

Solubilisation of Hydrocarbons in Surfactant Monolayers

Robert Aveyard,* Philip Cooper and Paul D. I. Fletcher

Surfactant Science Group, School of Chemistry, University of Hull, Hull HU6 7RX, UK

Hydrocarbons which do not spread macroscopically on aqueous surfactant solutions can nevertheless be incorporated (solubilised) in the adsorbed surfactant films, producing mixed monolayers. The surface concentration of alkane in these systems can be obtained semi-quantitatively from the lowering of surface tension caused by the solubilisation. For surfactant solutions above the c.m.c., alkane uptake is found to decrease with increasing alkane chain length, but to increase with increasing surfactant chain length. For a given surfactant, not only is the molar uptake of alkane greater the smaller the alkane, but also the volume uptake. Solubilisation does not significantly affect the surface concentration of surfactant, but rather it increases the monolayer thickness. As close-packed monolayers are progressively diluted, the alkane solubilisation is found to rise initially but then to fall rather rapidly when the surface concentration of surfactant is reduced to *ca.* half that at the c.m.c. The contact angles, θ , of all the alkanes on dodecyltrimethylammonium bromide solutions close to the c.m.c. are very low. As the surfactant monolayer is diluted, θ begins to rise rapidly when the monolayer becomes less than 'close-packed', finally approaching the value for alkane on pure water. For the system comprising sodium diethylhexylsulphosuccinate (AOT), aqueous NaCl and cyclohexane, increase in the salt concentration up to 0.025 mol dm⁻³ compresses the surfactant monolayer and as a result, hydrocarbon solubilisation is substantially reduced. Above this salt concentration solubilisation remains constant. Inversion of microemulsion type in this same system also occurs at 0.025 mol dm⁻³ NaCl and so it appears, for this system at least, that the hydrocarbon penetration is very similar at the oil/water and the air/water interfaces.

Solubilisation of various materials, including hydrocarbons, in aqueous micellar solutions has been very widely studied over the years.¹ Although the uptake of hydrocarbon vapours by insoluble monolayers has been reported,² it is surprising that solubilisation of hydrocarbons in planar surfactant monolayers appears to have been neglected. Such solubilisation (or penetration) of hydrocarbons at oil/water interfaces, although difficult to quantify directly, has a number of important consequences. Particularly interesting are the ways in which hydrocarbon penetration can affect the surface concentrations of suitable surfactants in close-packed monolayers at, say, alkane/water interfaces.³ Such solubilisation is believed to be an important element in determining the spontaneous curvature of surfactant monolayers and hence microemulsion phase behaviour in so-called Winsor systems.^{4,5} The different propensities of alkanes of different chain length to mix with surfactant chains in nonionic micelles may also be implicated in the rather complex effects which solubilised hydrocarbons have on cloud points.⁶

In a preliminary study⁷ we reported data for solubilisation of dodecane in adsorbed monolayers of dodecyltrimethylammonium bromide. We have now broadened the investigation to include other surfactants and hydrocarbons. We have determined how alkane solubilisation varies with alkane and surfactant chain lengths and with surface concentration of surfactant. We have also calculated the alkane volume uptake and, on the assumption of liquid density, the thickness of the hydrocarbon parts of the mixed monolayers. Finally, the effect of NaCl on solubilisation of cyclohexane in ionic

monolayers (of Aerosol OT) has been investigated. These results have been compared with microemulsion behaviour in the same system and the similarity between oil penetration at oil/water and air/water interfaces highlighted.

Experimental

Materials

The hydrocarbons were from various sources, and all had estimated purities by GLC of >99%. They were passed through chromatographic alumina shortly before use to remove polar impurities. Interfacial tensions against water at 25 °C were always in excellent agreement with previous literature values.⁸ Water was distilled once, passed through an Elgastat ion-exchange column and then through a Milli-Q-Reagent Water System. The surface tensions of random samples were checked and found always to be 71.8 ± 0.2 mN m⁻¹ at 25 °C. Sodium chloride was analytical grade and was used untreated. At the concentrations used it had little effect on the surface tension of water, and clearly was free of surface active impurities. Details of the surfactants used are summarised in Table 1. The c.m.c. values and areas per molecule in saturated films at the air/solution interface were obtained for sodium diethylhexylsulphosuccinate (AOT), and for cetyl- and dodecyl-trimethylammonium bromides (CTAB and DoTAB, respectively) from the data in Fig. 1. Similar data (not presented) were obtained for the decyl homologue (DTAB) in the linear part of the tension–ln (surfactant concentration) curve and above the c.m.c.

Table 1 Details of surfactants used

surfactant	source (purity)	treatment	c.m.c.	area
AOT	Sigma (99%)	used as received	2.8	1.15
DTAB	Eastman (99%)	2 ether extractions, recryst, from	64.0	0.60
DoTAB	Sigma (99%)	acetone-methanol, final recryst.	13.7	0.62
CTAB	Fluka (99%)	from methanol	0.97	0.63

c.m.c. values are in 10⁻³ mol dm⁻³; areas per molecule (at the air/water interface) at the c.m.c. are in nm².

