On Understanding Microemulsions

I. Interfacial Tensions and Adsorptions of SDS and Pentanol at the Cyclohexane/Water Interface

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We measured interfacial tensions using the spinning drop technique in two-phase oil/water (O/W) systems containing sodium dodecyl sulfate (SDS), *n*-pentanol, NaCl, cyclohexane, and water. The systems contained only small amounts of SDS (mostly <CMC). Surfactant activities were obtained from measured distribution data. Addition of pentanol decreases the adsorption of SDS, whereas the saturation adsorption of pentanol is almost not affected by the presence of SDS. Under conditions that also exist in W/O microemulsions a molar ratio pentanol/SDS of 2.4 at the interface is found from interfacial tension measurements. Similar values are obtained for the interface in microemulsions from dilution experiments. In the mixed monolayer, the total adsorption (pentanol + SDS) corresponds to approximately 25 Å^2/ molecule, whereas for pure SDS and pentanol the saturation adsorptions correspond respectively to a coverage of 54 and 36 Å^2/molecule. © 1987 Academic Press, Inc.

INTRODUCTION

Microemulsions are thermodynamically stable dispersions of oil and water in one another. In many cases these systems can be considered dispersions of monodisperse spherical droplets (1–3) in a continuous medium (W/O or O/W). The spontaneous formation and thermodynamic stability of microemulsions require a low interfacial tension between water and oil (4–6), that is obtained by the presence of a large amount of one or more surfactants.

An important class of microemulsions contains an ionic surfactant (e.g., a soap, an alkyl sulfate or sulfonate, a tetraalkylammonium salt) and a weakly polar cosurfactant (often a medium-chain-length aliphatic alcohol). The distribution of the surfactants among the droplets, the continuous medium and the (microscopic) interface separating them, is largely determined by their solubilities in the fluid media and their adsorbabilities (7).

Interfacial tensions and adsorption densities of the surfactants are essential quantities required for the understanding of microemulsions, their stability and phase equilibria, as will also be shown in forthcoming papers (8, 9) of this series. Unfortunately, the interfacial tension between the droplets and the continuous medium cannot be measured directly. It is, however, possible to measure interfacial tensions between macroscopic water and oil phases, that correspond in composition with the dispersed and the continuous medium in microemulsions. From such measurements the adsorptions, Γ_{sa} and Γ_{co}, of the surfactant (sa) and the cosurfactant (co) can be evaluated by application of the Gibbs adsorption equation for a multicomponent system,

$$\left(\frac{\partial \gamma}{\partial \ln a_i}\right)_{a_{j\neq i,1,T}} = -RT\Gamma_i^{(1)} \quad \text{(for } i \neq 1), \quad [1]$$

where γ is the interfacial tension, a_i and a_j are the activities of the components i and j, and $\Gamma_i^{(1)}$ is the relative adsorption of component i ($\Gamma_1^{(1)} \equiv 0$).

In microemulsions, almost all the surfactant ions are present in the interface, since the con-

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centration in the aqueous regions of the droplets is below the CMC. The amount of cosurfactant adsorbed at the interface between the droplets and the continuous medium can also be measured with the dilution procedure as described in the experimental section of this paper. In this way two independent evaluations of the ratio Γ_{co}/Γ_{sa} are thus possible.

This paper reports on a study of the effect of the surfactant (sodium dodecyl sulfate, SDS), the cosurfactant (n-pentanol), and salt (NaCl) on interfacial tensions (γ) and adsorptions (Γ_{sa}, Γ_{co}) at the macroscopic cyclohexane/water interface.

In a second paper (8) the thermodynamics of microemulsions and their phase equilibria will be considered. Experiments on phase behavior and confrontation with the theory will be reported in a third publication (9).

EXPERIMENTAL

Materials. Cyclohexane, n-pentanol, and NaCl were Baker "analyzed" reagents. Sodium dodecyl sulfate was purchased from BDH. Except in a few cases, these materials were used without further purification. Deionized water was doubly distilled for elimination of surface-active impurities. The absence of ionic and surface-active impurities was checked by electrical conductivity and surface tension measurements.

Sample preparation. Mixtures of oil and water for equilibration and subsequent measurements of interfacial tensions were prepared in 25-ml glass tubes with Teflon-sealed screw caps. Equilibration times (at $25 \pm 2°C$) of up to 1 month were used to assure attainment of equilibrium. The samples were weighed into the tubes and vigorous shaking was avoided to prevent formation of coarse emulsions which can be (kinetically) stable for a long time. Especially at low cosurfactant contents coarse emulsions were observed to persist for a long time. Only gentle shaking was applied during the first week of the equilibration time to homogenize both phases.

The samples contained 8.00 g of an oil phase

and 10.00 g of a water phase. The oil phase (to be referred to simply as oil) was a solution of the cosurfactant (n-pentanol) in cyclohexane. The initial composition was varied between pure cyclohexane and pure pentanol.

The initial concentration of SDS in the water phase (to be referred to simply as water) was varied from zero to concentrations which, after equilibration, reached the CMC in water or yielded a near zero value of the interfacial tension at high cosurfactant contents in the oil. The highest initial SDS concentration was $2.11 \times 10^{-2} M$ (at $0.30 M$ NaCl and 20% (w/w) pentanol in oil) and was equivalent to $32 \times$ CMC at the chosen salt concentration. Initial SDS concentrations above the CMC were necessary at high cosurfactant contents in the oil because a considerable part of the SDS dissolved in the oil.

The concentration of NaCl in the water was varied between 0 and $0.30 M$. As NaCl is practically insoluble and water dissolves only slightly in oil, the equilibrium concentration of NaCl in water may be equated to its initial concentration at low SDS contents.

