

Some Observations on Phase Diagrams and Structure in Binary and Ternary Systems of Didodecyldimethylammonium Bromide

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An account is given of the phase diagrams and structure in both binary and ternary systems formed with didodecyldimethylammonium bromide, dodecane and water. They form L_2 -phase (microemulsion) and various mesophases very different from ternary amphiphilic systems usually studied. Observations include two lamellar liquid crystalline phases (which can coexist) with very different water contents, of a liquid crystalline hexagonal phase, a highly variable microemulsion structure, a cubic phase with compositions intermediate to those of the L_2 -phase and the water-rich lamellar phase, and a very stable emulsion. Since the double-chained quaternary ammonium salts are often insoluble in water and oil, they reside at the oil-water interface, and microstructure is therefore much more easily elucidated. This is particularly so if phase behaviour and physical properties adduced from NMR diffusion, conductance and viscosity are combined with recent direct force measurements between bilayers of surfactants adsorbed on mica. The present system, at one end of the spectrum of solution behaviour, forms a well defined entry point to more complicated systems which can be generated by successive perturbations induced by other components.

Cationic surfactants like dialkyldimethylammonium halides have important applications *inter alia* as antistatic fabric softeners, hair conditioners and disinfection agents. In spite of the widespread use of these components, little research on fundamental aspects of their self-association behaviour has been carried out. This contrasts with the situation for double chain anionic surfactants, such as Aerosol OT, where phase behaviour and microemulsions have been very extensively studied by many research groups.^{1–10}

Renewed interest in quaternary ammonium surfactants has been stimulated by the recent dis-

covery that compounds like and including didodecyldimethylammonium salts, and corresponding single chain salts, e.g., pyridinium or hexadecyltrimethylammonium surfactants are potent immunosuppressants.^{11,12} The latter are widely used in the pharmaceutical industry in cough mixtures and other preparations such as bacteriocides. The mechanism of immunosuppression is similar to, and probably identical to, that of cyclosporin A, used widely as a drug to control organ transplant rejection. They appear to be more effective immunosuppressants than cyclosporin. In such applications, which represent the beginning of a new field of immunotoxicology, and in drug delivery problems, the nature of aggregates formed is a central issue.

Beyond that, double-chained quaternary ammonium halides are insoluble in both water and

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Dedicated to Professor Per Ekwall on his 90th birthday

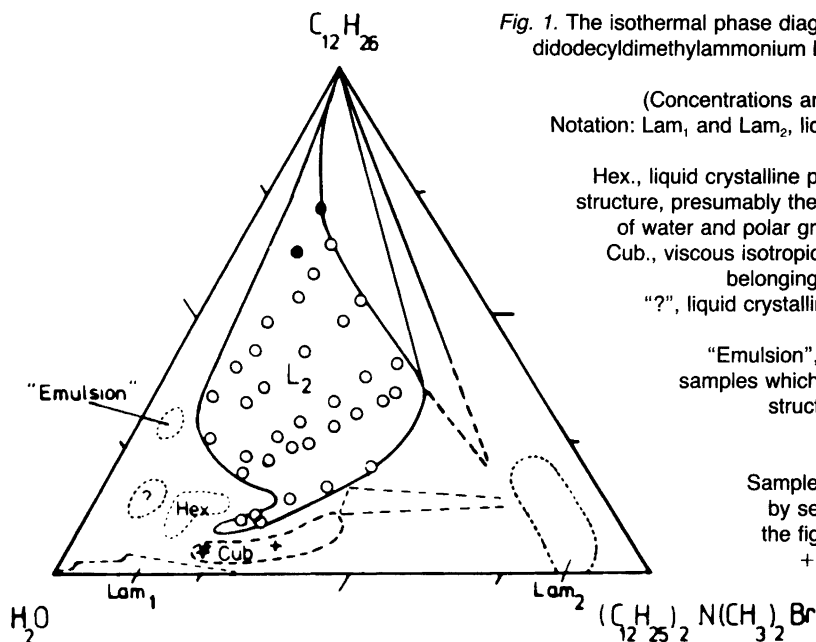


Fig. 1. The isothermal phase diagram for the ternary system didodecyldimethylammonium bromide/dodecane/water at 20°C.

(Concentrations are given in weight percent).

Notation: Lam₁ and Lam₂, liquid crystalline phases with lamellar bilayer structures.

Hex., liquid crystalline phase with a hexagonal rod structure, presumably the reversed variant with rods of water and polar groups in a hexagonal array.

Cub., viscous isotropic, cubic phase, presumably belonging to the space group Im3M.

