The Study of Surfactant Monolayers by Surface Pressure–Area Measurement

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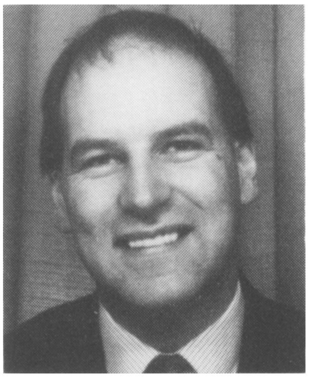
1 Introduction

Surfactant monolayers are relevant to a wide range of practical systems and processes, including detergency, paint manufacture, corrosion control, and foaming/defoaming applications. To give an everyday example, labels on food products often include the ingredient lecithin. This surfactant adsorbs at water/air (w/a) and water/oil (w/o) interfaces and is used to stabilize dispersions containing fats or oils and water. It also occurs naturally in cell membranes and is vital to the function of biological systems.

To be a surfactant, a molecule must consist of distinct hydrophobic and hydrophilic portions. A common example is a fatty acid comprising a long hydrocarbon chain attached to a $-COOH$ head group. The hydrophilic head group anchors in the water surface whilst the hydrophobic tail prefers to extend out of the water into the air (w/a interface) or into the oil (w/o interface). There are many examples of such materials, ranging from simple surfactants like the fatty acids and alcohols to complex polymeric systems.

This article is concerned specifically with surfactants which are insoluble in water. The term 'insoluble' is a vague one and in this context refers to surfactants which when placed at the w/a or w/o interface will remain there in preference to dissolving in the bulk water. Therefore, they tend to be materials dominated by a large hydrophobic portion with a relatively small hydrophilic head group.

Insoluble surfactants can be studied uniquely because their concentration at the interface is known directly, from the amount added to the interface. The technique most commonly used involves measuring the surface pressure (Π) as a function of the surface concentration. The surface concentration is usually expressed as the area available per surfactant molecule (A) at the interface and is readily calculated if the molecular weight of the surfactant is known. The existence of a surface pressure is easily demonstrated by placing a small amount of surfactant inside a loop of cotton on the surface of clean water. The loop is forced into a circle as the repulsion between neighbouring surfactant molecules causes the monolayer to expand and occupy the maximum available area. Thus, it can be seen that measurement of the surface pressure provides a way of studying the interaction forces between surfactant molecules at the interface.



Mark Aston obtained his M.Sc. in colloid and surface chemistry at Bristol University in 1981, and went on to study the theories of emulsion stability for his Ph.D. at the University of Reading. It was during this time that he became familiar with the Langmuir trough technique. Since joining BP in 1985, he has used colloid science to solve practical problems in many areas, and is currently working on environmentally friendly drilling fluids for oil and gas exploration. He is the author/co-author of ten scientific papers.

Surface pressure–area (Π–A) measurements can give valuable information about how surfactants pack together, which in turn relates to the intermolecular forces involved. For polymeric surfactants, information on the conformation of the polymer can be gained: *e.g.*, whether the polymer is coiled or uncoiled at the interface. Surfactant interactions in mixed films can also be studied, as can the interactions between monolayers and soluble additives present in the subphase.

2 Experimental Methods

Insoluble monolayers at the w/a and w/o interface are investigated using the so-called Langmuir Trough. Descriptions of the apparatus are given in standard surface chemistry texts (*e.g.* reference 1); Figure 1 shows a schematic diagram of an early form of trough. Modern troughs have automated computerized control systems with data logging facilities, but the principles of the method remain unchanged since the early work by pioneers such as Adam and Langmuir at the beginning of the century.

For measurements at the w/a interface, surfactant is added as a solution in a spreading solvent (*e.g.* hexane or petroleum ether) to the surface of the subphase. The solvent is allowed to evaporate, then barriers at the surface are moved to compress the spread film of surfactant. Film compression results in a lowering of the surface tension and a corresponding increase in the surface pressure as the surface concentration increases. Surface tension and surface pressure are related by the expression:

$$\Pi = \gamma_0 - \gamma \qquad (1)$$

where Π is the surface pressure, γ_0 is the surface tension of the clean surface (pure bulk phase), and γ is the surface tension in the presence of the surfactant monolayer. Successive additions of surfactant can be used to increase the surfactant concentration, rather than using barrier compression, if required.

