

SUB-ZERO TEMPERATURE BEHAVIOR OF WATER IN NON-IONIC MICROEMULSIONS

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Abstract

Sub-zero temperature DSC measurements were conducted to evaluate the behavior of water in non-ionic microemulsions. Two surfactant systems were studied. The first, based on ethoxylated fatty alcohol, octaethylene glycol mono *n*-dodecylether [hereafter referred to as $C_{12}(EO)_8$] and also containing water, pentanol and dodecane at a fixed weight ratio of 1:1. The second system, based on oligomeric ethoxylated siloxanes, water and dodecanol as oil phase. In both systems it was found that in up to 30 wt.% of the total water content, all water molecules solubilize in the amphiphilic phase and are bound to the ethylene oxide (hereafter referred to as EO) head-groups. No free water exists in the surfactant aggregates' core. Up to three molecules of water are bound to each EO group.

In the first system, the behavior changes significantly upon adding more water. The added pentanol allows further swelling and the water penetrates into the amphiphile structures and forms a reservoir of free water. Structures are deformed and grow from elongated channels (up to 15–20 wt.% water), via illdefined (one-dimensional growth) local lamellar structures (up to ca. 60 wt.% water) to spherical normal, O/W micelles (at ≥ 85 wt.% water).

In contrast, the oligomeric systems, due to geometrical restrictions of the amphiphiles and the nature of their curvature that prevents inversion, cannot further solubilize water in the surfactant aggregates' core, causing phase separation to occur.

Keywords: DSC measurements, sub-zero temperature, water in non-ionic microemulsions

Introduction

It has been long demonstrated that liquid water departs considerably from its average bulk behavior when near solid or liquid interfaces [1]. The investigation of possible interactions between water and such interfaces may help to gain some insight into the behavior of water in biomolecular processes [2, 3]. In this context, microemulsions may well serve as model systems for the investigation of water in confined spaces [3], since microemulsions may be envisaged as tiny

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droplets of water (or oil) dispersed in continuous oil (or aqueous) medium [1]. For example, membrane proteins, which are immersed in a lipophilic membrane while many water molecules are very close to the membrane surfaces [4], may be linked with water-oil interfaces, typical of microemulsions.

When describing the state of water in relation to any surface, a distinction is usually made between 'bulk' and 'bound' water. Bulk or free water is assumed to have physicochemical properties not much different from those of pure water. Thus, it should, for example, have a heat of fusion similar to that of ordinary water, freeze at approximately 0°C, and have heat capacities nearly the same as ice below this temperature and very close to those of water above this temperature [5].

'Bound' water, known also as 'hydration shell', 'solvent shell', 'hydration water' [6] or 'vicinal water' [1], may be defined by an operational definition or by a more precise and independent one. Definitions of the first kind refer to the water detected by a certain technique as having been influenced by the surface of the substrate in contact with the water. The presence of a nearby surface may alter thermodynamic properties (among others: melting point, enthalpy and heat capacity) and hydrodynamic and kinetic properties of the water. Thus, water whose properties differ detectably from those of 'bulk' water in the same system, as a result of the presence of a surface, may be defined as 'bound' water [5].

One such rather common operational definition derives from the low temperature behavior of the water. Water, whose thermodynamic properties have been sufficiently modified so as to remain unfrozen at sub-zero temperatures, may be called 'bound' water, 'non-freezing' or 'non-freezable' water [5]. In such cases a definite amount of water, unable to freeze into normal ice, is readily determined experimentally [5], with practically the same results obtained by different methods [6]. This water is clearly distinguishable from 'bulk' water.

A technique-independent definition considers bound water as that water associated with a surface of a substrate, at a level of hydration beyond which further addition of water leaves the system unchanged (except for a dilution effect). The same end point of the hydration process is obtained by various techniques [6].

This distinction between bound and bulk water is also relevant to the development of industrial microemulsions for which the evaporation rates of water incorporated in their microstructure are of significance.

The nature of water-substrate interactions and the extent to which water is bound, have been investigated using spectroscopic methods, such as NMR [7, 8], IR [9–11] or ESR [7], and calorimetric methods, which may be divided into ambient [12–14] and low-temperature measurements [7, 15–19].

In order to examine the possible water interactions at microemulsion interfaces, two sets of systems have been investigated. The first, being a non-ionic microemulsion system of water/pentanol/dodecane, and the monomeric ethoxylated surfactant C₁₂(EO)₈ as the amphiphile, and the other, being microemulsion of water and dodecanol stabilized with siliconic oligomeric amphiphiles, which also have ethoxylated side chains.