"?", liquid crystalline phase, presumably with a lamellar structure.

"Emulsion", region with opaque, white samples which had a very coarse droplet structure under the microscope.

L₂, isotropic liquid phase, "microemulsion".

Sample compositions investigated by self-diffusion are indicated in the figure: O, ● in the L₂ region, + in the cubic phase region.

oil, and must therefore reside, in the main, at the oil-water interface in ternary systems. This circumstance coupled with the considerable flexibility in imposed curvature which can be controlled by a range of oils of different chain lengths, allow microstructures to be elucidated very much more easily for these systems than for surfactants like Aerosol OT, which partitions between oil and water in a complex manner.

Kunieda and Shinoda¹³ have investigated the phase equilibria in two-component systems of a number of dialkyldimethylammonium chlorides and water and also noted the appearance of extensive isotropic solution phases in ternary systems with decanol and cyclohexane. In recent years, Evans, Ninham *et al.*¹⁴⁻²⁵ have examined in detail several aspects of double-chained cationic surfactants. In particular, they have demonstrated the existence of a large isotropic solution phase rich in hydrocarbon in the ternary systems of didodecyldimethylammonium bromide/straight chain alkane/water. This phase (here denoted by L₂, v. Fig. 1) has the unusual property that the electrical conductivity decreases with increasing water concentration.^{15,19} This feature is accompanied by parallel behaviour in viscosity and hydrocarbon and water self-diffusion.¹⁴⁻¹⁹ These observations confirm the existence of a bi-continuous structure consisting of water-filled in-

terconnected conduits at low water content, while, when the water content is increased, the structure changes to a water-in-oil droplet system. Indeed, many features of the phase diagrams, and accompanying microstructure, can be inferred from straightforward geometric packing arguments. Other phases have not been examined in detail and our only comment is that, when the phase boundary is passed in the direction of the water corner, then "toward the water corner the system forms clear viscous gels which become solid with increasing water content".¹⁵ Further exploration of this area is clearly desirable. We present in this paper some preliminary observations on the equilibria which exist in the triangular isothermal phase diagram. In addition, we present some results of self-diffusion studies that complement those of Blum *et al.*¹⁷ The extent of the L₂-phase is rather similar (Fig. 2) for systems containing the straight chain alkanes C₆ to C₁₂ which give qualitatively similar behaviour.¹⁷ We have therefore restricted our study to a representative system containing dodecane. At high surfactant content with shorter chained oils like cyclohexane or 1-hexene, which penetrates strongly into the surfactant tail region, there may well emerge some rather different microstructures.