Interfacial tensions. Interfacial tensions were measured with the spinning drop technique (10, 12). A drop of the less dense phase, embedded in the denser phase, is deformed by high speed rotation of a cylindrical glass sample tube around its axis. This technique is especially useful for measuring the low interfacial tensions that occur in microemulsion systems. The apparatus was built by Bailey Engineering, Windsor, England. Its maximum rotation speed is 10^4 rpm. All measurements were carried out in a thermostated room (25 $\pm 2°C$).

The interfacial tension was calculated from the expression

$$\gamma = \tfrac{1}{4} r^3 \Delta\rho\omega^2 \qquad [2]$$

which is equivalent to that given by Slattery and Chen (11) for a cylindrical drop and is also known as the approximation of Vonnegut (12). In this expression r is the radius of the cylindrical part of the drop, $\Delta\rho$ is the density difference of the phases, and ω is the angular

velocity of the drop and the surrounding phase. The approximation is valid if the diameter ($2r$) is less than one-quarter the drop length measured along the rotation axis. For low interfacial tensions this condition is already fulfilled at intermediate rotation speeds (<4000 rpm), but for high interfacial tensions a large drop volume is essential for the condition to be satisfied at sufficiently low rotation speeds. Therefore we used rotating tubes with a large internal diameter ($\approx$3 mm) for measurements of high interfacial tensions.

The rotation speed was constant at better than 0.5%. The diameter of the drop was measured with a microscope equipped with a calibrated eyepiece. Micrometer read-off errors correspond to about 3 μm in the diameter. Apparent drop diameters were corrected for the magnification introduced by the cylindrical glass tube. For diffuse illumination the correction factor equals the ratio of the refractive indices of the denser phase and the medium surrounding the sample holder (13, 14). As the external medium is air and the denser phase is almost pure water, this correction factor equals 1.33. The procedure was checked by measuring the apparent diameters of cylindrical solid "drops" (polyethylene) of known diameters in liquids of different refractive index.

Densities. Densities of the phases were measured with a Paar DMA 02 C digital precision density meter. Changes in the densities with varying surfactant concentration were neglected because the total amount of surfactant present was always very low. An experimental check on systems with high surfactant concentrations revealed that the error introduced is indeed negligible for all samples

Analysis of equilibrated phases. When necessary the equilibrium compositions of the phases were measured. For analysis of the liquid components gas chromatography was used. The oil phase and the water phase were analyzed for cosurfactant using a steel column, packed with a cross-linked polystyrene resin (Chromosorb 103 supplied by Chrompack B.V.) and a flame ionization detector (FID).

The analyses were carried out isothermally. The distribution coefficient of the cosurfactant was noted to depend strongly on its concentration in oil, indicating a strong association of pentanol in the oil. Association of other medium-chain-length aliphatic alcohols in nonpolar solvents was also observed with a variety of experimental techniques (15–17).

The concentrations of SDS in water and oil were measured colorimetrically (18, 19). An aqueous solution containing an excess of methylene blue was added to a sample of the phase to be analyzed. From aliquots of oil phase the oil was first evaporated and the residue was redissolved in water. The blue equimolecular complex of the dye and the surfactant was extracted in chloroform. Then the extinction at a wavelength $\lambda = 652$ nm was measured with a Bausch and Lomb/Shimadzu Spectronic 200 UV spectrophotometer. The lowest amount of SDS that could be detected was approximately 2×10^{-6} g which corresponds to a detection limit of 2×10^{-4}% (w/w) for 1.00-g aliquots of the water phase. The equilibrium concentration in water was used to calculate the adsorption of the surfactant from interfacial tensions via the Gibbs adsorption equation. From surfactant distribution data it was also possible to detect the onset of association (micellization) of the surfactant either in the water or in the oil, as at that point the distribution coefficient started to change.

Dilution procedure for W/O microemulsions. For W/O microemulsions the compositions of the interface and the continuous medium can be measured directly via a dilution method (20). Several authors used this method to produce microemulsions with different volume fractions and constant droplet size (1–3).

The basic assumption of the dilution method is that the compositions of the droplets, the continuous medium, and the interface do not depend on the volume fraction ϕ of the droplets. For W/O microemulsions that contain just enough cosurfactant to form a single-phase, optically clear system, the composition of the continuous medium can be de-

termined by alternately adding oil and cosurfactant (see Fig. 1).

When oil is added, the cosurfactant activity in the continuous medium decreases and a part of the cosurfactant will leave the interface of the droplets to maintain adsorption equilibrium. A sharp increase in the turbidity then indicates that the microemulsion becomes unstable and that the multiphase region is entered. The cosurfactant/oil ratio in the continuous medium can be restored by adding cosurfactant and the system clears up again. The net result of repeating this procedure is a dilution of the microemulsion with a cosurfactant/oil mixture having the composition of the continuous medium. This composition can be found from the slope of the line in Fig. 1. Extrapolation to zero oil content gives the ratio of the amounts of cosurfactant and surfactant in the droplets plus the interface. As the solubility of the cosurfactant in water is low this ratio may be equated to n_{co}^{σ}/n_{sa}, where n_{co}^{σ} is the amount of cosurfactant at the interface of the drops. This ratio is equal to Γ_{co}/Γ_{sa} as the concentration of surfactant inside the drops is also low.

FIG. 2. Effect of cosurfactant and electrolyte (NaCl) on interfacial tensions between cyclohexane and water in the presence of small amounts ($\approx$CMC) of SDS. ($\bullet$) 0.2% (w/w) SDS in water ($\approx$CMC), ($\square$) 0.2% (w/w) SDS in 0.03 M NaCl (>CMC), ($\triangle$) 0.2% (w/w) SDS in 0.10 M NaCl (>CMC), ($\bigcirc$) 0.019% (w/w) SDS in 0.30 M NaCl ($\approx$CMC).