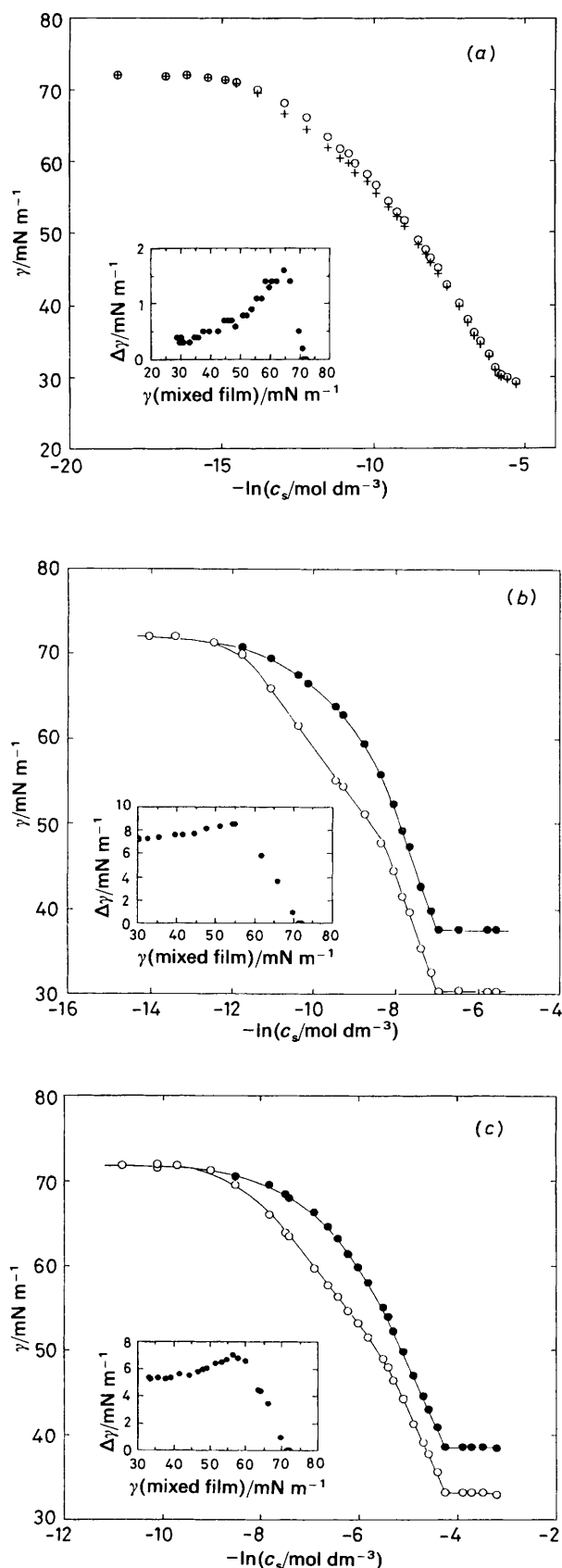


Fig. 1 Tensions of aqueous surfactant solutions at 25 °C as a function of surfactant concentration in the presence and absence of dodecane lenses on the surface. Insets show tension lowering caused by dodecane as a function of the tension in the presence of dodecane. (a) AOT with (+) and without (○) dodecane, (b) CTAB with (○) and without (●) dodecane, (c) DoTAB with (○) and without (●) dodecane

Methods

Air/solution tensions were measured using a Krüss K10 automatic tensiometer with a du Noüy ring attachment; the maximum pull method is employed with this instrument, and the ring does not become detached from the surface. The dish of the tensiometer was fitted with a split-glass cover with two small holes large enough only to allow the two wire ring supports to pass through. The cover is essential to stop evaporation of hydrocarbon from the mixed monolayers. If the cover was removed evaporation started immediately and the tension rose. When a small drop of hydrocarbon is placed on a surfactant solution, it sometimes appears to spread initially and then to retract, often breaking up into very small lenses, which can, however, be clearly seen. Initially therefore, the hydrocarbon was contained inside a filter paper cylinder passing through the surface. This allows hydrocarbon molecules to enter the surface outside the cylinder whilst keeping liquid from contact with the ring and possibly interfering with the measurement. However, we found subsequently that the small lenses on the open surface caused no problems with tension measurement.

Low oil/water interfacial tensions were determined using a Krüss spinning-drop tensiometer (SITE 04).

Results and Discussion

The alkanes decane and upwards do not spread on water or on aqueous solutions of the surfactants CTAB, DoTAB and DTAB, sodium dodecylsulphate (SDS) and AOT. These same alkanes are not adsorbed on the surface of pure water.⁹ They are, however, readily solubilised in the surfactant monolayers, causing a lowering of tension, $\Delta\gamma$, of the surfactant solutions which is related to the surface concentration of the hydrocarbon, Γ_a , in the mixed monolayer as discussed later. We show plots of tension (γ) vs. $\ln(\text{surfactant concentration } c_s)$ both in the presence and absence of dodecane lenses on the surface of solutions of CTAB, DoTAB and AOT in Fig. 1. The values of $\Delta\gamma$ (inset) are seen to depend on c_s and hence surface concentration, Γ_s , of surfactant. Above the c.m.c., however, $\Delta\gamma$ is independent of c_s . We now discuss, first, results for solutions above the c.m.c. and then present data for solutions below the c.m.c. In addition, we estimate the contact angles of alkanes with the surfactant solutions, and finally explore the possible relevance of the variation of solubilisation at air/water surfaces to inversion of microemulsions in two-phase systems.

(i) Systems above the c.m.c.

Equilibrium tension lowerings caused by a range of alkanes, chain length N_a , on various surfactant solutions above the c.m.c. are given in Table 2. We may obtain good estimates of Γ_a in the mixed films as follows. For the present systems at constant T and p , the Gibbs adsorption equation may be written

$$-d\gamma = \Gamma_a d\mu_a + \Gamma_s d\mu_s + \Gamma_w d\mu_w \quad (1)$$

where the μ are chemical potentials; subscript w denotes water. For addition of alkane to the surface of a surfactant solution at the c.m.c. (where solubilisation of alkane in bulk solution is absent) $d\mu_s = d\mu_w = 0$ so we may write

$$\Gamma_a = -(\partial\gamma/\partial\mu_a)_{\mu_s, \mu_w} = (a_a/RT)(d\Delta\gamma/da_a) \quad (2)$$

where a_a is the mole fraction activity of hydrocarbon.