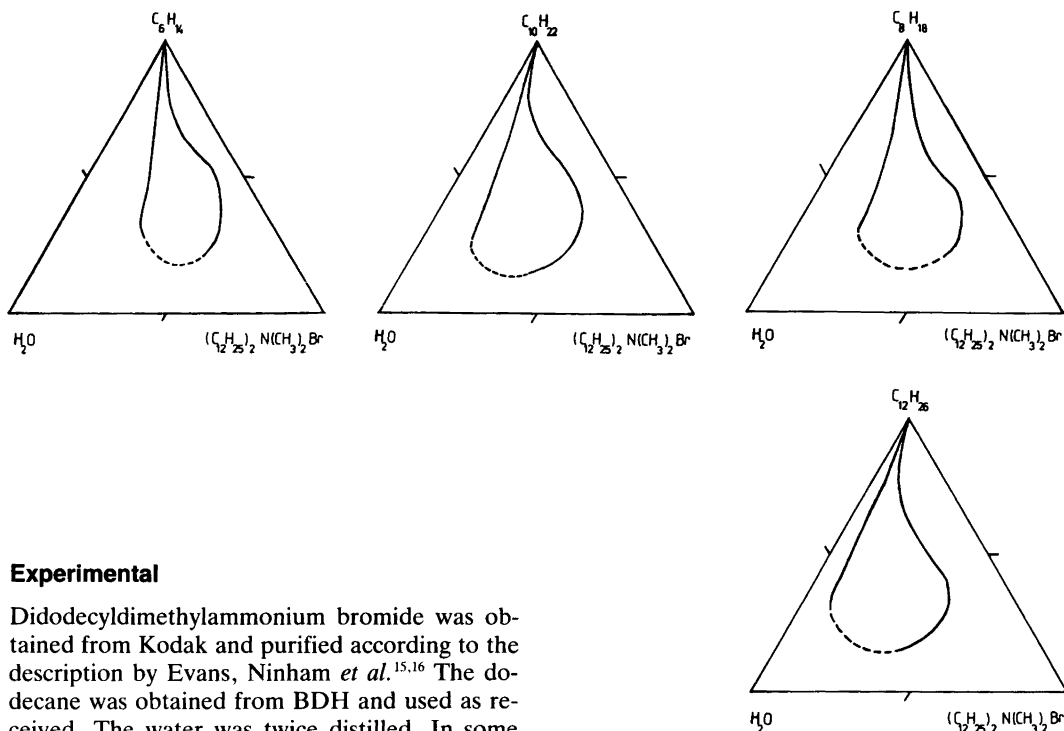


Fig. 2. The extent of the L_2 -regions in the ternary systems of didodecyltrimethylammonium bromide and water with the alkanes, hexane, octane, decane and dodecane, respectively. After Ref. 17.

Experimental

Didodecyltrimethylammonium bromide was obtained from Kodak and purified according to the description by Evans, Ninham *et al.*^{15,16} The dodecane was obtained from BDH and used as received. The water was twice distilled. In some samples, heavy water was used (Ciba-Geigy, 99.8%).

The samples were prepared by weight in glass ampoules, which were flame-sealed, heated to 100°C in order to obtain an equilibrium homogeneous system, and cooled slowly to room temperature. The samples were subsequently investigated macroscopically for birefringence between crossed polarizers; possible different phases were separated in a desk centrifuge and examined in a polarizing microscope. The structure inferred from the texture was checked by X-ray diffraction. ²H NMR spectra were recorded at a resonance frequency of 15.351 MHz with a modified Varian XL-100-15 pulsed spectrometer.

Self-diffusion coefficients of all the components of the microemulsions were obtained by the Fourier transform NMR pulsed gradient, spin echo, multicomponent, self-diffusion method which has been fully described elsewhere.²⁶⁻³⁰ A JEOL FX-60 FT NMR spectrometer operating in the ¹H mode at 60 MHz was employed and the field frequency lock was provided by internal D₂O. The temperature of the measurements was controlled to within ±0.5°C as determined by a precalibrated copper-constantan thermocouple.

The amplitude of the spin echo signal for each NMR line was fitted to the equation:

$$A_i = A_i^0 \exp[-\gamma^2 G^2 D_i \delta^2 (\Delta - \delta/3)] \quad (1)$$

using a nonlinear least squares routine. In this equation, A_i^0 is the value of A for $\delta = 0$, γ is the magnetogyric ratio of the proton, G is the strength of the applied field gradient, D_i is the self-diffusion coefficient of the i th species responsible for the NMR signal. The field gradient pulse duration, δ , was varied over the range 1–99 ms, and Δ , the time between the radio frequency pulses, was kept constant at 140 ms to minimize the J modulation effect according to a suggestion of Stilbs.^{26,29} The magnitude of G was determined

daily before and after every set of measurements by calibration experiments taking the self-diffusion coefficient of traces of HDO in D₂O at the experimental temperature from the literature.³¹ The error limits of *D*, determined as previously described,³² correspond to 80% confidence intervals, considering all deviations from eq. (1) as random errors. In almost all the cases, errors of less than 5% in the determined coefficients were found. Only in a few cases did larger errors exist but always less than 10%.

The evaluation of the diffusion coefficients from overlapping signals was accomplished by a procedure described before.³⁰ Due to short transverse relaxation times, it was not possible to measure the surfactant diffusion in all cases.

Phase equilibria

The binary system of didodecyldimethylammonium bromide and water at room temperature (20°C) is dominated by a lamellar liquid crystalline phase (Lam₁) extending from about 4 to 30 wt% of surfactant (Fig. 1). It is birefringent and has the typical mosaic texture of a lamellar liquid

crystalline structure, "coarse mosaic texture".³³ In the surfactant-rich part, this interpretation has been confirmed by X-ray diffraction which gives sharp diffraction peaks in the ratio 1:2 in the low-angle region besides the diffuse maximum in the wide angle region at 1/4.5 Å⁻¹. However, at lower surfactant content, the spacings are so large that it is not possible to record any values with our technique. The amphiphile bilayer thickness is about 23 Å and the cross-sectional area per hydrocarbon chain is about 34 Å². In the high surfactant part of the diagram, there is another lamellar phase (Lam₂) which is also birefringent with a "fine mosaic texture" in the polarizing microscope. The lamellar amphiphile thickness is about 26 Å and the cross-sectional area per hydrocarbon chain about 30 Å². The two lamellar phases are separated from each other by a wide two-phase zone. Fig. 3 a and b show water ²H NMR spectra of the two lamellar phases and these show the normal quadrupole splittings. The splitting is much larger for the water-poor phase than for the water-rich one because of a difference in the fraction of water molecules adjacent to the surfactant surfaces.^{34,35} In the two-phase re-