Surface pressure Π is measured directly on some troughs

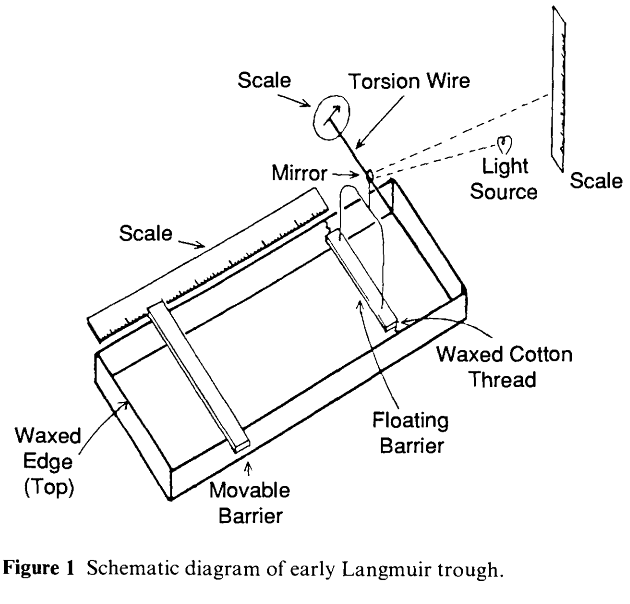


Figure 1 Schematic diagram of early Langmuir trough.

using a floating barrier and pressure transducer (or torsion wire) arrangement Alternatively, Π is calculated from measured γ values using equation 1 The direct measurement of Π has the advantage of minimizing wetting problems The measurement of γ is invariably made using a Wilhelmy plate, suspended from a microbalance, in the surface The plate, which is usually made of a small thin sheet of filter paper or roughened platinum, must be efficiently wetted by the subphase (*i e* the contact angle should be zero) However, this is not easy to ensure as surfactant will tend to adsorb onto the plate as the monolayer film is compressed Thus, direct measurement of Π is preferred

The surfactant area per molecule (A) is calculated from the trough area and the known surfactant addition A $\Pi - A$ curve is then constructed Figure 2 shows an idealized $\Pi - A$ isotherm which can be conveniently pictured as a kind of two-dimensional equivalent of a pressure–volume (PV) curve In the same way, it shows monolayer states and phase changes A fuller discussion of this will be given in Section 3

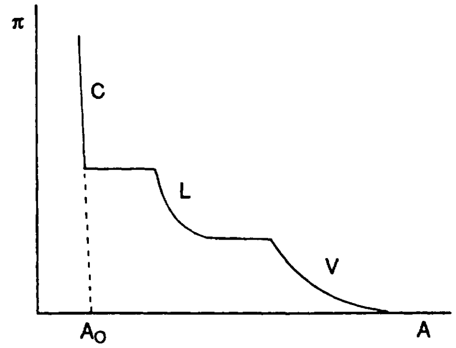


Figure 2 An idealized Π–A isotherm Three basic monolayer states are shown V = vapour, L = liquid, C = close-packed The horizontal sections represent phase transitions A_0 is the extrapolated minimum area per molecule

Considerable debate has taken place over the effect of the spreading solvent on the Π–A isotherm The possibility exists that solvent may not evaporate completely from the water surface so that some remains entrained within the surfactant monolayer This would influence surfactant packing at the interface and hence affect Π–A behaviour However, it is difficult to avoid the use of a spreading solvent since neat surfactant cannot be added in small enough quantities directly to the surface

Another important consideration is the rate of monolayer compression Rapid compression of the monolayer is likely to lead to non-equilibrium Π values To obtain equilibrium values of Π, stepwise compression is desirable, but it must be remembered that high molecular weight polymers may take several hours to reach equilibrium so this can make measurements very time-consuming As a check for equilibrium, it is useful to measure the change in Π during continuous compression, followed immediately by continuous expansion of the monolayer Hysteresis will then provide evidence of non-equilibrium Π values As an extension to this idea, it is possible to carry out relaxation experiments which involve compressing the monolayer to a given surface pressure, expanding quickly by a fixed amount, and then observing the decay/recovery in surface pressure This is particularly valuable for polymers and relates to their ability to respond to surface area changes This is relevant to emulsion stability and particularly emulsion formation where the requirement is for a polymer to respond rapidly to the creation of new surface as emulsion droplets are formed