We have determined values of $\Delta\gamma$ for the addition of (squalane-dodecane) mixtures, mole fraction x_a of dodecane, to the surfaces of solutions of DoTAB both above and below

Table 2 Tension lowering ($\Delta\gamma/\text{mN m}^{-1}$) of surfactant solutions above the c.m.c. caused by alkanes at 25 °C

N_a	DTAB (81 mmol dm ⁻³)	DoTAB (20 mmol dm ⁻³)	CTAB (1.6 mmol dm ⁻³)	SDS (10 mmol dm ⁻³)	AOT (3 mmol dm ⁻³)
10	5.9	7.2	9.0	6.8	—
11	4.9	6.2	7.9	5.9	—
12	3.8	5.4	7.4	4.5	0.4
13	2.9	4.3	6.6	3.9	—
14	2.2	3.5	6.2	2.9	—
15	1.6	2.7	5.7	—	—
16	1.2	2.3	5.0	2.1	—

the c.m.c. and of AOT below the c.m.c. Squalane (2,6,10,15,19, 23-hexamethylhexacosane), which is liquid at room temperature, does not spread on the surfactant solutions nor does it appreciably mix with the surfactant monolayers. Values of $\Delta\gamma$ produced by the hydrocarbon mixtures are shown as a function of x_a in Fig. 2. The $\Delta\gamma$ - x_a relationship is close to linear, but the curves are slightly concave upwards. For example, the data for 19.7 mmol dm⁻³ DoTAB are well fitted by the equation

$$\Delta\gamma = 0.33 + 4.25x_a + 0.71x_a^2 \tag{3}$$

The slope of the straight line joining the extremes of the curve generated by eqn. 3 is 4.91. The slope of the fitted curve at $x_a = 0$ is 4.25 and so the ratio of initial slope to the linear slope is 0.87. Since the infinite dilution activity coefficient of dodecane in squalane at 25 °C is 0.83,¹⁰ the observed curvature probably arises from the small non-idealities in the hydrocarbon mixtures. In the light of this, a good estimate of Γ_a when pure alkane ($x_a = a_a = 1$) is added to the surface is given by

$$\Gamma_a = \Delta\gamma/RT \tag{4}$$

The Γ_a for alkanes on the TAB solutions are shown in Fig. 3. Alkane uptake for a given surfactant decreases with increasing N_a ; for a given alkane Γ_a increases with increasing surfactant chain length, N_s . The Γ_a for all alkanes on all three TAB solutions are shown as a function of the difference in surfactant and alkane chain lengths, ($N_s - N_a$) in Fig. 4. All the data fall reasonably close to a common line. In a very simple way, the results can be understood in terms of a

volume-filling mechanism. The solubilisation might be considered hypothetically to occur in two stages. First, the surfactant chains in the pure monolayer become (more) extended and secondly, the alkane fills the space so generated.

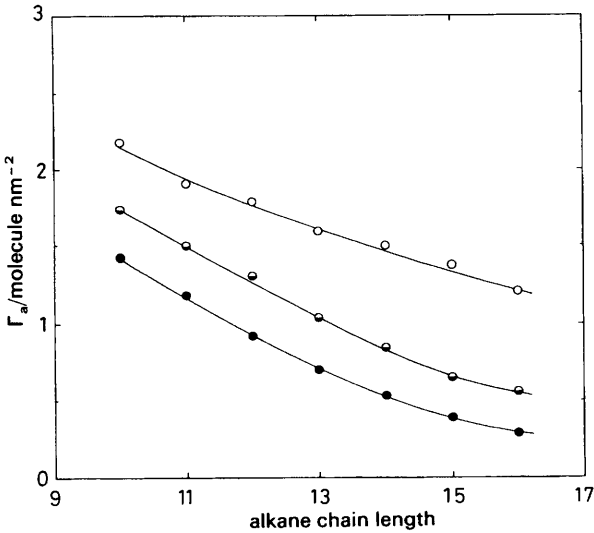


Fig. 3 Surface concentrations of alkanes on surfactant solutions at 25 °C as a function of alkane chain length: (●) DTAB, $c_s = 81 \text{ mmol dm}^{-3}$, (◐) DOTAB, $c_s = 20 \text{ mmol dm}^{-3}$ and (○) CTAB, $c_s = 1.6 \text{ mmol dm}^{-3}$

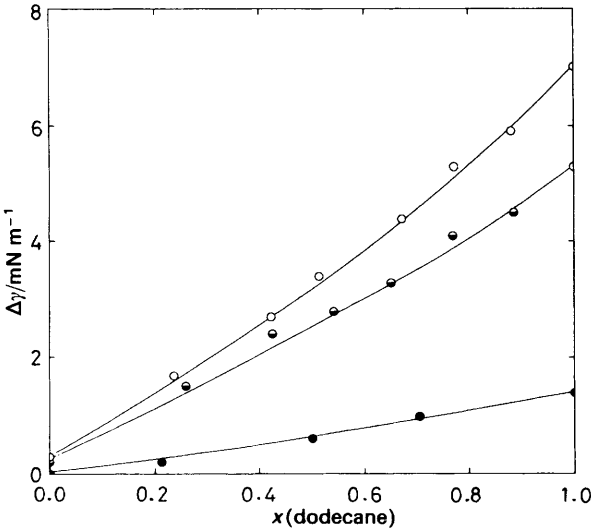


Fig. 2 Tension lowerings of AOT solutions, concentration $c_s = 0.025 \text{ mmol dm}^{-3}$ (●), and of DoTAB solutions, $c_s = 19.7 \text{ mmol dm}^{-3}$ (◐) and $c_s = 1.5 \text{ mmol dm}^{-3}$ (○), caused by lenses of (squalane-dodecane) mixtures of varying composition at 25 °C