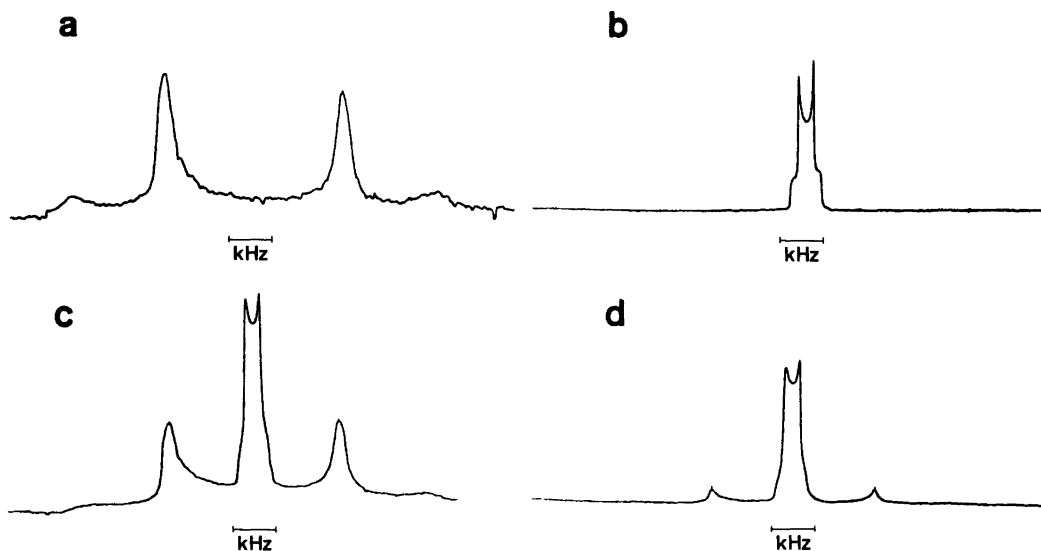


Fig. 3. ²H NMR spectra of four binary didodecyldimethylammonium bromide/water samples showing the quadrupole splittings.

a and **b**, one-phase samples with the compositions 89.9/10.1 and 30/70 respectively. **c** and **d**, two-phase samples with the compositions 69.95/30.05 and 49.91/50.09 respectively, showing the superposition of the two spectra from the phases Lam₁ and Lam₂.

gion, we observe superimposed spectra of the two phases and the two doublets give direct evidence of the coexistence of two lamellar phases (Fig. 3 c,d). For samples in the two-phase region, the splittings are constant, while the relative intensities change with the total sample composition.

The existence of two lamellar phases has previously been observed in some systems with divalent counterions where it can be understood in terms of attractive double layer forces³⁶ as also predicted by Monte Carlo simulations³⁷ and HNC calculations.³⁸ At low water contents, image charge forces are responsible for the swelling of the lamellar phase while for water-rich lamellar phases, the electrostatic repulsion between charged surfaces determines the swelling.³⁶ The present study seems to give the first observation of the coexistence of two lamellar phases, and thus also of attractive double layer forces, for a system with monovalent counterions and indicates particular bonding properties and locations of the bromide ions. At more than 96 wt % of water, the samples obtain a bluish tint which has an optical intensity maximum at about 98 wt % of water; simultaneously, the samples lose their birefringence.

It was not possible to find a clear two-phase zone between the liquid crystalline phase and the isotropic aqueous solutions. The saturation composition of the latter must be very low. Many of our observations for the water-rich part of the phase diagram parallel those of Ref. 13 for the dialkyldimethylammonium chlorides. Observations via video-enhanced differential interference microscopy³⁹ show that, as surfactant content decreases, large liposomes disperse into vesicle-type structures, polydisperse typically two or three closed layers which may also contain small micelles. At very low concentrations, the natural state of the system is probably a large, ~ 1000 Å, single layer vesicle, as it is for hydroxides, acetates and other strongly hydrated counterions which give soluble solutions up to 1 M – because of the enormous repulsive forces operating in these systems.²⁴

Density measurements in the water-rich lamellar liquid crystalline phase gave the value 1.0365 ml/g (at 20 °C) for the partial specific volume of the surfactant, while the corresponding value for water is close to 1.0018 ml/g (CRC Handbook of Chemistry and Physics, R.C. West, ed., 1982–

