For many binary systems, A + B, the surface tension follows the Szyszkowski relation:

$$\gamma = \gamma_A^\bullet - b\gamma_A^\bullet \ln(1 + c_B/a) \tag{4.1}$$

where a, b are constants and $\gamma_A^\bullet$ represents the surface tension of pure A.

Figure 4.5 shows that the butanol-in-water system follows the Szyszkowski relation at low concentrations, but deviates significantly at higher concentrations, a trend that can be attributed to competition from the solvent water.

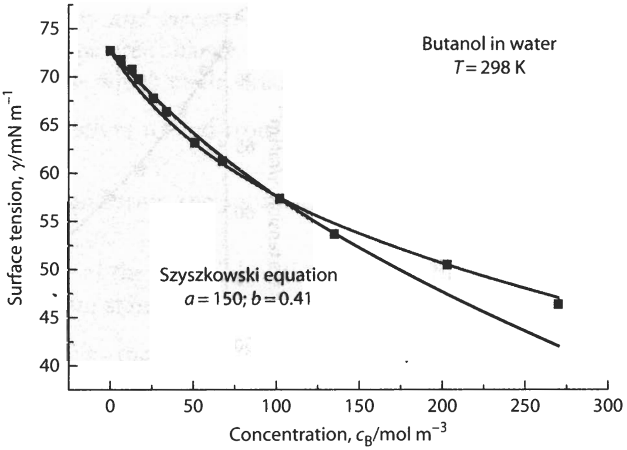

Figure 4.5. Fit of the Szyszkowski equation ($a = 150\,\mathrm{mol\,m^{-3}}$, $b = 0.41$) to experimental data (■) for the butanol + water system.

Differentiation of Eq. (4.1) and substitution in the Gibbs equation (3.32) gives

$$\begin{aligned}\Gamma_B &= \frac{c_B}{RT}\frac{b\gamma_A^\bullet/a}{1 + c_B/a}\\ &= \frac{\Gamma_B^\infty\ \alpha\ c_B}{1 + \alpha\ c_B}\end{aligned} \tag{4.2}$$

where

$$\alpha = \frac{1}{a};\ \Gamma_B^\infty = \frac{b\gamma_A^\bullet}{RT}.$$

A form suitable for linear plotting can be obtained:

$$\frac{c_B}{\Gamma_B} = \frac{1}{\Gamma_B^\infty \alpha} + \frac{c_B}{\Gamma_B^\infty}. \tag{4.3}$$

Equation (4.2) has the same form as the Langmuir adsorption isotherm, originally derived for the chemisorption of gases on solids and discussed in detail in Section 8.5.1. Equations (4.2) and (4.3) are sometimes called the Szyszkowski–Langmuir isotherm.

Again it is only the data at low concentrations that fit the Szyszkowski–Langmuir isotherm.

According to the Langmuir equation, at high concentrations $\Gamma_B \rightarrow \Gamma_B^\infty$, so the adsorption tends to a limiting value. The Langmuir equation was originally derived for adsorption at the gas–solid interface in which case the limiting behaviour corresponds to complete monolayer coverage. At the gas–liquid interface the limit is generally lower and may not be reached because of competition from the solvent (as in Figure 4.4). With butanol in water, for example, Γ_B^∞ is significantly lower than theoretical upper limit of about $8.3\,\mu\mathrm{mol\,m^{-2}}$ (see Figure 4.6).