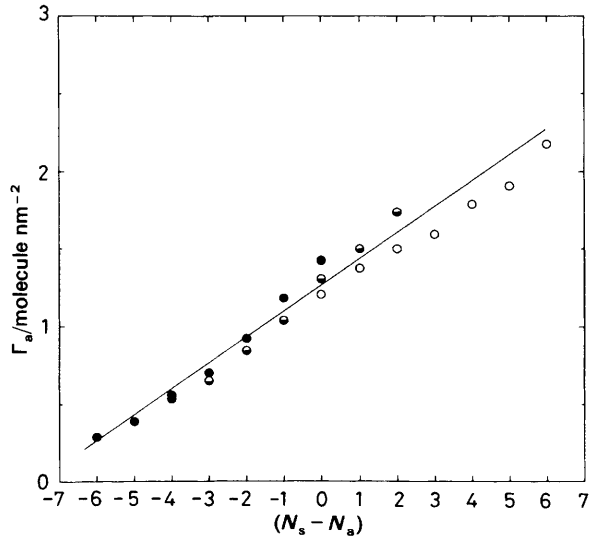


Fig. 4 Surface concentrations of alkanes at 25 °C on various surfactant solutions (concentrations as in Fig. 3) as a function of the difference in chain lengths of alkane and surfactant. ○, CTAB; ◐, DoTAB; ●, DTAB. Concentrations as in Fig. 3

Assuming that in the mixed films the lengths of the chains of the longer surfactants are greater than those of the shorter ones, a given alkane will be more strongly solubilised in the longer surfactant. For a given surfactant, obviously a given available volume will accommodate a larger (molar) amount of short alkane than long alkane. The picture is not so simple, however; as will be shown, it appears likely that the mean fractional extension of a surfactant chain depends on the length of the alkane solubilised. Further, if shorter alkanes are to swell out the tail region of a monolayer more than the longer homologues (as is believed to be the case when microemulsion systems are inverted by changing N_a), one would expect the volume of alkane solubilised to be greater for the shorter alkanes.

Assuming the chain region of the mixed monolayer to be liquid-like it is easy to show, noting the volume of a CH_2 group is 0.027 nm^3 and of a CH_3 group is double this [and as shown, Γ_a (molecule area^{-1}) = $\Delta\gamma/k_B T$], that the thickness δ of the hydrocarbon part of the monolayer and the volume v of hydrocarbon solubilised per unit area are given by

$$\delta/\text{nm} = 0.027[\Gamma_s(N_s + 1) + 0.242 \Delta\gamma(N_a + 2)] \quad (5)$$

and

$$\begin{aligned} v(\text{nm}^3 \text{ nm}^{-2}) &= 0.027\Gamma_a(N_a + 2) \\ &= 6.534 \times 10^{-3} \Delta\gamma(N_a + 2) \end{aligned} \quad (6)$$

In these equations, the Γ are in molecule nm^{-2} and $\Delta\gamma$ in mN m^{-1} . Knowing v and Γ_s , the volume fraction, Φ_a , of alkane in the hydrocarbon part of the mixed monolayer can be calculated. We show how Φ_a changes with N_a for the TABs in Fig. 5. The volume fraction of alkane rises sharply as N_a is reduced for the shorter-chain surfactants. This rise is less pronounced for CTAB. For decane, Φ_a is roughly coincident at around 0.5 for all three surfactants. Note that in general Γ_s changes only little on incorporation of alkane. For example for the DTAB–dodecane system Γ_s (pure film) = $1.67 \text{ molecule nm}^{-2}$ and Γ_s (mixed film) = $1.64 \text{ molecule nm}^{-2}$. The uptake of alkane therefore must cause an increase in the monolayer thickness, and presumably therefore in the mean extension of the surfactant chains.

The mean fractional extensions of the surfactant chain ($\delta/\text{length of fully extended chain}$) in monolayers containing various alkanes are depicted in Fig. 6. As seen, at most (*i.e.* in

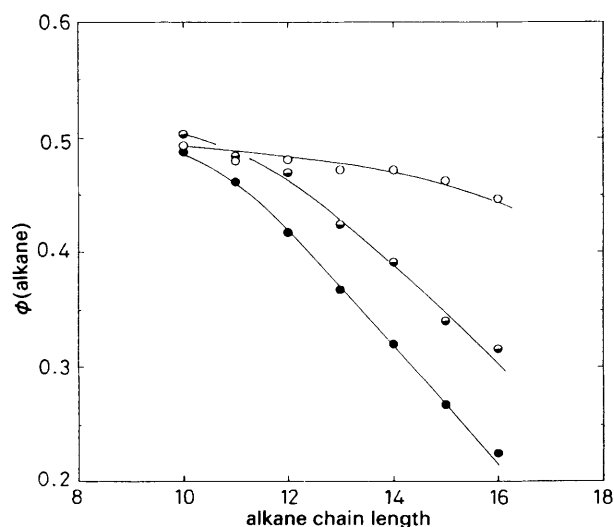


Fig. 5 Variation of volume fraction of alkane in surfactant monolayers at 25°C with alkane chain length for \bullet , DTAB; \bullet , DoTAB and \circ , CTAB. Concentrations as in Fig. 3