RESULTS AND DISCUSSION

We introduce the analysis and discussion of the interfacial tension measurements at the macroscopic oil/water interface b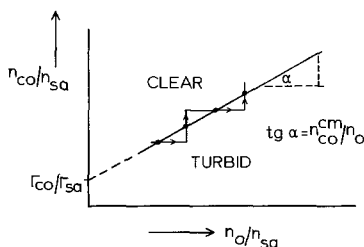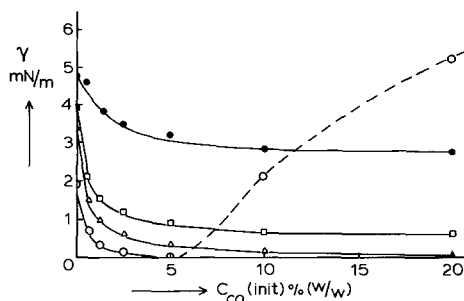y referring to Fig. 2. This figure gives a plot of the interfacial tension as a function of the initial cosurfactant concentration in the oil at different initial SDS concentrations in the water at different fixed values of NaCl concentration. The need for auxiliary surfactant distribution measurements, in order to derive adsorptions from the raw interfacial tension data, is also demonstrated by this figure.

For each curve the initial SDS concentration in water was chosen at or above the CMC for the corresponding NaCl concentration. So we are certain that, before any cosurfactant was added, the reduction of the interfacial tension by the SDS has reached its maximum value and that any further reduction is due to pentanol.

Both NaCl and pentanol lower the interfacial tension at a constant initial concentration of SDS. The deviating behavior at 0.30 M NaCl above 5% (w/w) pentanol is discussed below. An interesting observation is that in the absence of NaCl the lowest interfacial tension that can be reached with these surfactants is about 3 mN/m. Although this is a relatively high interfacial tension, microemulsions can easily be formed with these components without adding NaCl (2, 3). On the other hand, the interfacial tension for a system with pure cyclohexane and SDS in 0.30 M NaCl is seen to be lower ($\approx$2 mN/m). Microemulsions,

FIG. 1. Determination of compositions of continuous medium (cm) and droplet interface via the dilution procedure. The amount of cosurfactant (n_{co}) is plotted vs the amount of oil (n_o) for microemulsions at the phase boundary. The amounts are normalized with respect to the amount of surfactant (n_{sa}).

however, cannot be formed with SDS without the addition of cosurfactant, even if NaCl is added. From these facts we conclude that a low interfacial tension between oil and water may be necessary for microemulsion formation, but it is clearly not the only factor that determines whether stable microemulsions will form. The cosurfactant must have another important effect in addition to reducing the oil/water interfacial tension. In the next paper (8) it will be stressed that the curvature dependence of the interfacial tension is essential in microemulsion formation and that this is controlled by the concentration of cosurfactant and salt.

The major part of the reduction of the interfacial tension by pentanol occurs before $c_{co}(\text{init}) \approx 5\%$ (w/w). Very low interfacial tensions ($\approx 10^{-2}$ mN/m) are obtained at 0.10 M NaCl for cosurfactant concentrations above 10% (w/w) and at 0.30 M NaCl for 5% (w/w) cosurfactant. Surprising is the sharp increase in the interfacial tension above 5% of cosurfactant at 0.30 M NaCl. As we do not expect Γ_{sa} or Γ_{co} to change sign (21) or the cosurfactant activity to decrease upon adding cosurfactant, this observation can only be accounted for by a decrease in the surfactant activity. Presumably this happens by transfer of SDS to the oil phase, i.e., by the formation of a W/
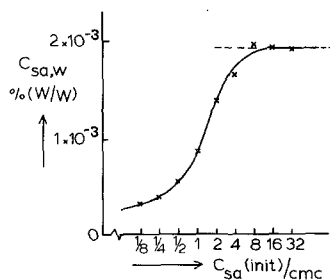

FIG. 4. Surfactant concentration in the aqueous phase versus the initial surfactant concentration in water. The initial cosurfactant concentration in cyclohexane was 20% (w/w). Water contains 0.30 M NaCl. Initial surfactant concentrations are given in units of the CMC in 0.30 M NaCl without oil and cosurfactant (CMC = $1.9 \times 10^{-2}\%$ (w/w) (Ref. (22)).

O microemulsion. We therefore measured the equilibrium concentrations of the surfactant in water ($c_{sa,w}$) and in oil ($c_{sa,o}$).

Distribution of SDS

Figure 3 gives a plot of the equilibrium concentrations of SDS in oil and water against the initial cosurfactant concentration in oil for the samples with 0.30 M NaCl and an initial SDS concentration in water of $1.86 \times 10^{-2}\%$ w/w ($\approx$CMC at 0.30 M NaCl).

At low initial cosurfactant concentrations all the surfactant is seen to remain in the water phase. No SDS could be detected in the oil phase, in agreement with the fact that SDS is not soluble in oil. At larger c_{co} the concentration of SDS in the oil phase gradually increases until, at high c_{co}, almost all SDS is present in the oil. The concentration in the water phase becomes very low, but finite. This finding is in agreement with the sharp rise of the interfacial tension in Fig. 2. At $c_{co} = 20\%$ (w/w), $c_{sa,w}$ is less than 5% of the CMC in 0.30 M NaCl. From data which will be discussed later we know, however, that $c_{sa,w}$ is still in the region where saturation adsorption for the surfactant exists. Figure 4 shows the equilibrium concentration of SDS in water as a function of its initial concentration, expressed as a fraction of the CMC. When more surfactant is added, $c_{sa,w}$ gradually increases. For the highest
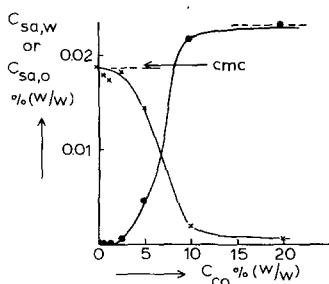