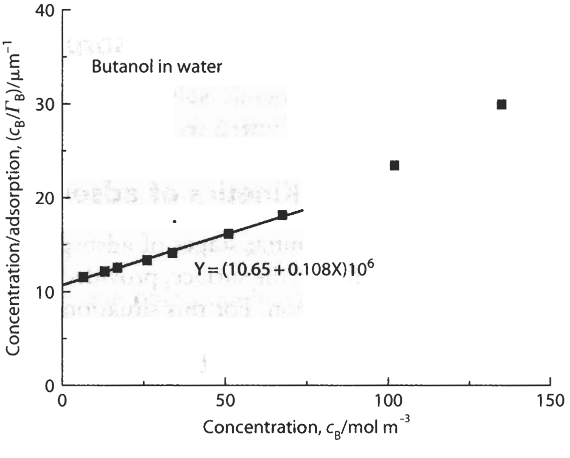

Figure 4.6. Test of Eq. (4.3) for the data in Figure 4.4. Note that only the data at low concentrations fit the straight line. From this line we obtain $\Gamma_B^\infty = 5.55\ \mu\text{mol m}^{-2}$ ($0.30\ \text{nm}^2\ \text{molecule}^{-1}$), $\alpha = 0.0101\ \text{mol}^{-1}\ \text{m}^2$.

4.4.3 Equations of state

The results of adsorption measurements may be expressed as an equation of state such as that formulated by Schofield and Rideal:

$$\Pi\left(\hat{A} - \hat{A}^\circ\right) = qkT \tag{4.4}$$

or

$$\Pi\hat{A} = qkT + \Pi\hat{A}^\circ \tag{4.5}$$

where $\Pi = \gamma_{\text{solvent}} - \gamma_{\text{solution}}$ is the surface pressure; $\hat{A}_i = 1/\Gamma_i$, is the area per molecule of i; and q is a constant giving a measure of the affinity of the adsorbed molecules for each other. Generally, the amount adsorbed is less than one monolayer. Plots of Eq. (4.5) for various unionized fatty acids show good linear relationships over much of the surface pressure range. Some of these data are shown in Figure 4.7.

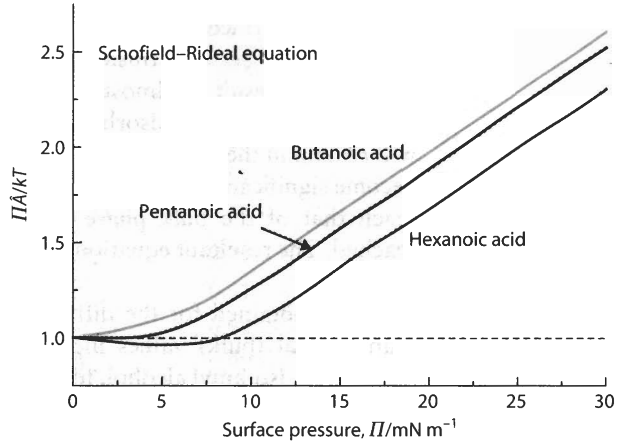

Figure 4.7. Tests of the Schofield–Rideal equation (4.5) for the adsorption of several unionized carboxylic acids at the air–aqueous solution interface. (Replotted from data of Schofield and Rideal, 1925.)

4.4.4 Negative adsorption

A few organic solutes are negatively adsorbed at the air–(dilute aqueou solution) interface. They include glycine and sucrose.

4.4.5 Kinetics of adsorption

In the initial stages of adsorption the rate is determined by diffusion of th solute to the surface, provided that there is no stirring and no energy barrier t adsorption. For this situation we can write:

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \left(\frac{D}{\pi}\right)^{1/2} ct^{-1/2} \qquad (4.6$$

so that

$$\Gamma = 2c(Dt/\pi)^{1/2} \qquad (4.7$$

where D is the diffusion coefficient and c is the concentration of the solute

Even though this equation only applies at the beginning of the adsorptio process it does suggest that small amounts of impurity in the solute can take long time to reach adsorption equilibrium and give rise to long-term drifts surface tension. We will see in Section 4.7.6 that this effect can be used as test for surfactant purity.

At later stages the back diffusion of solute away from the surface mu also be considered. The net rate of adsorption is then slower than give by Eq. (4.6) and has been described by the theory of Ward and Tord (1946). This theory also incorporates the possibility of an energy barrier adsorption. Their model postulates a subsurface region with a thickness only a few molecular diameters that is in instantaneous equilibrium with th surface. Effectively this enables the amount adsorbed at the surface to expressed as a bulk-type concentration and thus simplifies the diffusio problem.