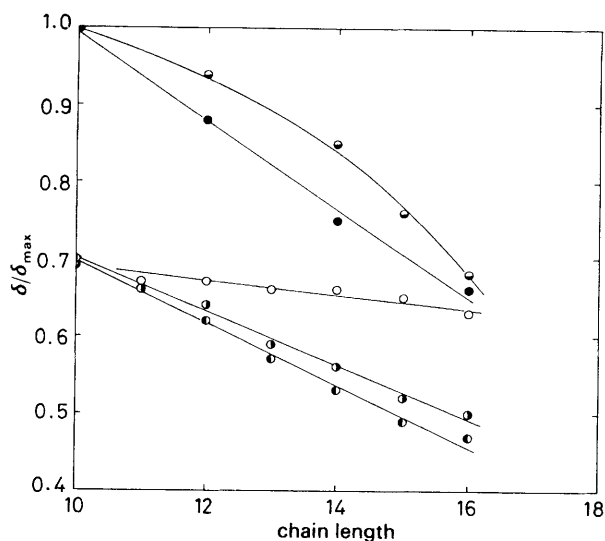


Fig. 6 Fractional extensions of surfactant chains ($\delta/\delta_{\text{max}}$) as a function of alkane chain length for \bullet , DTAB; \bullet , DoTAB; \circ , CTAB (all at concentrations as in Fig. 3), and (in BLM) \bullet , phosphatidyl choline and \bullet , monoolein

the case of decane as alkane) the surfactant chains are only 70% extended; the fractional extension falls as N_a increases, the largest effect being for the shortest surfactant. For comparison, data are also shown in Fig. 6 for half the hydrocarbon layer thickness in bimolecular lipid membranes (BLM) incorporating alkanes.¹¹ The BLM formed from both monoolein and phosphatidyl choline ('stabilisers') and incorporating decane have thicknesses corresponding to fully extended stabiliser chains. This is because the BLM are stabilised against thinning by only the small fraction of stabiliser chains which are fully extended. Even so, the bilayer thickness falls rapidly as N_a increases, and for hexadecane as alkane, half the thickness of the hydrocarbon part of the BLM is very close to the hydrocarbon layer thickness in the CTAB–hexadecane monolayers. We would remark that although we have assumed liquid alkane densities for the monolayer tail regions, there may well be a density gradient normal to the surface; if so true thicknesses will obviously exceed those given by eqn. 5.

(ii) Systems below the c.m.c.

Surface concentrations of dodecane, obtained from the data in Fig. 1 in conjunction with eqn. 4, vary with Γ_s as is evident from the insets in Fig. 1. Penetration into AOT monolayers is much smaller than for CTAB and DoTAB, as would be expected intuitively for a surfactant with two hydrocarbon chains. For all the surfactants, however, Γ_a increases with Γ_s , and passes through a maximum well before the c.m.c. is reached, and then falls as the c.m.c. is approached. The maximum solubilisation of alkane corresponds to the maximum molar ratios Γ_a/Γ_s shown in Fig. 7. For Γ_s up to that corresponding to this maximum ratio, the average film thickness (Fig. 7) increases rapidly, and thereafter increases much more slowly as Γ_a/Γ_s (and Γ_a) fall markedly. Some data for dodecane solubilisation are presented in Table 3; it appears that dodecane uptake is maximum when Γ_s is approximately half that at the c.m.c. When the monolayer becomes more dilute in surfactant than this, it rapidly becomes incapable of alkane solubilisation.

It is possible that the discontinuities in the curves of Γ_a/Γ_s and of δ against Γ_s reflect some kind of phase change within the monolayers, but from the present data alone we cannot learn more. For DoTAB and CTAB films at maximum

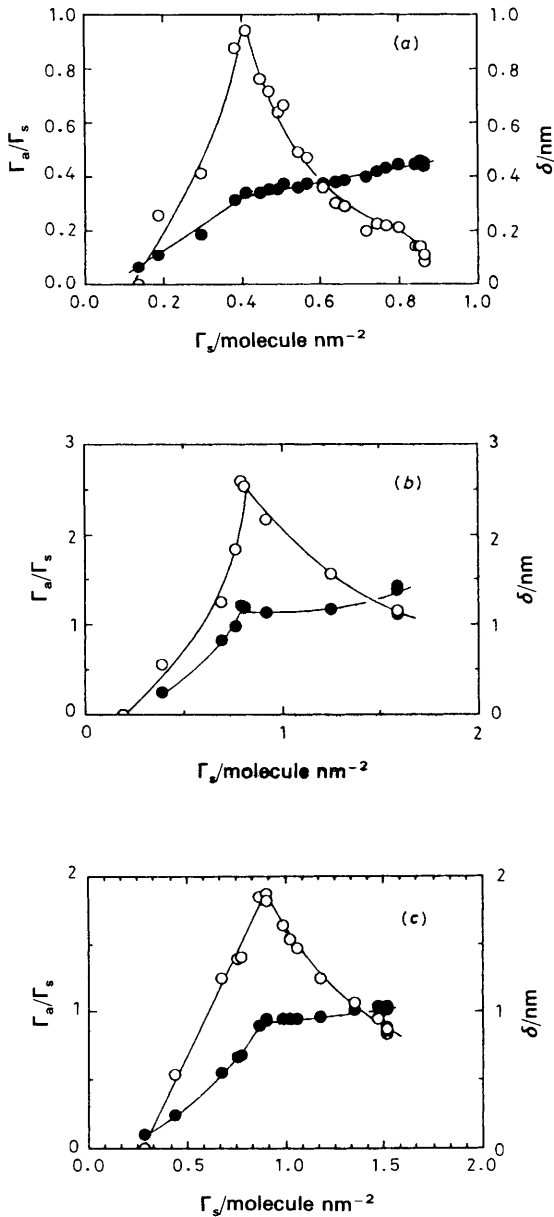


Fig. 7 Variation of molar ratio of alkane to surfactant in the surface (○) and of the hydrocarbon layer thickness (●) with surface concentration of surfactant in mixed films at 25 °C. (a) AOT, (b) CTAB, (c) DoTAB

Table 3 Parameters for penetration of dodecane into monolayers at the c.m.c. and at maximum alkane uptake

surfactant	Γ_a	Γ_s	δ	Γ_a/Γ_s
(a) at maximum alkane uptake				
AOT	0.39	0.41	0.34	0.9
DoTAB	1.69	0.90	0.96	1.9
CTAB	2.06	0.80	1.15	2.6
(b) at the c.m.c.				
AOT	0.09	0.86	0.44	0.1
DTAB	0.92	1.64	0.84	0.6
DoTAB	1.28	1.52	1.02	0.8
CTAB	1.77	1.59	1.40	1.1

Γ in molecule nm⁻²; δ in nm; Γ_s is for mixed film.

uptake of dodecane, the average film thicknesses are over double that expected for alkyl chains lying flat along the surface. For AOT, the corresponding thickness (0.34 nm) is less than that for a flat chain. This points to the possibility that the mixed films at low surfactant concentrations are not uniform, maybe consisting of condensed islands of greater thickness in equilibrium with ‘gaseous’ patches.