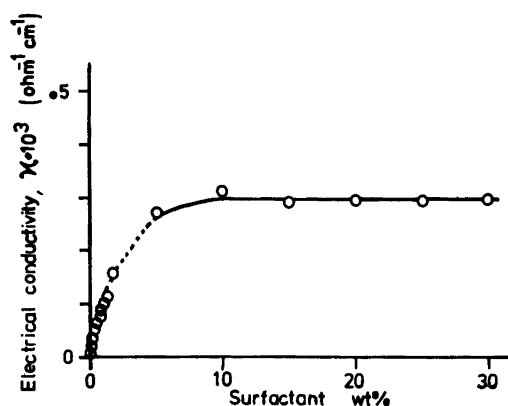


Fig. 4a. The electrical conductivity in binary didodecyldimethylammonium bromide/water samples for the region 0–30 wt % of surfactant.

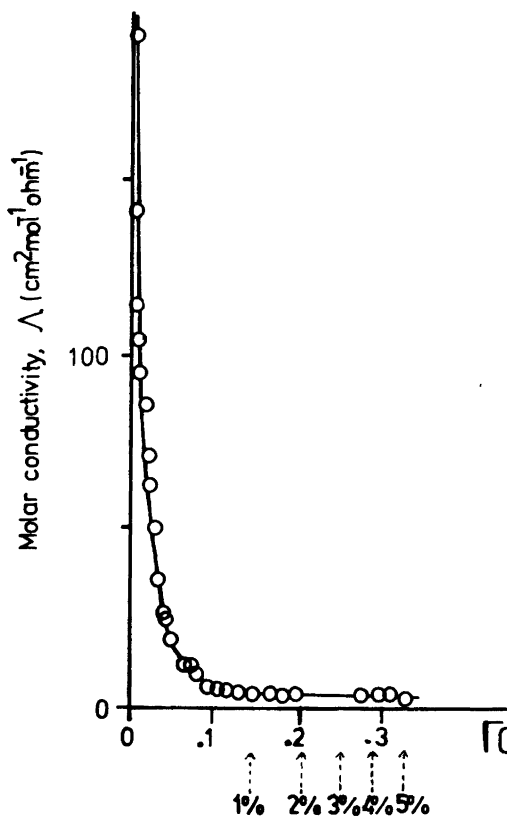


Fig. 4b. The equivalent conductivity versus the square root of the molar concentration in the concentration region 0–5 wt % of surfactant.

1983). In this phase, the electrical conductivity was rather low with constant κ -values of about $0.3 \cdot 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ (unoriented samples). Below about 4% of surfactant, the values decreased continuously to extremely low values (Fig. 4a). The equivalent conductivity increased smoothly with increasing water content without indication of any break due to the crossing of a phase boundary (Fig. 4b). The equivalent conductivity values were very high ($>200 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and the curve showed no maximum of the type postulated (and sometimes found) by Ralston et al.⁴⁰ in studies of the electrical conductivity in aqueous dialkyldimethylammonium chloride systems.

In the ternary system, one notices the existence of several different liquid crystalline phases in that region which was denoted "clear gel" by Ninham et al.¹⁵ The binary phase, Lam_1 , had the capability of incorporating up to 8 wt% of dodecane without losing its structure (Fig. 1). There was also a phase, (marked Cub), which contained between 21 to 54 wt% of surfactant, 2 to 11 wt% of dodecane and 46 to 75 wt% of water. This phase was optically isotropic; the consistency was rather stiff, although less rigid than for the cubic phases encountered in common soap/water systems. It was not possible to obtain satisfactory X-ray diffractograms for this phase. However, the pattern of the corresponding phase in the system containing hexane could be indexed based upon 5 reflections as a primitive cubic structure with a unit cell parameter of about 93 \AA . (D. Anderson, University of Minnesota, private communication, considers the structure of the dodecane-containing phase to belong to the body-centered space group $\text{Im}3\text{m}$). The self-diffusion of both water and dodecane in this phase of the system is rather high, $D = 5\text{--}9$ and $1.5\text{--}2.25 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively, indicating a continuous structure both with respect to oil (lipid) and water.