When a new surface is created the solute concentration in the subsurfa region will be the same as that in the bulk, but nearly instantaneous adsor tion to the surface itself will cause the concentration in the subsurface fall to nearly zero. Diffusion of solute from the bulk to the subsurfa will initially result in almost all of this material moving immediately to t surface, but as the adsorbed amount increases more and more solu will remain in the subsurface and back diffusion from subsurface to bulk w become significant. Eventually the solute concentration in the subsurface w reach that of the bulk phase and adsorption equilibrium will have be reached. The resultant equation requires graphical integration and will not given here.

Values obtained for the diffusion coefficient that are significantly low than normal (bulk) values indicate the existence of an energy barrier adsorption. Iso-amyl alcohol, for example, gives a value that is about 56 tim smaller than the normal value showing that diffusion is not the ra determining step in the adsorption process.

4.5 Adsorption of ionized solutes

When the solute is ionized the Gibbs equation must be used in the general form with a term for each species in solution. Using the Gibbs convention and a solute that ionizes completely to M^+ and X^-;

$$\frac{-\mathrm{d}\gamma}{RT} = \Gamma_{\mathrm{M}^-}\,\mathrm{d}\ln c_{\mathrm{M}^+} + \Gamma_{\mathrm{X}^-}\,\mathrm{d}\ln c_{\mathrm{X}^-}$$

If M^+ and X^- are the only ions in the solution then electrical neutrality requires that

$$c_{\mathrm{M}^+} = c_{\mathrm{X}^-} = c \text{ and } \Gamma_{\mathrm{M}^+} = \Gamma_{\mathrm{X}^-} = \Gamma$$

and

$$-\frac{\mathrm{d}\gamma}{RT} = 2\Gamma\,\mathrm{d}\ln c$$

or

$$\Gamma = -\frac{1}{2RT}\frac{\mathrm{d}\gamma}{\mathrm{d}\ln c} = -\frac{c}{2RT}\frac{\mathrm{d}\gamma}{\mathrm{d}c}. \tag{4.8}$$

Aqueous solutions of simple electrolytes often show a slight rise in surface tension with concentration. According to the Gibbs equation (4.8) this indicates negative adsorption of the solute: in other words the electrolyte is partly expelled from the surface. Some typical values of surface tension are shown in Table 4.1.

Table 4.1. Surface tension values of some aqueous solutions of simple salts at 20 °C (data from Weast, 1977).

Solute	Concentration, c_B/mol dm^{-3}	Surface tension, γ/mN m^{-1}
None		72.75
NaCl	0.10	72.92
NaCl	0.93	74.4
NaCl	4.43	82.55
KCl	0.93	74.15
NaBr	0.91	74.05
$NaNO_3$	0.92	73.95
$BaCl_2$	0.80	74.9
$MgCl_2$	0.91	75.75
Na_2CO_3	0.90	75.45
HCl	0.97	72.45
H_2SO_4	0.84	72.55

4.6 Adsorption of surfactants

4.6.1 Molecular structure of surfactants

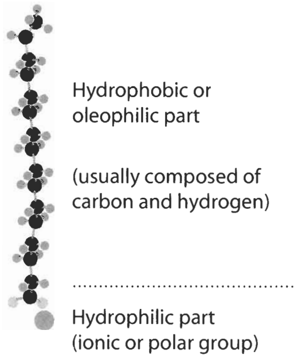

Figure 4.8. Structural features of a typical amphiphile (in this case sodium hexadecanoate).

Surfactants (an abbreviation for *surface active agents*) belong to a class of compounds known as **amphiphiles**. An amphiphile (from Greek: *loves both*[2]) is a substance that combines in the one molecule a segment that tends to be water insoluble and oil soluble, i.e. **hydrophobic** or **oleophilic**, and a segment that tends to be water soluble, i.e. **hydrophilic**. The balance between the hydrophobic and hydrophilic segments can cover a wide range: from molecules that are almost completely insoluble in water to ones that are highly soluble. This is sometimes referred to as the **hydrophilic–lipophilic balance** or HLB (see Section 6.3 for more details). The essential features of a typical amphiphile are shown in Figure 4.8.