FIG. 3. Concentrations of the surfactant in the water phase ($\times$) and the oil phase ($\bullet$) vs the (initial) cosurfactant concentration in the oil phase. Broken lines indicate initial concentration of SDS and theoretical maximum in oil (levels are different because concentrations are in % (w/w)). The initial surfactant concentration in 0.30 M NaCl is $1.86 \times 10^{-2}\%$ (w/w) ($\approx$CMC = $1.9 \times 10^{-2}\%$ (w/w) (arrow)).

initial surfactant concentrations $c_{sa,w}$ approaches a constant value of approximately $1.9 \times 10^{-3}\%$ (w/w), that corresponds to 10% of the CMC in 0.30 M NaCl. At all further additions the surfactant goes almost entirely into the oil phase. Because $c_{sa,w}$ is always relatively low we may regard the aqueous phase as a solution of surfactant monomers with an activity proportional to $c_{sa,w}$.

The observed CMC-like behavior (constant surfactant activity with increasing total concentration (see Fig. 4)) is an indication for the formation of surfactant aggregates in oil. This hypothesis is further confirmed when we plot $c_{sa,o}$ against $c_{sa,w}$ (Fig. 5).

The nonlinear behavior within the entire investigated concentration range ($>1/8$ CMC, 0.30 M NaCl) suggests that a gradually increasing association of SDS takes place in the oil phase. This may be considered as the onset of W/O microemulsion formation. Even in the absence of SDS, cyclohexane + 20% (w/w) pentanol takes up approximately 0.5% (w/w) of water; therefore the extra amount of water entrained with the SDS is in most cases too small to be detected. For the sample with an initial surfactant concentration of 16 times the CMC we observed an increase in the water content of the oil phase to about 1% (w/w). More detailed results on water uptake into the oil phase at higher surfactant concentrations will be given in the third paper of this series.
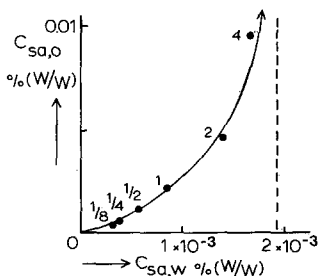
For 0.30 M NaCl solutions at lower cosur-

FIG. 6. Surfactant concentration in the oil phase versus surfactant concentration in the aqueous phase (c_{co}(init) = 5% (w/w), 0.30 M NaCl).

factant concentrations and for 0.10 M NaCl solutions at all cosurfactant concentrations a qualitatively different behavior is noted. As an example we give the data for 0.30 M NaCl and 5% (w/w) pentanol in cyclohexane (Fig. 6).

Here the surfactant distribution coefficient $c_{sa,o}/c_{sa,w}$ is much smaller and is constant within experimental error for low surfactant concentrations. These observations suggest the absence of surfactant association in water and in oil. Above a certain concentration in water ($\approx 3 \times 10^{-3}\%$ (w/w)) the concentration in oil becomes constant, indicating micellization (or microemulsion formation) in water. We note that at this point the surfactant concentration in the oil (probably monomers associated with pentanol and water) is much lower than that commonly present in microemulsions. The different behavior of 0.10 and 0.30 M NaCl systems and low and high cosurfactant content systems at 0.30 M NaCl is also noted in our study of microemulsion phase behavior (9). The distribution data show that it is always necessary to determine equilibrium concentrations of the surfactant in water before the concentration dependence of interfacial tensions can be interpreted.

Distribution of Pentanol

We also measured the distribution of the cosurfactant between the oil and the water phase. Figure 7 is a plot of its equilibrium concentration in water ($c_{co,w}$) versus the initial

FIG. 5. Surfactant concentration in the oil phase versus surfactant concentration in the aqueous phase (c_{co}(init) = 20% (w/w), 0.30 M NaCl). Numbers and broken line correspond respectively to initial concentrations (in units of CMC) and maximum $c_{sa,w}$ in Fig. 4.
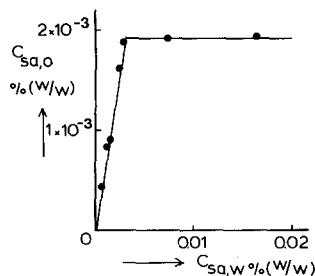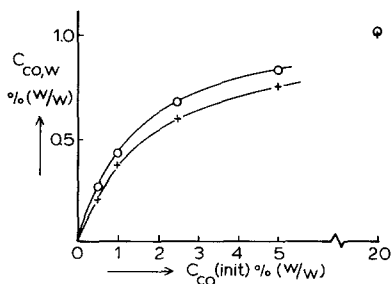
FIG. 7. Pentanol concentration in aqueous phase vs initial concentration in cyclohexane for cyclohexane/water systems (without SDS). (O) 0.10 M NaCl in water, (+) 0.30 M NaCl in water.

concentration in oil. The marked nonlinear behavior is an indication for gradually increasing association of pentanol in the oil phase. We obtained a rough estimate of the average aggregation number from the freezing point depression of solutions of pentanol in cyclohexane in the absence of water.[1] For pentanol concentrations above 5% (w/w) the average aggregation number was about 3.5. For 0.30 M NaCl Fig. 7 shows a slightly lower cosurfactant concentration in water than that for 0.10 M NaCl. This is probably a salting-out effect; therefore the approximate coincidence of the points for an initial cosurfactant concentration of 20% (w/w) is suspect. Even for pure pentanol as the oil phase and 0.30 M NaCl (not shown in the figure) the concentration in water is low (1.74% (w/w)). Therefore we may regard the aqueous phase as an ideal solution of pentanol in water. So for all initial concentrations in oil, the cosurfactant activity is proportional to its concentration in the aqueous phase. Furthermore we found that, for the low surfactant concentrations under study, the distribution coefficient of pentanol is independent of the surfactant concentration. These results are extremely useful for the interpretation of interfacial tension data, because for any sample, the cosurfactant activity can be read off Fig. 7 for a given initial cosurfactant concentration in oil.