Another phase, Hex in Fig. 1, occurred between 14 and 18 wt% of surfactant, 6 to 15 wt% of dodecane and 64 to 79 wt% of water. This phase was birefringent and showed a texture characteristic of a hexagonal structure in the polarizing microscope. The structure was confirmed by X-ray studies; the two-dimensional unit cell parameter is about 146 \AA . The structure is obviously of the reversed type with rods of water and the polar groups in a hexagonal arrangement in a

hydrocarbon matrix. Further towards the water corner, there is another birefringent phase, ? in Fig. 1, where texture under the microscope indicated a lamellar structure. The X-ray diffraction peaks were at such low scattering angles that it was not possible to confirm this conclusion. There were indications that this phase was separated from the lamellar liquid crystalline phase Lam_1 by a two-phase zone. Similarly, the hexagonal and cubic phases were separated from the lamellar phase by two-phase zones. There was also a three-phase triangle $\text{L}_2\text{--Hex--Cub}$. The lamellar phase in the high surfactant part of the phase diagram also had the capability of taking up dodecane without losing its structure. The borders of this phase were not located with any accuracy and the location of the corners situated in this phase of the three-phase triangles, dodecane- $\text{L}_2\text{--Lam}_2$ and Cub- $\text{L}_2\text{--Lam}_2$, respectively, not exactly known (v. Fig. 1).

An additional feature of the phase diagram is the spontaneous formation of white, rather stiff and opaque samples in a region around 5 wt% of surfactant, 30 wt% of dodecane and 65 wt% of water. Under the microscope, the samples looked like a coarse dispersion. It was not possible to break this dispersion. The existence of such an "emulsion" adds further support for the emerging consensus that the older distinction between emulsions and microemulsions, the one metastable, the other thermodynamically stable, is not subtle enough.

The extension of the hydrocarbon-rich solution phase L_2 agrees in general with that reported by Blum et al.¹⁷ The borders towards the water corner were ill-defined as these authors have reported. A peculiar feature is the finger that extended between the hexagonal and cubic phases (Fig. 1).

Self-diffusion in the microemulsion (L_2) phase

In order to characterize the microscopic structure of the L_2 phase, we performed multicomponent self-diffusion studies. Sample compositions investigated are indicated in Fig. 1 and self-diffusion coefficients are reported in Table 1. The self-diffusion behaviour of the different components can be summarized as follows.

Table 1. Self-diffusion coefficients in the L_2 -phase of the system didodecyldimethylammonium bromide-dodecane-water at 26 °C (the samples were made up with D_2O containing traces of H_2O ; the compositions are recalculated on molar basis)

Molar ratio surfactant surfactant + oil	Composition (% wt.)			$D_w(10^{-10} \text{ m}^2 \text{ s}^{-1})$	$D_{oil}(10^{-10} \text{ m}^2 \text{ s}^{-1})$	$D_{surf}(10^{-10} \text{ m}^2 \text{ s}^{-1})$
	DDAB	n-dodecane water				
0.047	10.0	75.0	15.0	0.52±0.02	6.90±0.06	
0.054	9.8	63.6	26.6	0.07±0.01	6.43±0.16	
0.085	16.0	67.0	17.0	2.50±0.03	5.81±0.04	
	15.0	60.0	25.0	0.54±0.02	6.20±0.09	
	15.8	55.0	29.2	0.34±0.02	5.79±0.06	
	12.0	51.0	37.0	0.05±0.01	5.49±0.07	
	12.7	44.3	43.0	0.05±0.01	5.52±0.06	
	10.7	43.0	46.3	0.05±0.01	5.65±0.03	
	10.0	35.0	55.0	0.06±0.01	4.99±0.09	
0.156	26.1	54.3	19.6	3.63±0.06	4.69±0.02	0.31±0.03
	25.0	49.9	25.1	3.11±0.04	4.84±0.03	0.47±0.05
	21.0	44.0	35.0	1.01±0.04	5.25±0.04	
	18.0	37.0	45.0	0.18±0.01	5.02±0.03	
	16.0	34.0	50.0	0.10±0.02	5.12±0.05	
	13.0	27.0	60.0	0.02±0.01	4.38±0.06	
	0.250	37.9	42.0	20.1	3.65±0.06	3.73±0.04
34.2		39.1	26.7	3.51±0.06	3.96±0.04	0.36*
30.3		34.7	35.0	2.70±0.07	3.99±0.03	0.28*
26.9		30.7	42.3	2.04±0.08	4.58±0.09	0.36±0.03
24.9		27.3	47.8	1.21±0.08	4.13±0.09	
21.0		24.0	55.0	0.31±0.02	4.01±0.14	
0.306		40.1	35.1	24.8	3.95±0.09	3.78±0.03
	38.6	33.8	27.6	3.56±0.07	3.72±0.02	
	35.7	31.2	33.1	3.46±0.04	3.80±0.03	0.78±0.10
	32.7	28.6	38.7	3.16±0.03	3.85±0.07	
	30.2	25.7	44.1	2.89±0.11	3.71±0.02	
	28.4	24.2	47.4	1.13±0.07	3.70±0.01	
	25.2	22.4	52.4	1.09±0.01	3.61±0.02	
	22.9	19.5	57.6	0.33±0.01	3.72±0.05	
	0.468	44.9	20.2	34.9	4.32±0.10	2.72±0.06
38.0		17.0	45.0	3.63±0.13	2.30±0.07	0.73±0.07
32.9		14.6	52.5	4.02±0.03	2.58±0.02	
30.0		10.0	60.0	5.86±0.13	2.32±0.03	
27.9		12.0	60.1	5.75±0.13	2.54±0.16	
25.9		11.0	63.1	4.97±0.11	2.30±0.12	

*Graphically determined.

