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Structural Changes Induced By Addition Of A Hydrocarbon To Water/amphiphile Mixtures

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Structural changes induced by addition of a hydrocarbon to water/amphiphile mixtures

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Abstract: The phase conditions in a system of water, hexadecane, sodium dodecyl sulphate, and di-ethylene glycol dodecyl ether showed the *W/O* microemulsions to be obtained first after destabilization of a liquid crystalline phase by addition of the hexadecane. The original lamellar liquid crystalline phase was moved towards higher surfactant/cosurfactant ratios and a new phase with inverse amphiphile cylinders in a hexagonal packing appeared.

Key words: Microemulsions, liquid crystals, micellar solutions, hydrocarbon solubilization.

Introduction

The microemulsion phenomenon has been the center of an intensive research effort in the last ten years due to the interest in tertiary oil recovery [1, 2]. The discussion about the structure and the stability of the microemulsions has been intense, with initial suggestions of the stability depending on the interfacial properties only [3–5]. This hypothesis was fairly early shown to be insufficient [6]; later, more complete treatments [7, 8] showed the importance for stability of the different terms in the total free energy.

Paralleling these efforts, Gillberg [9], Shinoda [10], and Ahmad [11] showed *W/O* microemulsions to be direcly obtained from the cosurfactant inverse micellar solution [12] by the addition of hydrocarbon. In fact, the solubility region of water, when calculated as a fraction of the non-hydrocarbon constituents only, remained constant at hydrocarbon contents less than fifty percent by weight [13].

An exception to this rule was found in the microemulsion systems with a nonionic surfactant as cosurfactant which were introduced by Sagitani [14]. These cosurfactants did not form the typical inverse micellar solution with a water solubilization maximum versus the surfactant fraction. Instead, the *W/O* microemulsions were formed first when the hydrocarbon was added to the system.

These kinds of microemulsions may find use in technical applications for which the biological aggressivity of the normal cosurfactants such as pentanol are prohibitive. With this in mind, we found a more complete investigation into the phase conditions of a system with combined anionic/nonionic surfactants to be of value. The nonionic surfactant was chosen as the di-ethylene glycol dodecyl ether since earlier investigations [14] demonstrated the oxyethylene chain length to be critical in order to obtain the *W/O* microemulsions.

Experimental

Materials

The sodium dodecyl sulphate (BDH Chemicals, Ltd., specially pure) was recrystallized twice from ethanol. Di-ethylene glycol dodecyl ether (Nikkon Chemical Company) was > 98% pure according to gas chromatography, the hexadecane was Aldrich spectrometrically pure, and the water was twice distilled.

Phase diagrams

The solubility regions were determined by visual inspection of samples in glass vials thermostated at 30 ± 0.1 °C. The presence of liquid crystals in the samples was detected using crossed polarizers and confirmed by observations and polarized light in an optical microscope.

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X-ray diffraction

The X-ray diffractograms were recorded by means of low angle equipment (Siemens Crystalloflex 4) equipped with a Tennelec PSD-100 detector. The signal was separated using a multichannel analyzer (Packard, Model 901).

Light scattering

The light scattering measurements were made on a Sofica Photo Gonio Diffusometer, Model 42,000, at 30 °C at a wave length of 546 nm. The cells were cleaned in a concentrated chromosulphuric acid for 15 hours, followed by several rinses with distilled water.

The solvents, benzene and water, were both filtered through Millipore filters at 0.22 μm to remove dust prior to preparation of samples. In addition, the solutions were centrifuged for 3 hours at 35,000 g before the measurements.

The light scattering intensity scale was chosen with benzene giving 100 units.

Results

Phase regions

The phase diagrams for the systems water, sodium dodecyl sulphate, di-ethylene glycol dodecyl ether, and hexadecane are presented by figures 1 and 2. Figure 1 shows the system with no hydrocarbon;

figure 2 reveals the changes caused by the partial substitution of the amphiphiles by the hydrocarbon.