The surfactants are water-soluble amphiphiles and are strongly adsorbed at surfaces. The driving force for this strong adsorption comes from the amphiphilic nature of the surfactant molecule; for example, at the air–aqueous solution interface the hydrophobic portion of the molecule can be in the vapour phase out of the water while the hydrophilic portion can be immersed in the water (as in Figure 4.9). Such adsorbed films are known as **Gibbs monolayers** (*monolayer* because there is normally only one layer).

The use of a circle and line to represent a surfactant molecule is sometimes criticized because it does not adequately represent the relative sizes of the head group and the tail. Often the head group is actually smaller in cross-section than the tail. However, this is not the complete picture as the hydrophilic head group will have water molecules associated with it, increasing its effective size. Nevertheless it is useful to examine space-filling molecular structures to get a better perspective. Images of some such structures are shown in Figure 4.10.

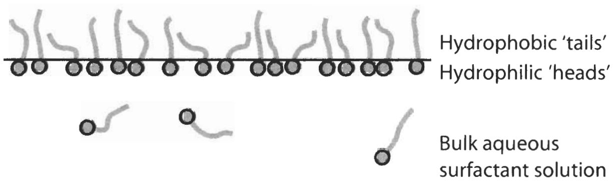

Figure 4.9. Schematic illustration of a Gibbs monolayer. It is a common convention to draw amphiphiles with a circular dot to represent the hydrophilic 'head' group and a line (irregular or straight) to represent the hydrophobic 'tail' section.

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[2] The terms *amphiphilic* and *amphipathic*, although opposite in literal meaning, apply to identical molecular types. The first term means *loves both*, the second means *hates both*. Thus, for example, a polar group 'likes' water but 'hates' non-polar solvents, an alkyl chain 'hates' water but 'loves' non-polar solvents. Until fairly recently the term *amphipathic* was normally used, but as love is always better than hate, *amphiphilic* is now preferred.

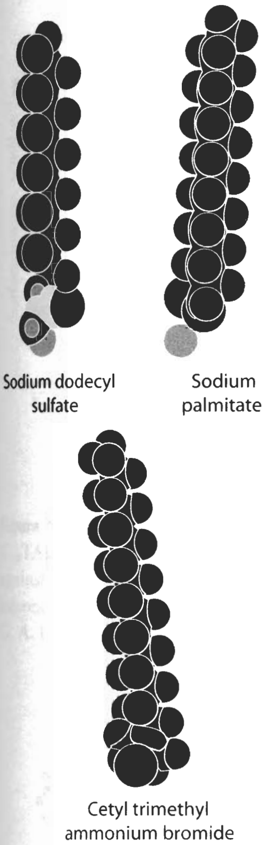

Figure 4.10. Space-filling molecular models of several amphiphiles.

Many of the common amphiphiles have trivial names and some of these are given in Table 4.2 and Table 4.3.

There are three classes of surfactant, defined by the ionic nature of the surface active species: **anionic, cationic,** and **non-ionic.** Some examples are shown in Figure 4.11.

4.6.2 The surface tension of surfactant solutions

The *surface tension* of a surfactant solution, when plotted against concentration, usually falls smoothly to a lower limit after which it remains constant (see Figure 4.12). The curve is nearly linear at very low concentrations and the Gibbs equation (4.8) indicates that the adsorption is then proportional to the concentration. When the surface tension is plotted against $\ln c$ there is a linear fall just before an abrupt change to the constant value of surface tension. The Gibbs equation shows that where the γ–$\ln c$ curve is linear the absorption is constant, suggesting that the adsorption has reached a limit. This is often called the **saturation adsorption.** However, recent neutron reflectivity and surface tension data have brought the concept of saturation adsorption into question (Simister *et al.*, 1992; Barnes *et al.*, 1998).