Contact Angles of Alkanes with Surfactant Solutions

Although the alkanes used here do not spread macroscopically on the surfactant solutions, lower alkanes do and so presumably the contact angles, θ , of the higher alkanes are almost zero, at least close to the c.m.c. For a three-phase system (aqueous solution α , alkane δ , and vapour phase β) at equilibrium¹²

$$\gamma_{\alpha\beta} \leq \gamma_{\alpha\delta} + \gamma_{\beta\delta} \tag{7}$$

The equality corresponds to spreading of the alkane, and the inequality to the formation of lenses. For simplicity we suppose the $\alpha\delta$ (oil/aqueous) interface is coplanar with the $\alpha\beta$ (air/solution) interface, i.e. that the solution is non-deformable. We may then calculate the (hypothetical) contact angles of the non-wetting alkanes with surfactant solutions from the relationship

$$\theta = \cos^{-1}[(\gamma_{\alpha\beta} - \gamma_{\alpha\delta})/\gamma_{\beta\delta}] \tag{8}$$

From eqn. 8, for θ to become zero the difference between the surface tension of the surfactant solution in equilibrium with alkane lenses and the oil–aqueous solution tension must approach the value of the alkane–vapour tension.

We have determined values of $\gamma_{\alpha\delta}$ for alkane/surfactant solution interfaces just above the c.m.c. for DoTAB solutions in contact with a range of alkanes. The surface tensions of the alkanes have been taken from the literature.¹³ The various tensions are given in Table 4, from which it is seen that, within experimental error ($\gamma_{\alpha\beta} - \gamma_{\alpha\delta}$) is equal to the alkane surface tension in all cases. Hence θ is very close to zero for all the alkanes.

Clearly, if the surfactant concentration is reduced θ must eventually start to rise, finally attaining the value for alkane on pure water. In Fig. 8 we show $(\gamma_{\alpha\beta} - \gamma_{\alpha\delta}) = \Delta\gamma^*$ as a function of $\ln(\text{surfactant concentration, } c_s)$ for the DoTAB–dodecane system. $\Delta\gamma^*$ rises as c_s increases up to $\ln c_s = -5.5$ (the c.m.c. is at $\ln c_s = -4.2$). Values of θ , calculated using eqn. 8, are shown in the inset as a function of c_s . The contact angle approaches zero around the surfactant concentration where Γ_s in the mixed monolayer becomes effectively constant, i.e. close-packed.

(iii) Alkane Penetration and Microemulsion Inversion

As mentioned, in a system consisting of, say, equal volumes of an aqueous phase and an alkane phase with an appropriate surfactant, so that one of the phases is a microemulsion, it

Table 4 Various tensions (mN m⁻¹), relevant to the spreading behaviour, for the systems (alkane–aqueous DoTAB) above the c.m.c. ($c_s = 19.7 \text{ mmol dm}^{-3}$)

N_a	$\gamma_{\alpha\beta}$	$\gamma_{\alpha\delta}$	$(\gamma_{\alpha\beta} - \gamma_{\alpha\delta})$	$\gamma_{\beta\delta}$
10	31.4	7.9	23.5	23.4
11	32.4	8.2	24.2	24.2
12	33.2	8.4	24.8	24.9
13	34.3	8.7	25.6	25.6
14	35.1	8.9	26.2	26.1
15	35.9	9.1	26.8	26.6
16	36.3	9.3	27.0	27.0

See text for symbols

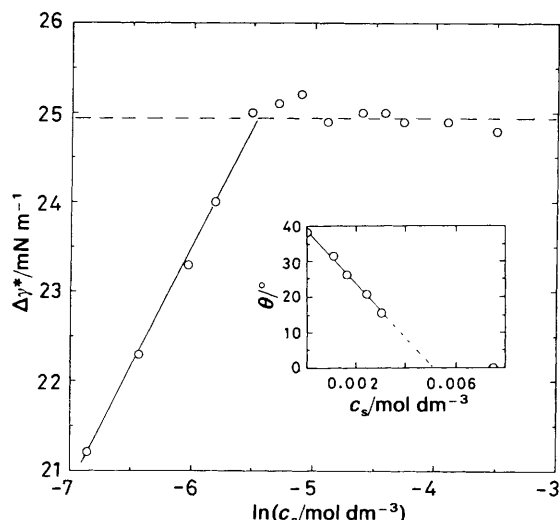


Fig. 8 Variation of tension difference $\Delta\gamma^*$ (see text) with surfactant concentration c_s for the (DoTAB-dodecane) system at 25°C. Dashed horizontal line represents the surface tension of dodecane at 25°C. Inset shows variation with c_s of contact angle of dodecane with aqueous DoTAB