The normal micellar region L_1, in figure 1 at increased surfactant concentration is continued by a liquid crystalline phase, H, with a structure of hexagonally arranged cylinders. An increased fraction of the nonionic surfactant gave a huge area of a lamellar liquid crystal, N. The extremely high water solubilization capacity in the lamellar liquid at high nonionic/ionic surfactant ratios is remarkable. Higher weight fractions of the nonionic, 0.93 − 0.97, resulted in the formation of an optically isotropic liquid crystal, O. Finally, the liquid nonionic emulsifier dissolved 25% water and only small amounts of the ionic surfactant. The addition of water/ionic surfactant molecular ratio of 7 enhanced the solubility of the ionic surfactant to 25% by weight. The unmarked area to the right in the figure was not characterized due to the difficulty with solid/liquid and solid/liquid crystal equilibria.

The partial substitution of the amphiphiles by the hydrocarbon led to a phase diagram according to figure 2. The micellar solution, L_1, and the liquid crystal, H, with no nonionic surfactant present could not solubilize the hydrocarbon to a hydrocarbon/ionic surfactant ratio of 0.25. A minimum nonionic/
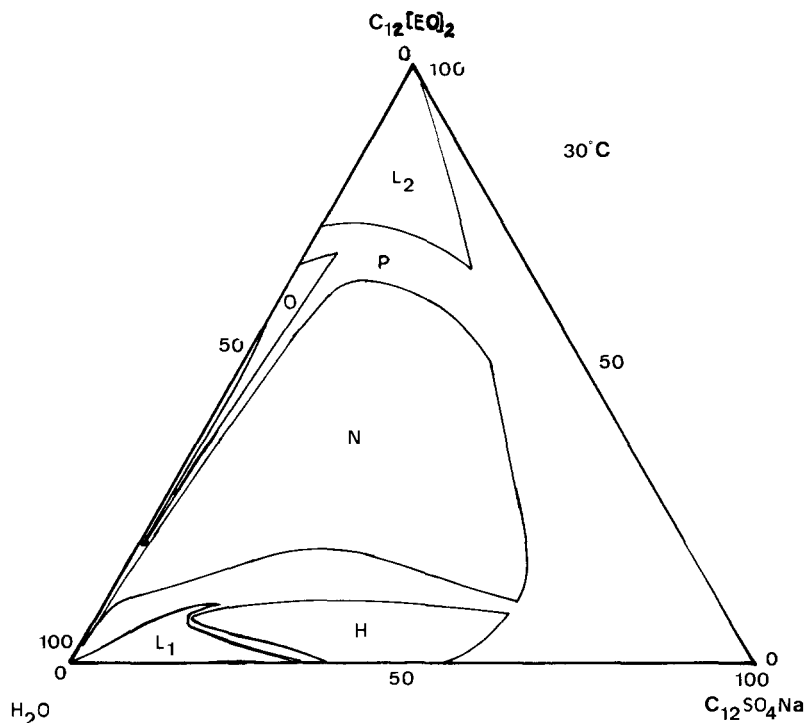