Water/oil measurements are notoriously difficult to do, the main difficulties being wetting problems and surfactant dissolution effects The major difficulty is the tendency for the surfactant to dissolve in one or other of the bulk phases as the surfactant film is compressed Clearly, a surfactant which is selected on the basis of being water insoluble is likely to be highly soluble in the oil Reliance is placed on the surfactant having a preference for the interface Arguably, it is essential to do both compression and expansion cycles in w/o systems to look for hysteresis as evidence for loss of surfactant into the water or oil phases

In comparing w/a and w/o isotherms it is generally found that the monolayer becomes more expanded in the presence of the oil The expansion is caused by solvation of the hydrocarbon chains of the surfactant by the oil, leading to a reduced van der Waals attraction between the chains At high states of compression the w/o isotherm may become more condensed than the w/a one,[2] but surfactant dissolution into the oil at high surface pressures can be responsible for this apparent effect

3 Monolayer States

The analogy of the behaviour of two-dimensional surfactant films with the phase behaviour of three-dimensional systems is useful In three-dimensional systems one talks of gases being highly compressible, undergoing a phase change to the liquid state and under certain conditions forming a solid phase which is more condensed than the liquid Reference to Figure 2 shows that this scheme is followed by an 'ideal' insoluble surfactant monolayer At large A (low surface concentration) the surfactant molecules are widely separated and in general are considered to lie quite flat at the surface This is the gaseous state In the liquid state, the monolayer is compressed such that the molecules are oriented more or less vertically Further compression produces a close-packed solid film which is highly incompressible Attempts to compress this further will lead to film collapse, sometimes causing the formation of a bilayer at the surface

Very often, no phase changes are observed and merely a gradual decrease in compressibility is seen as the molecules become more closely packed This is the case with most polymers in which reorientation of loops and trains can occur as the film is compressed In fact, phase changes are normally best observed in pure non-polymeric systems A good example is pentadecanoic acid (Figure 3) which has been studied in pure form by Pallas and Pethica [3] This shows a well-defined first-order liquid–close packed transition, but it is interesting that this was masked in the early work of Harkins[4] using impure material

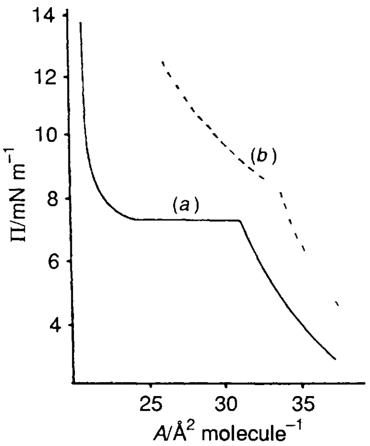


Figure 3 Π A isotherms for pentadecanoic acid monolayers (25 °C) at the 0 01 M HCl/air interface (a) determined by Pallas and Pethica[3] using high purity surfactant (b) determined by Harkins[4] using impure surfactant

Note that, although phase changes are quite commonly observed in surfactant monolayers, it is not always easy to relate the phase changes to specific reorientations within the monolayer In some cases the phase change is attributed to head group effects, but, more commonly, changes in hydrocarbon tail orientation are considered to be responsible A good example is hydroxyoctadecanoic acid The hydroxy (−OH) group is located in the C_{17} hydrocarbon tail of the acid If it is sufficiently far from the head group it acts as a strong anchoring point for the tail and holds it parallel with the water surface When the surface pressure is raised sufficiently, the tail can no longer be held and it 'flips' to a vertical orientation This results in a clear transition in the Π–A isotherm [5]

A number of conventions exist in the field of insoluble monolayers, and one of these is subdividing liquid states into 'liquid-expanded' and 'liquid-condensed' states Although still widely adopted, this is probably an unnecessary complication As suggested by Pallas and Pethica,[3] it is simpler and more appropriate to consider transitions from gas to liquid and liquid to close packed rather than trying to identify two separate liquid states