is possible to invert the microemulsion type by changing the alkane chain length. For example in alkane-0.068 mol dm⁻³ aqueous NaCl systems containing AOT above its c.m.c. at 25°C,³ for alkanes with $N_a < 9$ a water-in-oil microemulsion exists in equilibrium with the aqueous phase. As N_a is increased through nonane the microemulsion droplets form in the aqueous phase and the equilibrium systems are now oil-in-water microemulsions in equilibrium with an alkane phase. It is also possible to cause an inversion in microemulsion type, using a given alkane, by varying the salt concentration.¹⁴ In all cases, at the inversion condition the planar oil/water interfacial tension (γ_c) passes through a very low minimum, which is indicative of the inversion process. On a simple picture, inversion occurs when the cross-sectional areas a_h and a_c of the head and chain groups of the surfactant molecules are equal. Alkanes affect a_c by the penetration process already described. Salt concentration modulates the value of a_h for ionic surfactants such as AOT; salt screens the lateral head-group repulsions within the monolayers, hence reducing a_h . The question we wish to address here is if the hydrocarbon solubilisation process at the air/solution interface is closely related to microemulsion behaviour. If so it may be possible ultimately to obtain useful quantitative information relevant to microemulsion systems which is not otherwise readily accessible.

The system we have chosen to investigate consists of cyclohexane (a strongly penetrating hydrocarbon), aqueous NaCl, concentration m_c , and AOT above its c.m.c. Microemulsions are formed in this system and their type can be inverted by changing m_c . Characteristically, the tensions γ_c are low, and pass through a minimum at $m_c = 0.025$ mol dm⁻³ (Fig. 9). For low m_c , oil-in-water microemulsions are given, and at high m_c the system is inverted giving water-in-oil microemulsions.

We have already seen for systems with low contact angles, the chain/air surface in a mixed monolayer is energetically very similar to the surface of pure alkane [*i.e.* $\Delta\gamma^* = \gamma(\text{alkane})$]. This implies that the alkane penetration at the air/aqueous solution interface is very similar to that at the oil/aqueous solution interface. If so then we expect that alkane solubilisation in the monolayer at the air/solution interface (and hence $\Delta\gamma$) will fall as m_c is increased (a_h is reduced) until, at the salt concentration giving minimum γ_c at

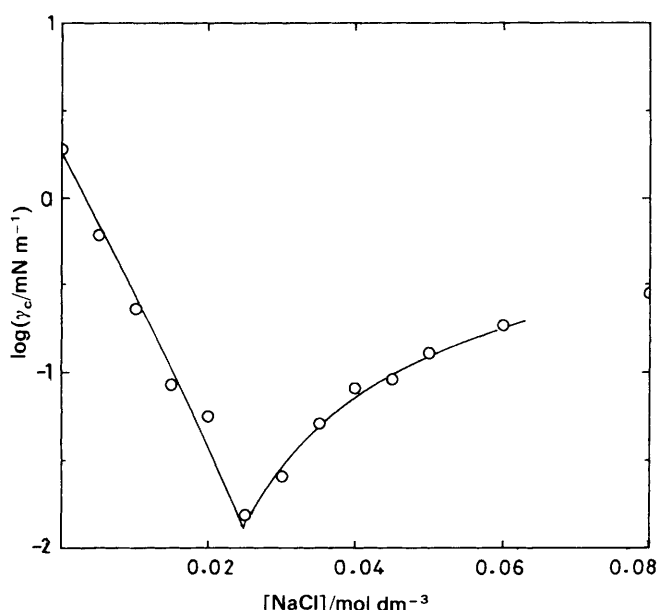


Fig. 9 Post-c.m.c. oil/water tensions, γ_c , vs. salt concentration in the system 3.76 mmol dm⁻³ aqueous AOT-cyclohexane at 25°C

the oil/solution interface (where a_c begins to determine the area per surfactant), $\Delta\gamma$ should become constant. This indeed is what is observed experimentally, as shown in Fig. 10. At low salt concentration $\Delta\gamma$ (and Γ_s) falls until, for m_c between 0.02 and 0.03 mol dm⁻³, the cyclohexane lenses on the AOT solutions become cloudy, indicating the uptake of AOT by the oil and the tendency to inversion. For $m_c > 0.03$ mol dm⁻³ the lenses become clear again and $\Delta\gamma$ remains constant.

It is possible to estimate the film compositions and thicknesses as follows. We may suppose for m_c up to 0.025 mol dm⁻³, where Γ_s is determined by the head groups, that Γ_s for AOT in the mixed monolayer at the air/solution interface is equal to that at (say) the heptane/water interface at the same salt concentrations (where a_h also determines Γ_s). We know that Γ_s for AOT at the cyclohexane/0.1 mol dm⁻³ NaCl interface is 1.25 molecule nm⁻²,¹⁵ which means at inversion $a_h = a_c = 0.80$ nm². Since, as seen, inversion occurs at 0.025 mol dm⁻³ NaCl, we expect the area per AOT molecule at the heptane 0.025 mol dm⁻³ NaCl interface also to be *ca.* 0.80 nm². Experimentally it is found to be *ca.* 0.81 nm².³ Thus,

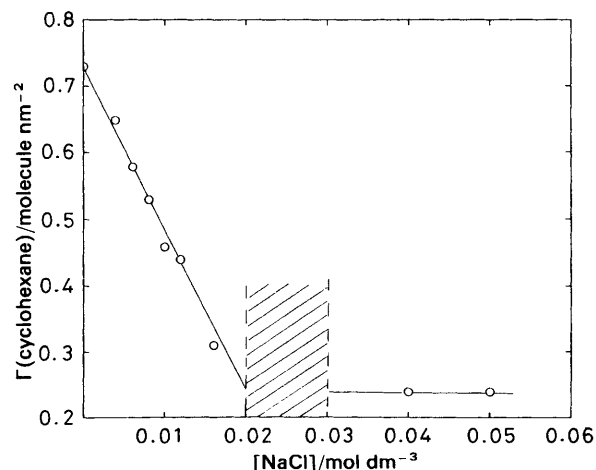


Fig. 10 Uptake of cyclohexane in AOT monolayers on 3.76 mmol dm⁻³ AOT solutions in aqueous NaCl as a function of salt concentration at 25°C. The shaded area represents the range of salt concentration where the cyclohexane lenses become cloudy