Fig. 1. Phases in the system water (H₂O), sodium dodecyl sulphate (C₁₂SO₄Na), and di-ethylene glycol dodecyl ether (C₁₂(EO)₂). L_1 = normal micellar solution, L_2 = inverse micellar solution, H = liquid crystal with hexagonal array of cylinders, N = liquid crystal with lamellar structure, O = liquid crystal with isotropic structure. Point P s. text
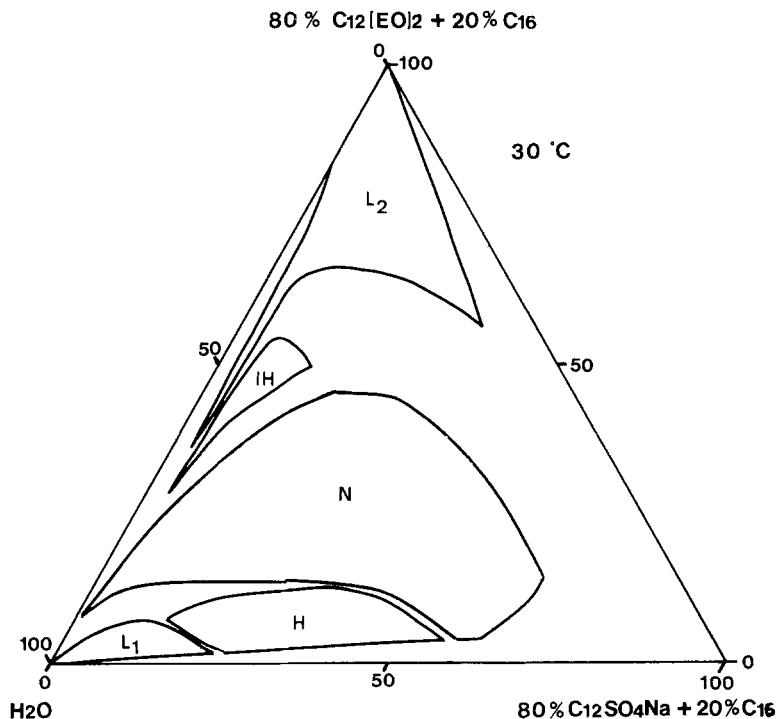
Fig. 2. Phases in the system water (H₂O), sodium dodecyl sulphate/hexadecane 4/1 mixture (80% $C_{12}SO_4Na$ + 20% C_{12}) and diethylene glycol dodecyl ether/hexadecane 4/1 mixture (80% $C_{12}(EO)_2$ + 20% C_{16}). L_1 = normal micellar solution, L_2 = inverse micellar solution, H = liquid crystal with hexagonal array of cylinders, N = liquid crystal with lamellar structure, IH = liquid crystal with hexagonal array of "inverse" cylinders

ionic surfactant weight ratio of 0.08 was necessary for the solubilization. This limit is marked by a straight line in figure 2. The upper limit of the nonionic surfactant fraction for these two phases was not changed to a significant degree. The lamellar phase, N, on the other hand, was stabilized at a slightly lower nonionic fraction and its upper limit was found to be at a considerably lower nonionic fraction. Without hydrocarbon, figure 1, the nonionic/ionic surfactant weight ratio for maximum solubility of the nonionic surfactant (point P, fig. 1) was 1.8. With hydrocarbon present (fig. 2) the corresponding weight ratio was 0.8, less than half the value. A new liquid crystal with a hexagonal organization of inverse cylinders, IH, was obtained at higher nonionic/ionic surfactant ratios. The liquid nonionic surfactant solution, L_2, of the water and the ionic surfactant showed an identical area to the system without hydrocarbon (fig. 1), but now in addition (fig. 2) extended in a narrow water solubilization maximum with a nonionic/anionic surfactant fraction of 0.93–0.96. This result was sufficiently interesting to merit a light scattering determination.

Light scattering

The light scattering (fig. 3) from the L_2 region gave a low intensity within the area found in the part of the area that was identical to the one with no hydrocarbon. The compositions within the narrow region with high water solubilization showed a pronounced increase of the scattering intensity.

Low angle X-ray diffraction

The low angle X-ray diffraction results showed excellent compatibility between the two surfactants in the lamellar liquid crystal for the system without hydrocarbon, figure 4. The interlayer spacing extrapolated to zero water content, 29 Å, was similar for all nonionic/ionic surfactant ratios. An increase of the nonionic surfactant fraction caused a more pronounced increase of the interlayer spacing with added water.