4.6.3 Adsorption of surfactants

Adsorption values can be calculated from such surface tension data using the Gibbs equation (3.32 or 3.33). Usually it is the logarithmic form of the equation that is used, as calculation of the slopes is easier. The adsorption isotherm for $C_{16}TAB$ calculated from the data in Figure 4.12 is shown in Figure 4.13.

There are two approximations that may be useful for calculating adsorption when the data are sparse. At low surfactant concentrations (indicated by values of surface tension only slightly lower than that of water) the slope $d\gamma/dc$ is nearly constant, and at concentrations just below the region of constant surface tension the slope $d\gamma/d\ln c$ is nearly constant.

Table 4.2. Systematic and common names of some fatty acids and alcohols. Note that that some of these amphiphiles are not sufficiently soluble in water to be classed as surfactants.

No. of carbons	Alcohol			Acid		
	Systematic name	Common name	Abbreviation	Systematic name	Common name	Abbreviation
12	dodecan-1-ol	lauryl alcohol	$C_{12}OH$	dodecanoic acid	lauric acid	$C_{11}COOH$
14	tetradecan-1-ol	myristyl alcohol	$C_{14}OH$	tetradecanoic acid	myristic acid	$C_{13}COOH$
16	hexadecan-1-ol	cetyl alcohol	$C_{16}OH$	hexadecanoic acid	palmitic acid	$C_{15}COOH$
18	octadecan-1-ol	stearyl alcohol	$C_{18}OH$	octadecanoic acid	stearic acid	$C_{17}COOH$
20	eicosan-1-ol	arachic alcohol	$C_{20}OH$	eicosanoic acid	arachidic acid	$C_{19}COOH$
22	docosan-1-ol		$C_{22}OH$	docosanoic acid	behenic acid	$C_{21}COOH$

Table 4.3. Names of common unsaturated and ionic surfactants.

Systematic name	Common name	Abbreviation
9-octadecenoic acid (*cis*)	Oleic acid	
9-octadecenoic acid (*trans*)	Elaidic acid	
9,12-octadecadienoic acid	Linoleic acid	
Sodium dodecyl sulfate	Sodium lauryl sulfate	SDS
Hexadecyl trimethyl-ammonium bromide	Cetyl trimethyl ammonium bromide	$C_{16}TAB$
Dodecyl penta(ethylene oxide)		$C_{12}E_5$

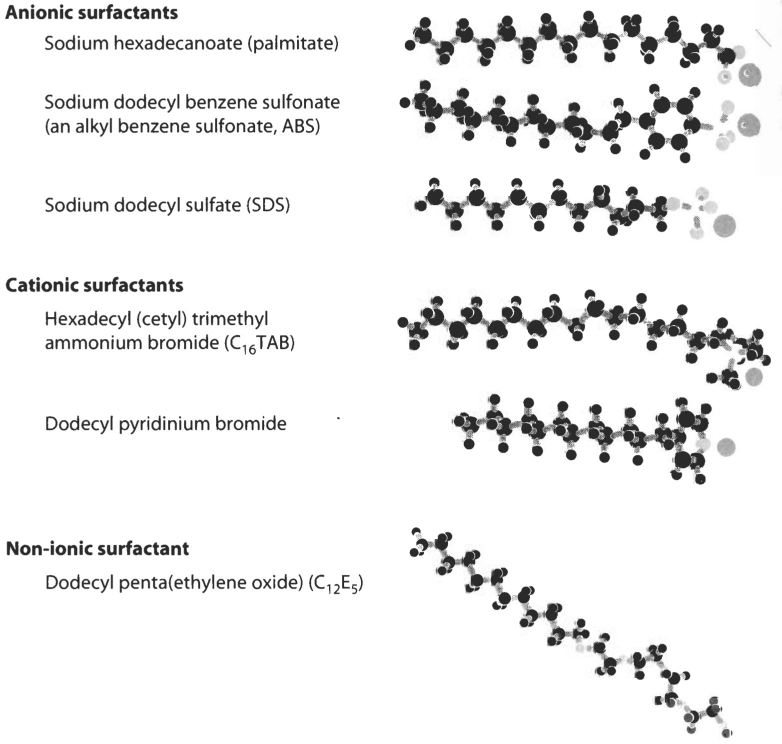

Figure 4.11. Examples of surfactants.