[1] The pentanol in these experiments was dried over magnesium sulfate.

Analysis of the Interfacial Tension Data

Figure 8 shows interfacial tensions of pentanol solutions in cyclohexane vs the logarithm of $c_{co,w}$. These systems do not contain SDS. From the slope of the linear part of the curve we obtain $-(1/RT)/(\partial\gamma/\partial \ln c_{co,w}) = (4.62 \pm 0.08) \times 10^{-6}$ mole/m^2. In making this calculation we omitted the point for pure pentanol that deviates from the linear plot and also the point for $c_{co} = 0.5\%$ (w/w) because saturation adsorption has probably not been reached at this concentration. Subject to the above restrictions a value of 35.9 ± 0.7 Å^2/molecule is obtained for the area per pentanol (σ_{co}) at the interface in the absence of SDS. It should be noted, as discussed in some detail in Appendix A, that the excess quantity measured by the slope of the γ vs ln $c_{co,w}$ plot does not give the relative or Gibbs adsorption $\Gamma_{co}^{(w)}$ of the cosurfactant. It determines the excess of cosurfactant relative to the two bulk phases which contain all of the oil and water components. Only at low cosurfactant concentrations in oil (<5% (w/w)) will the observed quantity correspond to $\Gamma_{co}^{(w)}$,

Figure 9 shows the dependence of the interfacial tension at 0.30 M NaCl on the equilibrium concentration of the surfactant in water for fixed initial cosurfactant concentrations in oil of 0, 1, 5, and 20% (w/w). Because the distribution of the cosurfactant does not de-
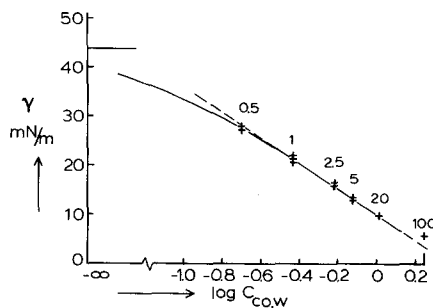

FIG. 8. Interfacial tension between cyclohexane and 0.30 M aqueous NaCl in the presence of pentanol vs logarithm of the pentanol concentration in the aqueous phase ($c_{co,w}$ in % (w/w)). Numbers in figure are initial cosurfactant concentrations in the oil (c_{co}(init) in % (w/w)). Slope corresponds to 35.9 Å^2/molecule for pentanol.
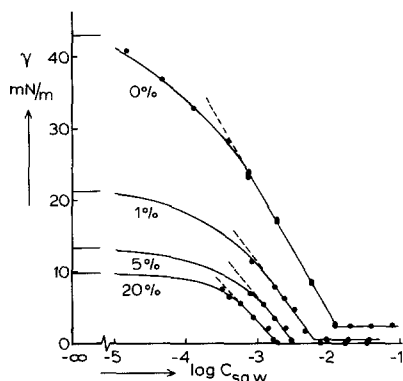
FIG. 9. Interfacial tension between cyclohexane and 0.30 M NaCl in the presence of pentanol and SDS vs logarithm of the SDS concentration in the aqueous phase ($c_{sa,w}$ in % (w/w)). Numbers in the figure are initial cosurfactant concentrations in oil. Interfacial tensions above the observed CMCs are 2.42 mN/m (0% co), 0.54 mN/m (1% co), and 0.036 mN/m (5% co). Lowest measured interfacial tension for 20% co: 0.066 mN/m. The corresponding point in the figure represents measurements at three different initial surfactant concentrations (8, 16, and 32 × CMC).

pend on the surfactant concentration, the co-surfactant activity is constant along each curve and Γ_{sa} can be obtained from the slopes of the curves. Information about the region where no saturation adsorption exists is meager because the analysis for surfactant is not sensitive enough. For very low surfactant concentrations the interfacial tensions approach the values shown in Fig. 8.

The value of 43 mN/m for the interfacial tension in the absence of both surfactants is somewhat lower than the value of 50 mN/m reported for the cyclohexane/water interface (23). This difference remains unexplained. It might be due to the presence of traces of surface-active impurities in the oil. Our observed CMC for an oil/water interface without co-surfactant (1.2×10^{-2}% (w/w)) is lower than the value of 1.9×10^{-2}% (w/w) found by Huisman (22) for an air/water interface at the same salt concentration (0.30 M NaCl, 21°C). Rehfeld (23) also observed a decrease in the CMC of SDS in going from an air/water interface (0.24% (w/w)) to a cyclohexane/water interface (0.22% (w/w)). This decrease was rel-

atively smaller than that in our experiments. A direct comparison is, however, not justified because Rehfeld's measurements were made without salt.

We note that the CMC is progressively decreased with increasing cosurfactant content, which may be explained by the formation of mixed micelles (24, 25). The curve at 20% (w/w) cosurfactant does not show the break, characteristic of a CMC in water. Under these conditions the concentration of SDS in water becomes constant (see Fig. 4) before the CMC is reached.

Saturation Adsorption

At surfactant concentrations higher than about 10% of the observed CMCs the slopes of the curves become constant, indicating saturation adsorption. For a dilute solution of an ionic surfactant in the presence of a cosurfactant and excess salt Eq. [1] assumes to a very good approximation (see Appendix A) the form

$$\left(\frac{\partial \gamma}{\partial \ln c_{sa,w}}\right)_{a_{co}} = -RT\Gamma_{sa}^{(w)}. \qquad [3]$$

From the data displayed in Fig. 9 we calculated surfactant saturation adsorptions at the different cosurfactant concentrations. Table I summarizes the results.