Another convention is the extrapolation of the close-packed region of the isotherm to zero pressure to determine a close-packed (*i e* minimum) area per molecule (see Figure 2) This works for conventional surfactants and gives values which agree with those obtained from *X*-ray data on three-dimensional solids For example, in Figure 3 the close packed area for pentadecanoic acid is about 21 Å^2 per molecule, which is the expected cross-sectional area for a straight chain fatty acid However it can be argued that extrapolation is meaningless in polymeric systems where chain segments may be desorbed or the polymer substantially coiled as it is compressed The close-packed area per molecule in this case should be read directly and not extrapolated to zero pressure The validity of extrapolation to zero pressure to obtain molecular areas for liquid states is also questionable since the liquid isotherm is usually non-linear

Many attempts have been made to fit equations of state to Π A isotherms A detailed account is beyond the scope of this article but a few are worth mentioning Equations of the form

$$\Pi A = \iota kT \qquad (2)$$

where ι is a constant are analogous to the ideal gas equation and, as expected, are only applicable at very large areas (low pressures) Modifications to this equation to introduce excluded area and excluded pressure terms have been made,[6,7] with greater success, and virial equations have also been tried [8] The main problem is that these approaches do not take into account the influence of the subphase This was remedied by Gaines[9] who produced a rigorous thermodynamic treatment The equation fits experimental data fairly well, even into the liquid region, but generates constants (activity coefficients) which may not have real physical meaning in some cases There is certainly a need for further theoretical development to fit the curves into the liquid and solid regions

4 Mixed Monolayers

Most systems of practical interest involve complex mixtures of surfactants and these are very often impure The interactions between the components can often be studied using insoluble monolayer techniques

If two (or more) surfactants are mixed on a Langmuir trough the area per molecule for 'perfect' mixing is given by

$$A = x_1A_1 + x_2A_2 \quad \text{at constant } \Pi \qquad (3)$$

where x_1 and x_2 are the mole fractions of each surfactant and A_1 and A_2 are the molecular areas of the single component monolayers This is known as the additivity rule By comparing the theoretically predicted mixed monolayer Π–A isotherms with the experimentally determined ones, any deviations from additivity can be observed A displacement of the experimental curve to lower areas (condensation) would imply an unexpectedly high packing efficiency, while a displacement to higher areas (expansion) would imply poor packing of the surfactants

Obviously, the packing effects are likely to vary with the surface pressure A common method of analysis is to plot the experimental average area per molecule at a given surface pressure, against the monolayer composition A good example is given by the early work of Shah and Schulman (Figure 4) They investigated the interaction between dipalmitoyl lecithin and cholesterol monolayers at the w/a interface As the data suggest, at low surface pressures negative deviations from additivity occur This was attributed to the cholesterol occupying cavities in the lecithin monolayer Each lecithin molecule has two hydrocarbon chains and the cavities are produced by an angled orientation of these At high surface pressures the cavities disappear because the lecithin hydrocarbon chains are forced into a vertical configuration the additivity rule is then obeyed

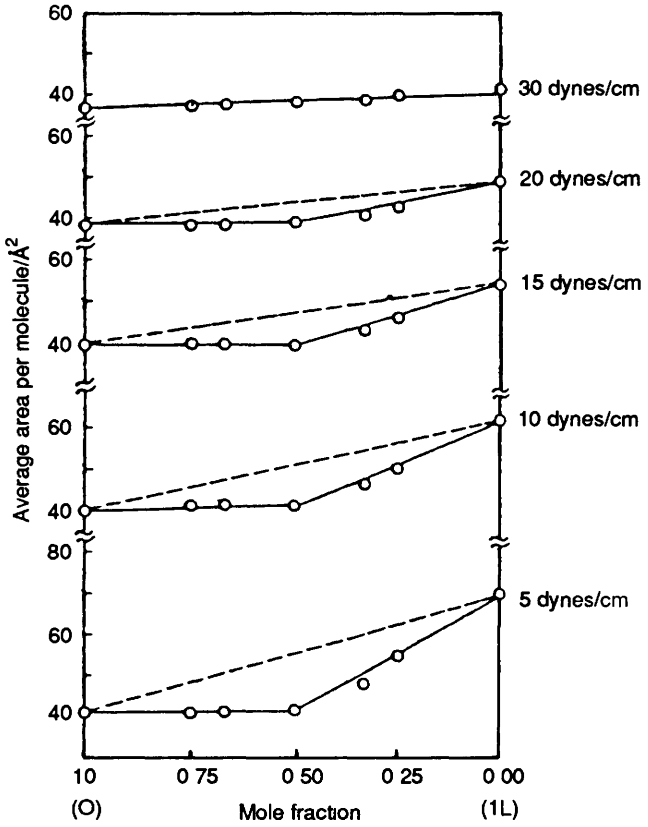


Figure 4 Deviations from additivity for dipalmitoyl lecithin–cholesterol monolayers at various surface pressures at the w/a interface (Shah and Schulman[10]) The broken line is the additivity rule line