With 20% hexadecane present, figure 5, the value extrapolated to zero water content was 39 Å and the
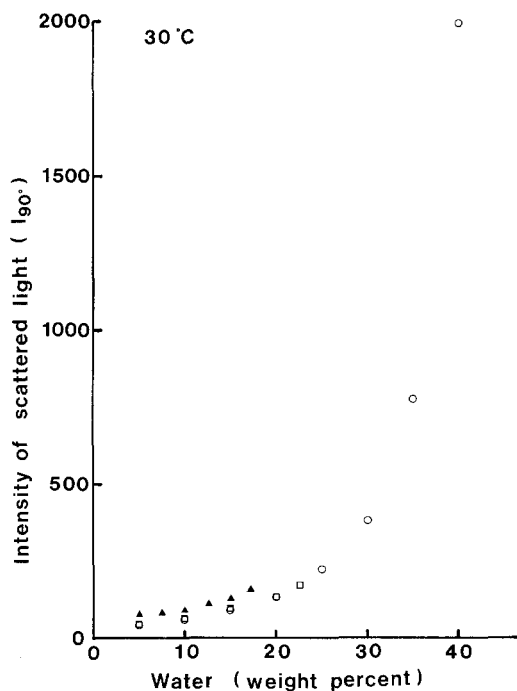
Fig. 3. Light scattering from L_2, figure 1 ($\blacktriangle$, $\square$), and figure 2 ($\bigcirc$). $C_{12}(EO)_2/C_{12}SO_4Na$ (weight ratio). $\square$ — 95/5, $\blacktriangle$ — 90/10, $\bigcirc$ — along the narrow solubility region
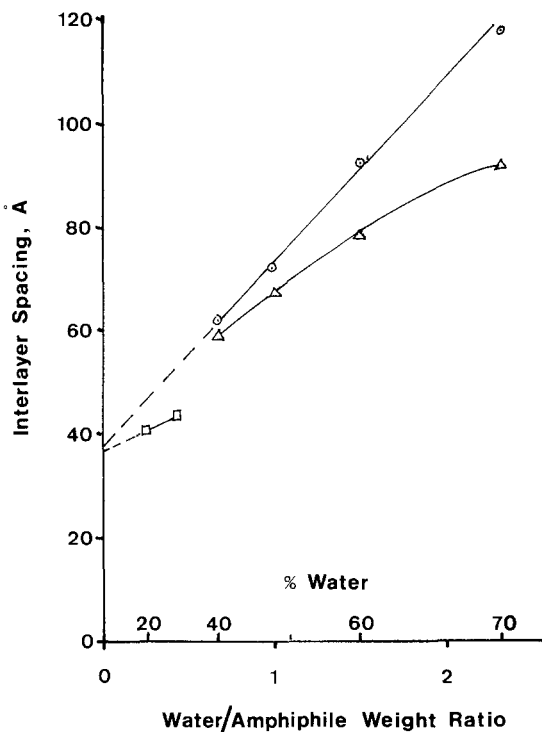

Fig. 5. Interlayer spacing in phase N, figure 2.

	$C_{12}SO_4Na$:	$C_{12}(EO)_2$	(weight ratio)
$\odot$ 1	0.3	0.7	
$\triangle$ 2	0.5	0.5	
$\square$ 3	0.7	0.3	

reduction in the shape, $\partial d/\partial(m_W/m_A)$, was pronounced with increased fraction of ionic surfactant.

Discussion

The results showed decisive changes brought forward by the addition of hydrocarbon, implying considerable structural reorganizations. A comparison with Ekwall's extensive contributions on corresponding systems with an ionic surfactant only [12] is interesting. Ekwall investigated the consequences of the addition of hydrocarbon to association structures fromed by ionic surfactants only in aqueous solution. For such systems a limited solubilization was found, and there was no change of the association structure; excess hydrocarbon in equilibrium was present in pure form.

As a contrast, in water/nonionic surfactant systems [15–19] the presence of hydrocarbon has the most pronounced influence on the association structures. The present results display the changes caused by the presence of the nonionic surfactant in nonionic/anionic surfactant mixtures, and it is interesting to
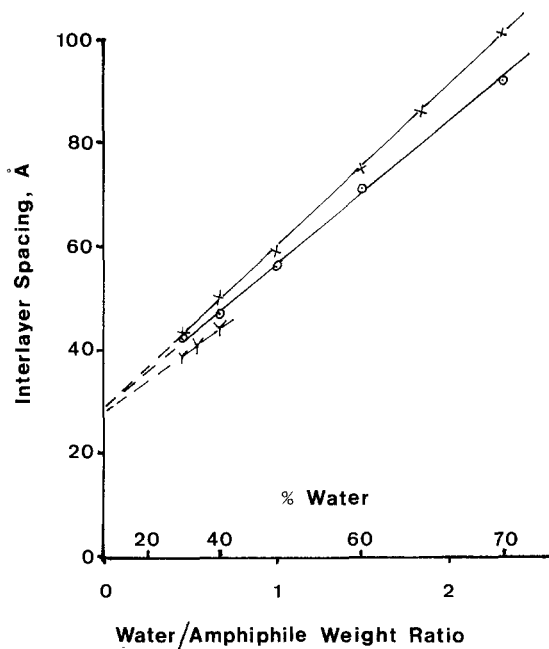

Fig. 4. Interlayer spacing in phase N, figure 1.