The value of 54 Å^2/molecule for the area per headgroup in systems without cosurfactant is in agreement with values for SDS at other

TABLE I

Saturation Adsorption (Γ_{sa}) and Area per Molecule of the Surfactant (σ_{sa}) at Different Initial Concentrations of the Cosurfactant

c_{co} % (w/w)	Γ_{sa} (μmole/m^2)	σ_{sa} Å^2/molecule	
0	3.07 ± 0.02	54.1 ± 0.4	
1	2.4 ± 0.3	69 ± 9	[75]
5	2.0 ± 0.2	83 ± 8	
20	1.82 ± 0.10	91 ± 5	[106]

Note. These results are obtained for 0.30 M NaCl. The numbers in square brackets are obtained in similar experiments with 0.10 M NaCl.

hydrocarbon/water interfaces (e.g., 53.4 Å^2/molecule for the *n*-heptane/water interface (26)). It deviates from a value of 48.3 Å^2/molecule for the cyclohexane/water interface (23), but the latter value was obtained for a system without excess electrolyte by fitting an empirical nonlinear relation, because the concentration region of saturation adsorption is small in the absence of excess electrolyte. Addition of cosurfactant lowers the saturation adsorption of the surfactant to about 60% of the value without cosurfactant. The larger part of this change occurs below 5% (w/w) of cosurfactant. In the range of cosurfactant concentrations often encountered in the continuous medium of microemulsions (>5% (w/w)), Γ_{sa} varies only slightly with the cosurfactant concentration. For 0.30 *M*, the observed surfactant adsorptions are slightly higher than those for 0.10 *M* NaCl. Although for systems without cosurfactant the effect of electrolyte on the maximal adsorption is small or absent (26), we may expect an increased adsorption at higher electrolyte concentrations due to screening of the electrostatic repulsions between the ionic headgroups of the surfactant.

The decreased adsorption of surfactant in systems with cosurfactant is apparently caused by adsorption of the cosurfactant which pushes the surfactant ions apart.

The adsorption of the cosurfactant in the presence of surfactant can also be obtained from our data. In Fig. 10 we plotted interfacial tensions versus the logarithm of the cosurfactant concentration in water for different fixed surfactant activities. These data were obtained by interpolation from the data in Fig. 9. The upper curve shows a part of the data for surfactant-free systems that were already given in Fig. 8.

Given the limited number of experimental measurements, the data nevertheless suggest that for cosurfactant concentrations above 5% (w/w) the adsorption of the cosurfactant is almost independent of the surfactant activity. At lower cosurfactant concentrations, saturation adsorption of co in systems with SDS is probably not reached.
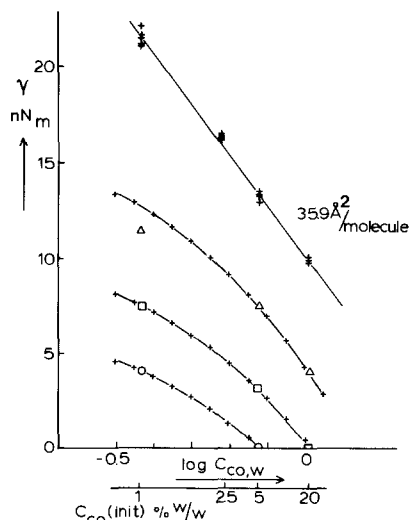

FIG. 10. Interfacial tensions vs logarithm of the cosurfactant concentration in the aqueous phase ($c_{co,w}$ in % (w/w)). Symbols $+$, $\square$, $\triangle$, and $\bigcirc$ correspond to respectively 0, 8.07×10^{-4}, 1.99×10^{-3}, and 3.47×10^{-3} $c_{sa,w}$ % (w/w). Data ($\triangle$, $\square$, and $\bigcirc$) are on the solid curves in Fig. 9. The curves ($— \times —$) are calculated by interpolation, assuming saturation adsorption for sa.

With an average value of $\Gamma_{sa} = 1.9 \times 10^{-6}$ mole/m^2 (Table I) and $\Gamma_{co} = 4.62 \times 10^{-6}$ mole/m^2 (independent of the surfactant activity) one finds $\Gamma_{co}/\Gamma_{sa} \approx 2.4$ for mixed monolayers of pentanol and SDS when $c_{co} \geq 5\%$ (w/w). As the area per SDS molecule is approximately 85 Å^2, this implies that per 85 Å^2 of the interface about 3.4 hydrocarbon chains are adsorbed. This results in quite high packing densities of hydrocarbon chains (≈ 25 Å^2/chain) when compared to values for pure SDS (54 Å^2/chain) and pure pentanol (36 Å^2/chain).

Results of the Dilution Procedure

An independent check of the ratio Γ_{co}/Γ_{sa} can be obtained from dilution experiments involving W/O microemulsions. Table II shows compositions of the continuous medium and the interface of microemulsions with different water/surfactant ratios and two different NaCl concentrations in water.

For microemulsions prepared with 0.30 *M* NaCl, Γ_{co}/Γ_{sa} is in acceptable agreement with

TABLE II

Compositions of the Interface and Continuous Medium in Microemulsions with Different Water/Surfactant Ratios

n_w/n_{sa} mole/mole	0.30 M NaCl		0.10 M NaCl	
	Γ_{co}/Γ_{sa}	c_{co}^{cm} % (w/w)	Γ_{co}/Γ_{sa}	c_{co}^{cm} % (w/w)
20	3.3	7.5	3.3	9.0
35	2.0	7.0	2.6	9.3
50	2.3	6.4	2.7	11.5
70	2.3	6.4	3.2	13.7

Note. Results obtained by the dilution procedure.

the value of 2.4 that was obtained from interfacial tension measurements. For the smallest water/surfactant ratio ($n_w/n_{sa} = 20$) we find a somewhat larger Γ_{co}/Γ_{sa} possibly due to curvature effects on the adsorption at the droplet surfaces.