Application of the Gibbs equation

Comparisons of adsorption values determined by the Gibbs equation and values determined by more direct methods occasionally reveal discrepancies.

Surface hydrolysis is clearly illustrated by the following example (Sally *et al.*, 1950). Adsorption measured by radio labelling of the anionic surfactant 'Aerosal OTN' (sodium di-*n*-octyl sulfosuccinate) with ^{35}S showed that Eq. (4.8) should be used without the factor $\frac{1}{2}$. This suggested that Na^+ was not being adsorbed and further measurements with $^{22}Na^-$ confirmed this. Apparently the Na^+ was being replaced at the surface by H^+, a phenomenon

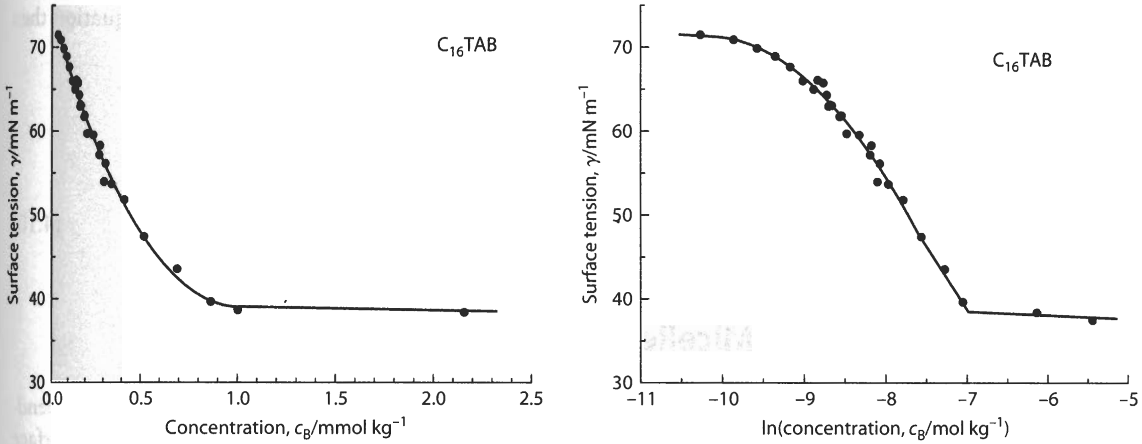

Figure 4.12. Surface tension of C_{16}TAB solutions plotted against concentration and ln(concentration). (Data of G. A. Lawrie.)

now called *surface hydrolysis*. Applying the full Gibbs equation (3.30) (with $Na^+ = M^+$) gives:

$$-\frac{d\gamma}{RT} = \Gamma_{M^+} \, d\ln(c_{M^+}) + \Gamma_{X^-} \, d\ln(c_{X^-}) + \Gamma_{H^+} \, d\ln(c_{H^-}).$$

But $\Gamma_{M^+} = 0$ and c_{H^+} is constant (the amount of H^+ lost to the surface is negligible compared to the total amount in the bulk solution), so the equation becomes

$$-\frac{d\gamma}{RT} = \Gamma_{X^-} \, d\ln(c_{X^-}). \quad (4.9)$$

Indifferent electrolyte

Sometimes the solution also contains a relatively large concentration of an indifferent electrolyte with the same counterion as the amphiphile (e.g. M^+Y^-). This avoids the ambiguities that may arise with surface hydrolysis and often