Diffusion of the oil. The values of the diffusion coefficient of n-dodecane are in the range $2.3\text{--}6.9 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for all L_2 -samples. This means that the diffusion of oil is rather invariant even for large changes in microemulsion composition. The diffusion of pure n-dodecane was calculated from Ref. 41 to be $8.8 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ at 26 °C.

Diffusion of the surfactant. Only in some samples, was it possible to measure the self-diffusion coefficient of the didodecyldimethylammonium ions. The D value was in the range between 0.25 and $0.78 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, thus an order of magnitude below that of the hydrocarbon.

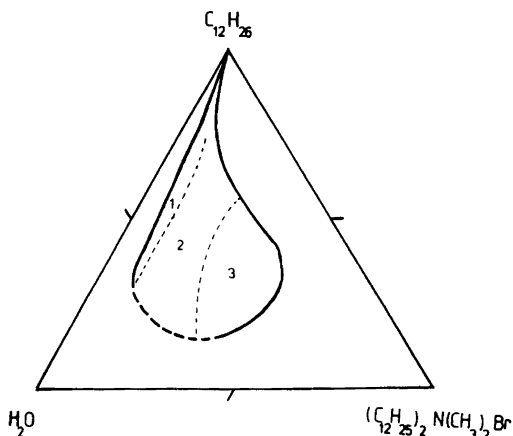


Fig. 5. Division of the L_2 region into 3 subareas on the basis of the values for the water self-diffusion coefficient.

Region 1, 2 and 3, D_w values of about $5 \cdot 10^{-12}$, $5 \cdot 10^{-11}$ and $1-4 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively.

Diffusion of water. The L_2 -region can be divided into 3 areas on the basis of the magnitude of their water self-diffusion coefficients. For region 1, the D_w values are about $5 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$, in region 2, about $5 \cdot 10^{-11} \text{ m}^2 \text{ s}^{-1}$ and region 3, in the range $1-4 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Fig. 5).

Molecular self-diffusion coefficients for motion over long distances can be interpreted in terms of microemulsion structure, since they are very sensitive to confinement into closed domains.^{42,43} On the other hand, the D values of molecules of a continuous medium are relatively less dependent on the shape of obstructing particles.⁴⁴ The principles of the self-diffusion approach and microemulsion structure have recently been reviewed in some detail.²⁷ Besides Fig. 5, the discussion is preferably based on plots of D versus water content for different ratios between surfactant and hydrocarbons (v. Fig. 6).

First of all, we note that D_{hc} is high throughout, so that over the entire range, the microemulsion phase is oil-continuous. D_w is highly concentration-dependent and we have regions which are