For microemulsions prepared with 0.10 M NaCl the corresponding ratios are somewhat larger (average $\Gamma_{co}/\Gamma_{sa} = 2.8$ for the largest water/surfactant ratios). For $c_{co} = 20\%$ (w/w) and 0.10 M, the observed ratio ($\Gamma_{co}/\Gamma_{sa} = 3.2$) together with the area per SDS molecule derived from interfacial tension measurements (106 Å^2/molecule, see Table I), give a packing density of approximately 25 Å^2/chain. This value was also found for the macroscopic interface in systems with 0.30 M NaCl. Apparently the increased screening of the electrostatic repulsions between the ionic headgroups at a higher salt concentration favors a higher relative amount of the ionic surfactant at almost constant total packing density.

CONCLUSIONS

Adsorption of SDS and of pentanol at the cyclohexane/water interface was determined from interfacial tension data. In order to interpret the interfacial tension measurements, we took into account the self-association of the cosurfactant in cyclohexane and the solubility of the surfactant in cyclohexane in the presence of cosurfactant.

At saturation adsorption of both surfactants, the packing density of lipophilic chains at the interface is quite high (25 Å^2/chain). This

packing density is independent of the salt concentration. Dilution experiments (see Table II) show that the ratio Γ_{co}/Γ_{sa} is lower at a higher salt concentration. More ionic surfactant is therefore adsorbed at the expense of the cosurfactant at the higher salt concentration. This is probably due to the more effective screening of the charges of the adsorbed surfactant.

The observed area per SDS molecule (σ_{sa}) in the presence of pentanol is considerably higher than the value in the absence of pentanol ($\sigma_{sa} = 83 \pm 8$ Å^2/molecule for c_{co}(init) $= 5\%$ (w/w)) and 54.1 $\pm$ 0.4 Å^2/molecule for pure cyclohexane (Table I). Under conditions that are also present in microemulsions (5% $< c_{co} < 20\%$), σ_{sa} increases only slightly with increasing cosurfactant concentration in the oil and the interfacial tension decreases monotonically with increasing activities of both surfactants. In this concentration range, as will be shown in Ref. (9), a transition from a Winsor type I (O/W + O) to a Winsor type II equilibrium (W/O + W) occurs. A general conclusion may therefore be that the nature of the interface in these two types of system is the same and that the observed interfacial tension minimum (see Fig. 2) is the result of a gradually decreasing surfactant activity.

APPENDIX A: THE GIBBS ADSORPTION EQUATION FOR AN INTERFACE SEPARATING TWO LIQUID PHASES

For a multicomponent (k components), two-phase (α, β) system at constant temper-

ature T and pressure p, the Gibbs adsorption equation reads

$$d\gamma = -\sum_{i=1}^{k} \Gamma_i d\mu_i, \qquad [A1]$$

where Γ_i is the surface excess concentration of component i for an arbitrary choice of the Gibbs dividing surface of zero thickness as expressed by the condition

$$\sum \bar{V}_i \Gamma_i = 0. \qquad [A2]$$

$\bar{V}_i$ is the partial molar volume of component i in the interface. On considering two homogeneous liquid solutions at equilibrium across a flat interface, it is convenient to retain both temperature and pressure as independent variables. In order to satisfy the phase rule we must therefore eliminate from Eq. [A1] two chemical potentials, say μ_1 and μ_2. This elimination may be achieved with the aid of the Gibbs–Duhem relations for the two homogeneous phases:

$$dp - s^\alpha dT - \sum c_i^\alpha d\mu_i = 0,$$

$$dp - s^\beta dT - \sum c_i^\beta d\mu_i = 0, \qquad [A3]$$

where s is the entropy per unit volume and c_i is the concentration of component i in the specified phase.

We then find for the appropriate form of the adsorption equation at constant pressure and temperature

$$d\gamma = -\sum_{i=3}^{k} \Gamma_{i(1,2)} d\mu_i, \qquad [A4]$$

where

$$\Gamma_{i(1,2)} = \Gamma_i - \Gamma_1 \left(\frac{c_i^\alpha c_2^\beta - c_i^\beta c_2^\alpha}{c_1^\alpha c_2^\beta - c_1^\beta c_2^\alpha} \right)$$
$$- \Gamma_2 \left(\frac{c_i^\beta c_1^\alpha - c_i^\alpha c_1^\beta}{c_1^\alpha c_2^\beta - c_1^\beta c_2^\alpha} \right). \qquad [A5]$$

We may also derive an analytical expression for the excess quantity $\Gamma_{i(1,2)}$ to show that it is (as it should be) independent of the particular location of the dividing surface. Following the Gibbs prescription for surface excess quantities (n^s) we write the materials balance expressions

$$n_1 = n_1^s + c_1^\alpha V^\alpha + c_1^\beta V^\beta$$

$$n_2 = n_2^s + c_2^\alpha V^\alpha + c_2^\beta V^\beta$$

$$n_i = n_i^s + c_i^\alpha V^\alpha + c_i^\beta V^\beta, \qquad [A6]$$

where the total volume V of the system is divided into two parts V^α and V^β by the arbitrarily placed dividing surface and Eq. [A2] is implied.