	$C_{12}SO_4Na$:	$C_{12}(EO)_2$	(weight ratio)
$\times$ 1	15	85	
$\odot$ 2	30	70	
Y 3	66.5	33.5	

observe the consequence of the structure conversions to be limited to high nonionic/anionic ratios. As an illustration should be noticed the structural changes invoked by the addition of hydrocarbon to the liquid crystalline phases with lamellar (*N*, fig. 1) and hexagonal (*H*, fig. 1) structure. The latter phase is characterized by a low nonionic/surfactant ratio and the presence of hydrocarbon gave no significant change of the maximum limit of the nonionic/anionic surfactant ratio. The amounts of nonionic surfactant are small, and the structural influence of the added hydrocarbon is insignificant, in accordance with Ekwall's results [12].

The lamellar phase, on the other hand, with its high content of nonionic surfactant, displayed drastic structural changes in the part with high nonionic/anionic ratio. There, a complete conversion was found in the formation of a liquid crystal with an inverse hexagonal structure. Furthermore, the isotropic liquid crystalline structure (*O*, fig. 1) was changed to an isotropic solution, joining the nonionic surfactant solution to form a *W/O* microemulsion area with a narrow nonionic/anionic surfactant fraction range.

This appearance of a pronounced water solubilization maximum to form *W/O* microemulsions first after addition of the hydrocarbon is a behavior at variance with the traditional systems with a medium chain length alcohol as a cosurfactant [13]. For such systems the water solubilization in the cosurfactant proper shows an identical solubilization maximum versus the cosurfactant/surfactant ratio to the one found in the microemulsions containing hydrocarbon. In fact, for such systems the addition of hydrocarbon changes but little the water solubilization counted as a fraction of water, surfactant, and cosurfactant; the hydrocarbon may be viewed as having a passive role of dilutant. In the present case, with a long chain nonionic/cosurfactant the hydrocarbon was a necessary component to break the ordered liquid crystalline structure to give the microemulsion area.

It is interesting to observe that the nonionic surfactant solution, L_2, in the system without hydrocarbon showed only a low intensity light scattering (fig. 3), indicating no colloidal association structures to be present [20–29]. The rise of the scattering intensity typical of such structures was found first in the narrow region of the strong water solubilization maximum in the presence of hydrocarbon (L_2, fig. 2).

The influence of the nonionic surfactant was reflected also in the dependence of the dimensions of the liquid crystals on the water and hydrocarbon content. Figure 4 and, to a higher degree, figure 5 directly illustrate a higher spacing dependence on the amount

of water with enhanced content of hydrocarbon. A comparison of the slopes reveals the fact that a higher nonionic surfactant ratio gave a higher increase of the interlayer spacing also with added hydrocarbon. The results point to a role of the nonionic surfactant as predominantly a hydrophobic part of the system, a role similar to the long chain alcohols in the systems earlier investigated [12].

This penomena of a polyethylene glycol dodecyl ether with a short oxyethylene chain behaving as a hydrophobic amphiphile has an interesting parallel in the results of the determinations of critical micellization concentrations (cmc) of ether sulphates by Schwuger and Lange [30]. They found the oxyethylene chain inserted between the alkyl chain and the sulphate group to cause a reduction of the cmc's of the surfactant e. g. act as a hydrophobic moiety. Our present and earlier [14] results indicate the polyethylene glycol alkyl ethers with short oxyethylene chain to function mainly as a hydrophobic cosurfactant, when combined with an ionic surfactant.

The difference in interlayer spacing (figs. 4 and 5) can also be used to evaluate the location of the hydrocarbon in the lamellar structure. Assuming the hydrocarbon to be localized between the layers, a direct calculation using volume ratios gives an increase of the interlayer spacing by 9.5 Å. The results show an increase of 10 Å for the extrapolated values to zero water content. For high nonionic/anionic ratios this trend was further enhanced with added water; low ratios gave the opposite.

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