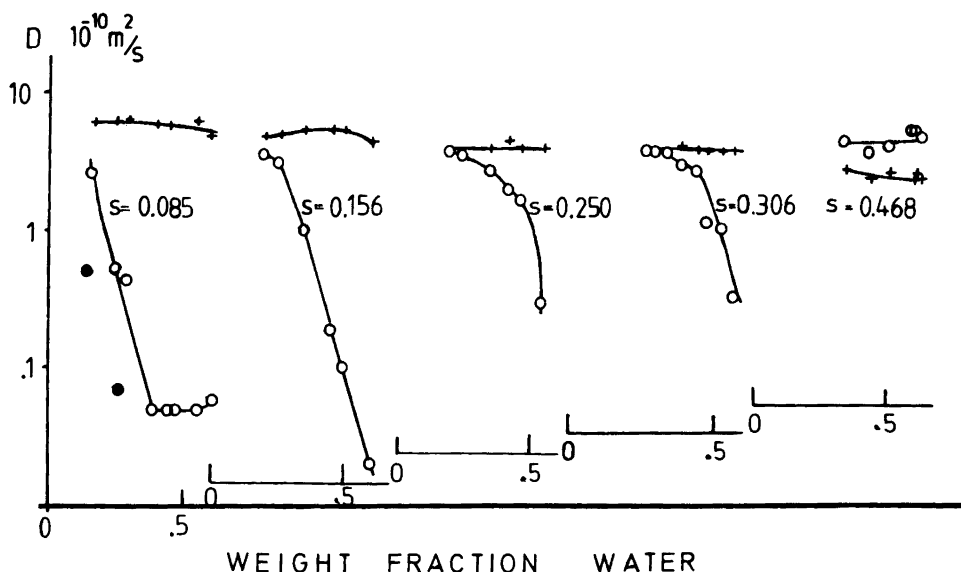


Fig. 6. Plot of water and oil self-diffusion coefficients, respectively versus water content for 5 series with almost constant molar ratios surfactant to surfactant + oil. The molar ratios are 0.085, 0.156, 0.250, 0.306 and 0.468. The locations of the individual points are given in Fig. 1.

○, water self-diffusion; and +, oil self-diffusion.

●, water self-diffusion miscellaneous points, marked in Fig. 1 with the compositions: s 9.8%, o 63.6%, w 26.6% s 10.0%, o 75.0%, w 15.0%.

distinctly water-continuous and other regions where water molecules are confined to closed domains. Measured values of D_{surf} are low and at no stage do we encounter situations with molecularly dissolved surfactant (Table 1). As would be expected for a balanced surfactant like didodecyldimethylammonium bromide and as already remarked, the surfactant molecules should have a strong tendency to occur at the oil-water interfaces. The solubility of the surfactant in isotropic solution is very low in both water and hydrocarbon [$<1\%$ by weight].

In Fig. 6, we note that at low water content and not too high surfactant concentration, both D_{hc} and D_{w} are high, corresponding to a bicontinuous structure. (This is supported by values of D_{surf} which approach $1 \cdot 10^{-10} \text{ m}^2 \text{ s}^{-1}$, a value found for bicontinuous structures in a number of different surfactant systems.²⁷) A very striking observation^{15,17} is the transition from bicontinuous to water-in-oil droplet structure as water content increases. This occurs in series with surfactant to oil + surfactant molar ratios of 0.085, 0.16 and 0.25. At the ratio 0.31, the water diffusion drops only at the highest water contents while at the ratio 0.47, water diffusion is rapid throughout. In the latter case, the microemulsions are bicontinuous for all water contents.

It is instructive to correlate the changes in self-diffusion behaviour with water content with the phase diagrams. In particular, we note that the microemulsions are of the water-in-oil type for the case where the microemulsion is transformed to a reversed hexagonal phase at higher water contents. At high surfactant content, the microemulsions remain bicontinuous and are transformed into a bicontinuous cubic liquid crystalline phase on further increase of the water content. Almost certainly this system has zero net curvature.

Summary

The picture which emerges for the L_2 phase of this ternary system is unambiguous and devoid of those uncertainties which afflict anionic systems studied previously. The surfactant, being insoluble in oil and water, resides at the oil-water interface. Oil uptake into the surfactant hydrocarbon, which varies systematically with alkane chain length and can be accounted for quantitatively by NMR and theories of chain packing,

tends to impose on the system a curvature appropriate to that of a reversed micellar phase. This is opposed by head group interactions. With increasing water and fixed S/O at the boundary of the L_2 phase, it is possible to strike a free energetic balance, and the system forms a bicontinuous network of tubular nature. With further water increase, corresponding to counterion dilution and more head group repulsion, the net reverse curvature set by the balance of forces decreases. At sufficiently high water and less surfactant, a situation is reached where, because the interface is now fairly flexible, the system breaks off into more stable water-in-oil droplets. With even more water, and low surfactant, the system rearranges to form surfactant-oil multilamellae surrounding large macroscopic droplets of water. At higher surfactant/oil ratios, oil uptake enforces a high rigidity on the interface. Water uptake can eventually be accommodated here by formation of a (eventual) zero net curvature system which is the cubic phase. At intermediate S/O ratio, with increasing water, head group repulsion can oppose oil uptake to squeeze out excess oil. The hexagonal phase forms because of packing constraints. Fine details and the equilibrium between different phases depend on interactions, as is evident from the coexistence of two lamellar phases in the binary system. The rôle of interactions can properly be resolved only by studies of phase diagrams with different counterions, binary and ternary, coupled with further direct force measurements.

The usefulness of such studies is clear. These systems provide a well defined entry point to the complex problem of solubility in multicomponent systems which is at one end of the spectrum of possibilities encompassed by Ekwall's work. By introducing further components, like cosurfactants of single-chained surfactants, it is possible to perturb the curvature of the system, and gain a more general insight into microstructure.

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