On solving for n_i^s ($=A\Gamma_i$) with the aid of Eq. [A6] we find the desired analytical expression for $\Gamma_{i(1,2)}$,

$$\Gamma_{i(1,2)} = \frac{1}{A} \left[n_i - \frac{c_i^\alpha c_2^\beta n_1 - c_i^\alpha c_1^\beta n_2}{c_1^\alpha c_2^\beta - c_2^\alpha c_1^\beta} \right.$$
$$\left. - \frac{c_i^\beta c_1^\alpha n_2 - c_i^\beta c_2^\alpha n_1}{c_1^\alpha c_2^\beta - c_2^\alpha c_1^\beta} \right]. \qquad [A7]$$

If we elect the Gibbs convention for locating the dividing surface, that is, $\Gamma_1^{(1)} = 0$, then it follows from [A5] that

$$\Gamma_{i(1,2)} = \Gamma_i^{(1)} - \Gamma_2^{(1)} \left(\frac{c_i^\beta c_1^\alpha - c_i^\alpha c_1^\beta}{c_1^\alpha c_2^\beta - c_1^\beta c_2^\alpha} \right) \qquad [A8]$$

and from Eq. [A4] we derive that

$$\left(\frac{\partial \gamma}{\partial \mu_i} \right)_{T, p, \text{ all } \mu\text{'s except } \mu_1, \mu_2, \text{ and } \mu_i} = -\Gamma_{i(1,2)}$$

$$= -\left[\Gamma_i^{(1)} - \Gamma_2^{(1)} \left(\frac{c_i^\beta c_1^\alpha - c_i^\alpha c_1^\beta}{c_1^\alpha c_2^\beta - c_1^\beta c_2^\alpha} \right) \right]$$

$$= -\left[\Gamma_i^{(1)} + \frac{c_i^\beta c_1^\alpha - c_i^\alpha c_1^\beta}{c_1^\alpha - c_1^\beta} \left(\frac{\partial \gamma}{\partial p} \right)_{T, \text{ all } \mu\text{'s except } \mu_1, \mu_2} \right].$$
$$[A9]$$

The physical significance of the adsorption quantity $\Gamma_{i(1,2)}$ may now be made clear. We consider the distribution of the components of the two-phase system among the volumes V_{I}^α, V_{II}^β, and V_{III}^A that in combination equal the total volume of the system including the interfacial region separating the bulk phases α and β. Let volumes V_{I}^α and V_{II}^β have the same composition as the homogeneous phases α and β respectively and in addition also contain the total amounts of components 1 and 2. Volume V_{III}^A then contains the excess amounts (positive

or negative) of the other components. For the amount n_i^A of component i in this "surface layer" we then derive the expression

$$n_i^A = n_i - c_i^\alpha V_I^\alpha - c_i^\beta V_{II}^\beta$$

$$= n_i - \frac{c_i^\alpha (c_2^\beta n_1 - c_1^\beta n_2)}{c_1^\alpha c_2^\beta - c_2^\alpha c_1^\beta} - \frac{c_i^\beta (c_1^\alpha n_2 - c_2^\alpha n_1)}{c_1^\alpha c_2^\beta - c_2^\alpha c_1^\beta}.$$

$$[A10]$$

We may now combine these three volumes to create our system. Volume V_{III}^A may be mixed with parts of volumes V_I^α and V_{II}^β to constitute the transition region inside which the interface will be located, provided that this mixing process does not entail a change in the total volume V of the system.

A comparison of Eqs. [A7] and [A10] shows that $\Gamma_{i(1,2)}$, which is derived experimentally from the partial derivative $\partial\gamma/\partial\mu_i$ (see Eq. [A9]), is exactly equal to n_i^A/A. This excess quantity is seen to be determined partly by the Gibbs excess density $\Gamma_i^{(1)}$ and partly by that amount of i already present in the neighborhood of the interface before adsorption and that remains there after the adsorption of i has expelled other components from this region.

For our two-phase, four-component system; oil (o), water (w), surfactant (sa), and cosurfactant (co), water is only slightly soluble and surfactant is practically insoluble in the oil phase (O) and oil may be assumed insoluble in the water phase (W). If we let water be component 1, oil component 2, cosurfactant component 3, and surfactant component 4 then according to Eq. [A9]

$$\left(\frac{\partial\gamma}{\partial\mu_{co}}\right)_{T,p,\mu_{sa}}$$

$$= -\left[\Gamma_{co}^{(w)} + \Gamma_o^{(w)}\left(\frac{c_{w,O} \cdot c_{co,W}}{c_{w,W} \cdot c_{o,O}} - \frac{c_{co,O}}{c_{o,O}}\right)\right] \quad [A11]$$

$$\left(\frac{\partial\gamma}{\partial\mu_{sa}}\right)_{T,p,\mu_{co}} = -\Gamma_{sa}^{(w)} - \Gamma_o^{(w)}\left(\frac{c_{sa,W} \cdot c_{w,O}}{c_{w,W} \cdot c_{o,O}}\right). \quad [A12]$$

As both surfactant and cosurfactant are known to accumulate strongly in the interface one would expect oil and water to be expelled

from it (negative adsorption), thereby leaving a layer that will contain essentially surfactant and cosurfactant.

In our experiments the ratio, $(c_{w,O} \cdot c_{co,W})/c_{w,W}$, is approximately equal to 10^{-5} and much smaller than $c_{co,O}$. It therefore follows that

$$\Gamma_{co(w,o)} \approx \Gamma_{co}^{(w)} - \frac{c_{co,O}}{c_{o,O}}\Gamma_o^{(w)}.$$

This approximation again illustrates that the excess adsorption $\Gamma_{co(w,o)}$ is not equal to the Gibbs adsorption density $\Gamma_{co}^{(w)}$ but approaches the latter in magnitude at low cosurfactant concentrations in the oil phase. According to Eq. [A12] and the experimental conditions, the Gibbs adsorption density $\Gamma_{sa}^{(w)}$ is a reasonable approximation for the excess adsorption $\Gamma_{sa(o,w)}$.

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