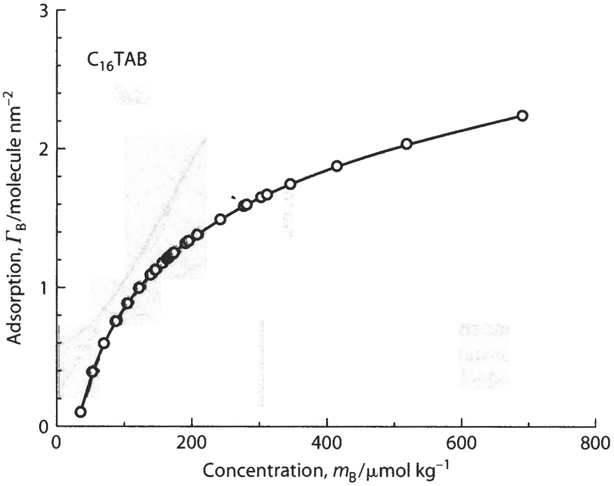

Figure 4.13. Adsorption isotherm for C_{16}TAB.

the electrolyte is added deliberately for this reason. The Gibbs equation then becomes:

$$-\frac{d\gamma}{RT} = \Gamma_{M^+} d\ln(c_{M^+}) + \Gamma_{X^-} d\ln(c_{X^-}) + \Gamma_{Y^-} d\ln(c_{Y^-}).$$

But $\Gamma_{Y^-} = 0$ and $d\ln(c_{M^+}) \approx 0$, resulting in:

$$-\frac{d\gamma}{RT} = \Gamma_{X^-} d\ln(c_{X^-}). \quad (4.10)$$

4.7 Micelles

Above a certain critical concentration the surface tension becomes independent of concentration, leading to a clear change in slope of the plot of surface tension against concentration (Figure 4.12), and is particularly marked in the logarithmic plot. This and other evidence indicates the formation of large aggregates known as **micelles.** The critical concentration is called the **critical micelle concentration** or **cmc**, and can be easily determined by the intersection of extrapolations of the linear regions each side of the change in slope (Figure 4.14). In an aqueous solution the amphiphile molecules in the micelles are arranged with their hydrophilic groups outwards and their hydrophobic segments inside, thus satisfying the amphiphilic requirements of the surfactant. In this structure the surface of the micelles is hydrophilic and consequently the micelles do not adsorb at the air–solution interface.

If X_s represents single (non-ionic) surfactant molecules in solution and X_m the micelles, the Gibbs equation becomes:

$$-\frac{d\gamma}{RT} = \Gamma_{X_s} d\ln(c_{X_s}) + \Gamma_{X_m} d\ln(c_{X_m}). \quad (4.11)$$

But $\Gamma_{Xm} = 0$ and c_{X_s} remains nearly constant above the cmc because all of the excess amphiphile goes to form micelles (implying that $\ln c_{X_s}$ is constant and therefore $d \ln c_{X_s} = 0$). Thus both terms in Eq. (4.11) vanish, and the surface tension becomes independent of concentration.

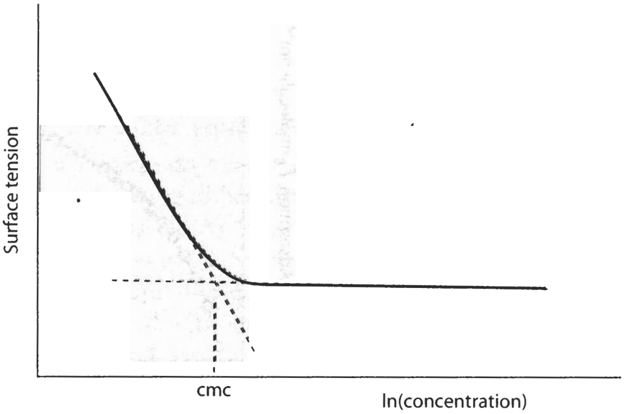

Figure 4.14. Above the cmc the surface tension remains constant. The intersection of the dashed lines extrapolated from the data allow a determination of the cmc from experimental data.