Similar condensation effects have been observed with many mixed surfactant systems For example, Puggelli and Gabrielli[11] have shown that stearic acid, methyl stearate, and stearyl amine all lead to the condensation of poly-2-vinylpyridine monolayers Such condensation effects, which imply a negative free energy of mixing, may help to explain why mixed surfactant monolayers often produce more stable emulsions and dispersions, *i e* by giving rise to a more coherent monolayer

Positive deviations from additivity are less common and imply a positive free energy of mixing resulting in a relatively unstable monolayer On a molecular level, these effects can sometimes be interpreted in terms of poorly packed surfactant hydrocarbon chains, *e g* when *cis* and *trans* isomers are mixed In cases where charged head-groups are involved, electrostatic repulsions may be responsible

The miscibility of the monolayer components is a factor often considered in studies of mixed surfactant monolayers As a test for miscibility, some workers (*e g* Tomoaia-Cotisel and Chifu[12]) have studied the collapse pressures of mixed monolayers According to the two-dimensional phase rule, the collapse pressure should be proportional to the monolayer composition if the monolayer behaves as an ideal two-dimensional solution If the monolayer components are immiscible so that 'islands' exist at the interface, the collapse pressure will not be proportional to the monolayer composition and the component with the lowest collapse pressure will be preferentially squeezed out from the interface. The main difficulty with this approach is that a well-defined collapse pressure is often not observed. Note also that inhomogeneous mixed films may or may not obey the additivity rule, depending upon the nature of the intersection between neighbouring micelles or islands.

5 Influence of the Subphase

The interaction of subphase components with the spread monolayer can be studied, and this has received much attention in relation to biological systems. Various workers have studied the interactions of divalent ions with phospholipid (lecithin) monolayers. As another example, Pezron *et al.*[13] have noted how the presence and nature of the cation dramatically influence the rate of collapse of arachidic acid monolayers. In order of increasing stability they find $H^+ < Li^+ < Na^+ << Ca^{2+} < Mg^{2+}$ for the choloride salts at 10 mM concentration.

Non-biological studies include those by Nordli *et al.*[14] on the influence of pH and water-soluble aromatic solvents on the behaviour of interfacially active fractions extracted from crude oils. The aromatic fractions are found to interact strongly with the monolayers.

However, care is required in the interpretation of the effects of additives on the monolayer. If the soluble additive is appreciably surface active it can interfere with the interpretation of the Π–A data. The study in effect becomes a combined 'insoluble monolayer' plus 'adsorption from solution' study. Some workers will argue that any direct effect of the soluble component on surface tension is taken into account by equation 1. For example, say a soluble species (an electrolyte) raises the surface tension of the monolayer-free surface from γ_0 to γ_0', then the surface pressure in the presence of the monolayer becomes:

$$\Pi = \gamma_0' - \gamma \qquad (4)$$

Thus, the higher initial surface tension (γ_0') is taken into account in the calculation of Π.

However, this approach is not actually valid because the influence of the soluble component will vary with monolayer surface coverage. In other words, γ_0' is not really a constant in equation 4. A full thermodynamic treatment has been given by Aston and Herrington.[15] The conclusion is that a plot of surface tension *versus* A is more appropriate than Π *versus* A in these cases. Figures 5 and 6 show data for a polymeric surfactant (B246) on a subphase containing high concentrations of ammonium nitrate. The polymer is a PHS–PEO–PHS block copolymer, where PHS is poly(12-hydroxystearic acid), and PEO is polyethylene oxide. The Π–A curves wrongly suggest monolayer expansion with increasing electrolyte concentration. The γ–A data show that there is in fact no expansion, as the curves converge. The absence of a polymer–electrolyte interaction is supported by the collapse surface tensions and the fact that the areas at collapse are approximately independent of the electrolyte concentration.

Of course, when the subphase additive is used at concentrations at which it has no direct effect on the surface tension (*e.g.* low electrolyte concentrations) the conventional Π–A plot is valid, and can provide very useful information on surfactant–additive interactions. But it is recommended that the influence of the additive on surface tension in the absence of the monolayer is established first.