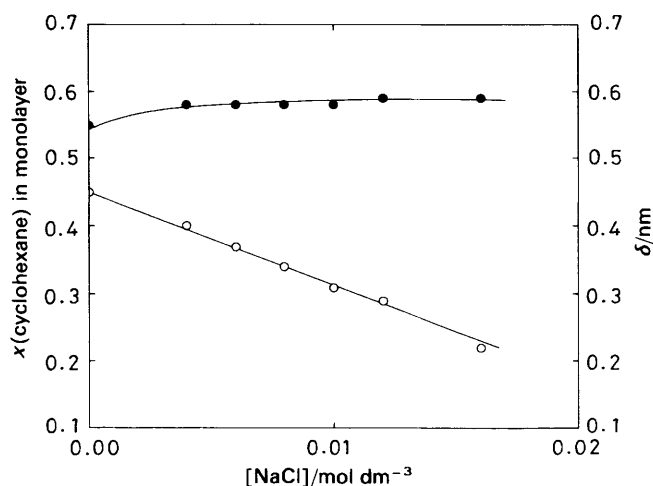


Fig. 11 Variation with salt concentration of the mole fraction of cyclohexane in mixed monolayers with AOT (○) and of hydrocarbon layer thickness (●) at 25°C

assuming values of Γ_a and knowing $\Delta\gamma$ we can calculate the film compositions and the thicknesses of the hydrocarbon parts of the monolayers using eqn. 5. We show the mol fraction x^σ of cyclohexane in the mixed monolayers [$x^\sigma = \Gamma_a/(\Gamma_a + \Gamma_h)$] and the hydrocarbon layer thickness δ as a function of salt concentration in Fig. 11. It is interesting to note that although x^σ falls very markedly with m_s , δ remains essentially unchanged at around 0.58 nm. It appears then that the surfactant tail extension remains unchanged as the monolayer is compressed by salt, and that the cyclohexane simply fills in the space available.

Conclusions

(1) Solubilisation of non-spreading alkanes in surfactant monolayers at the air/solution interface can be determined semi-quantitatively from the tension lowering caused by the mixing of surfactant and alkane at the surface.

(2) For systems at or above the c.m.c. the surface concentration of alkane, Γ_a , remains constant with respect to surfactant concentration. At equilibrium, Γ_a decreases with increasing alkane chain length and increases with increasing surfactant chain length. On the assumption that the hydrocarbon part of the mixed monolayers is liquid-like, both the volume uptake of hydrocarbon and the hydrocarbon layer thickness are readily calculated. For a given surfactant the thickness falls as alkane chain length increases.

(3) As a close-packed monolayer is 'opened up' by dilution of the solution, alkane uptake initially rises and then, when the area per surfactant reaches approximately twice that in the close-packed film, falls rapidly.

(4) The contact angles of alkane lenses with surfactant solutions close to the c.m.c. are almost zero. As the surfactant

films become more dilute however, the contact angles begin to rise quite rapidly.

(5) Addition of NaCl to AOT solutions initially reduces the area per surfactant at the surface and concomitantly the surface solubilisation of cyclohexane. For salt concentrations above 0.025 mol dm⁻³ hydrocarbon solubilisation remains constant. Significantly, in a similar system but containing roughly equal volumes of hydrocarbon and aqueous surfactant, microemulsions are formed and the oil/water tension reaches an ultralow minimum at the same salt concentration. Inversion of microemulsion type also occurs around 0.025 mol dm⁻³ NaCl.

We will report shortly on an investigation of two-dimensional solubilisation of dodecane in tetradecyltrimethylammonium bromide monolayers using low-angle neutron reflection.

The authors gratefully acknowledge the award, by Rhone-Poulenc (Bevaloid Ltd.), of a PhD Studentship for P.C. under which this work was carried out.

References

- O. Bayer, H. Hoffmann and W. Ulbricht, *Surfactants in Solution*, ed. K. L. Mittal and P. Botherel, Plenum, New York, 1986, vol. 4, p. 343. This paper gives many useful references on solubilisation in micellar solutions.
- K. E. Hayes and R. B. Dean, *J. Phys. Chem.*, 1953, **57**, 80.
- R. Aveyard, B. P. Binks and J. Mead, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 1755.
- S. Mukherjee, C. A. Miller and T. Fort, *J. Colloid Interface Sci.*, 1983, **91**, 223.
- R. Aveyard and T. A. Lawless, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2951.
- R. Aveyard, B. P. Binks, S. Clark and P. D. I. Fletcher, *J. Chem. Tech. Biotechnol.*, 1990, **48**, 161.
- R. Aveyard, P. Cooper and P. D. I. Fletcher, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 211.
- R. Aveyard and D. A. Haydon, *Trans. Faraday Soc.*, 1965, **61**, 2255.
- F. Hauxwell and R. H. Ottewill, *J. Colloid Interface Sci.*, 1970, **34**, 474.
- M.-H. Guermouche and J.-M. Vergnaud, *J. Chromatogr.*, 1973, **81**, 19.
- R. Fettiplace and D. A. Haydon, *Physiol. Rev.*, 1980, **60**, 510.
- B. Widom, *J. Chem. Phys.*, 1975, **62**, 1332.
- Selected properties of hydrocarbons and related compounds, API Project 44, Thermodynamics Research Center, Texas, vol. 2.
- R. Aveyard, B. P. Binks and J. Mead, *J. Chem. Soc., Faraday Trans. 1*, 1985, **81**, 2169.
- R. Aveyard, B. P. Binks and J. Mead, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2347.

Paper 0/02708A; Received 18th June, 1990