6 Studies using Solid Particles

The Langmuir trough is well-suited to the study of the interactions between solid particles at the water/air interface. One reason for studying such systems is that particles can play an important role in stabilizing (or destabilizing) emulsions and foams. For example, the presence of wax particles in crude oils can significantly enhance the stability of water-in-crude oil emulsions.

An obvious requirement for a Langmuir trough study of particulates is that the particles must float on the water surface. This is helped if the particles are less dense than the subphase, and if they are hydrophobic. Early work by Sheppard and Tcheurekdjian[16] showed how compression of a film of solid particles can be used to estimate the particle size, from the collapse area of the monolayer. The theory has recently been extended by Clint and Taylor[17] who have carried out experiments on overbased detergents. These are small particles, usually having a calcium carbonate core, stabilized by a grafted layer of surfactant. They are used in engine oils to neutralize acid combustion products. According to the theory of Clint and Taylor, it is possible to calculate a force–distance curve from the

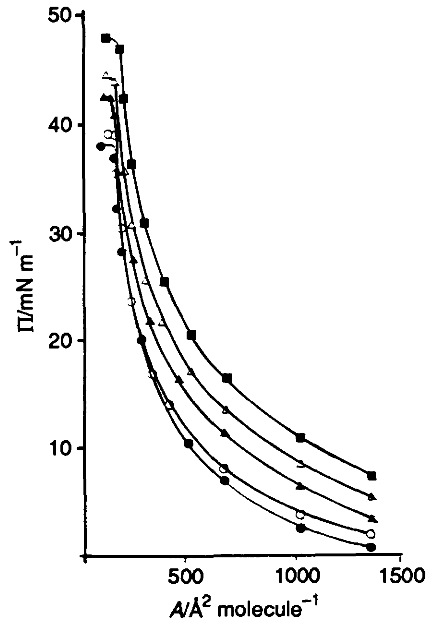


Figure 5 The effect of ammonium nitrate on the B246 w/a Π–A isotherm at 25 °C. The concentration of ammonium nitrate in mol dm is: (●) 0.00, (○) 1.25, (▲) 4.00, (△) 6.25, (■) 8.75.

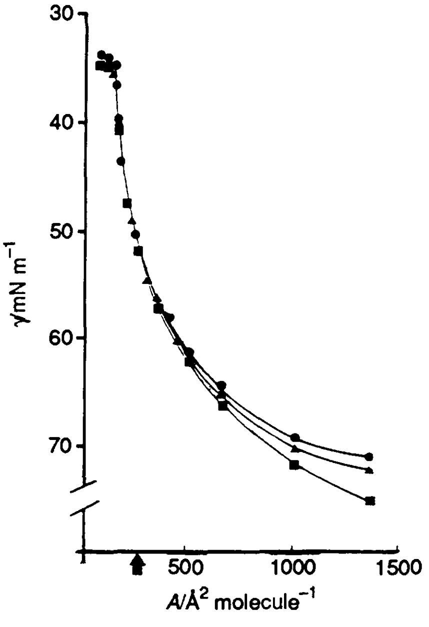


Figure 6 The effect of ammonium nitrate on the B246 w/a γ–A isotherm at 25 °C. The concentration of ammonium nitrate in mol dm is: (●) 0.00, (▲) 4.00, (■) 8.75.

Π–A data and to determine the contact angle as well as the particle size They find excellent agreement between the force–distance curves and experimental data in the literature, obtained using crossed mica cylinders The contact angle is obtained from the critical surface pressure attributed to close-packing of the particles

7 Concluding Remarks

It is hoped that the above will have given an indication of the scope and potential areas of application for insoluble monolayer studies It is a fact that practical applications of the technique in industry are often hidden because of commercial sensitivity The technique has great value as a tool to gain better understanding of the behaviour of monolayers at water/air and water/oil interfaces, and as such is probably under-used

Rather than looking at high purity single-component systems (which has been traditional) much is to be gained by investigating commercial surfactants, particularly as mixed films, and by studying the interactions of soluble components with monolayers The latter requires further theoretical study as well as practical data It is becoming clear that for these systems it is necessary to combine the theories for both soluble and insoluble surfactant monolayers

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