Experimental

Materials

Monomeric amphiphilic system

The oil phase was *n*-dodecane (Aldrich Inc., USA, 99% purity); the amphiphile was octaethylene glycol mono-*n*-dodecylether, C₁₂(EO)₈ (from Nikko Chemicals, Japan) and the coemulsifier was 1-pentanol, (Aldrich, purity 99%).

Polymeric systems

The oil phase consisted of either *n*-dodecane (Sigma, USA) or in most cases (for the reasons that will be explained in the text) of 1-octanol, 1-decanol or 1-dodecanol (Sigma, USA). The cosolvents were 1-propanol, 1-butanol or 1-pentanol (Aldrich). All the reagents were minimum 99% pure.

Table 1 Composition and surface properties of the PHMS-POE copolymers (Silwets)

Silwet surfactant	Molecular weight	EO content/ wt. %	Silicone/ wt. %	Estimated HLB/ range	Surface tension*/ 0.1 wt.%, mN m ⁻¹	Cloud point °C
L-77	600	62	38	5–8	20.5	–
L-7602	3000	40	60	5–8	26.6	39
L-7604	4000	55	45	13–17	25.4	50
L-7607	1000	75	25	13–17	23.4	58
L-7600	4000	74	26	13–17	25.1	64
L-7605	6000	73	27	13–17	30.2	93

*0.1 wt. % surfactant in water.

Table 1 lists the polymeric amphiphiles used in this research. The surfactants are based on polymethylhydrogensiloxans (PHMS) grafted with polyoxyethylenes (POE). The amphiphiles will be termed in short PHMS-POE or by their commercial trade names 'Silwets'. The products are commercially available from Union Carbide, USA and ICI, England. The Silwet molecular weight ranges from 600 to 6000 and has 25–60 Si atoms and 40 to 60 wt. % EO groups are grafted onto the polymeric backbone. The products estimated HLB's are 5 to 13 and the cloud points range from 39 to 93°C.

Water was double distilled. In all systems (monomeric and oligomeric) D20 was used to identify thermal water peaks. It was 99.8% minimum (Merck, Germany).

Phase diagram

The first model system chosen was *n*-dodecane/C₁₂(EO)₈/1-pentanol/water. Predetermined amounts of C₁₂(EO)₈, dodecane and pentanol were titrated with

water in order to detect phase transitions characteristic of the system. The detailed procedure is described elsewhere [20–22].

Since the behavior of four components is to be depicted on a pseudoternary phase diagram, the relative concentration of two of the components must be kept constant for all the experiments. Although phase diagrams of such quaternary systems are generally based on constant ratios of surfactant-to-water or cosurfactant-to-surfactant, we preferred to use a fixed weight ratio of oil-to-cosurfactant, which is also quite common, particularly among solubilization researchers [see our paper [23] and references therein]. We have used pentanol and dodecane at a fixed weight ratio of 1:1. The phase diagram is given in Fig. 1.

The main feature of the phase diagram is a continuous monophasic area extending from the water apex to the opposite edge, bordered by a two-phase region on the one side, and by a liquid crystalline domain on the other. This is an example of a U-type microemulsion [24].

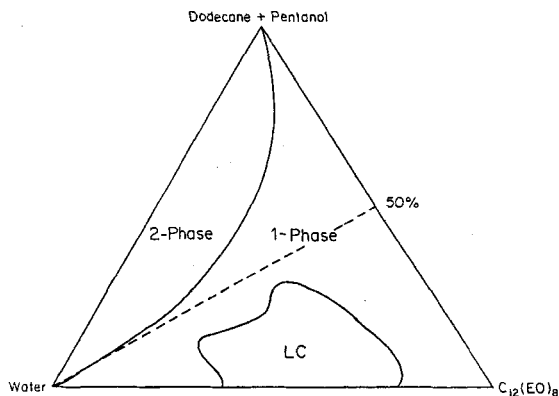


Fig. 1 Phase diagram for the system *n*-dodecane/ $C_{12}(EO)_8$ /1-pentanol/water. (27°C, weight ratio dodecane/pentanol = 1). No attempt was made to further identify the liquid crystals or any other phase within the LC area. The dashed line represents the water dilution line in which the mass ratio of dodecane:pentanol: $C_{12}(EO)_8$ is kept constant at 1:1:2, respectively

If we draw a line from the water corner to the midpoint of the side that connects the pentanol/dodecane and the surfactant apexes, it will represent system compositions for which the initial concentration of $C_{12}(EO)_8$ is 50% (wt.). This is the dilution line marked as '50%' in Fig. 1. It can be seen that the amount of water contained in the monophasic systems represented along this line may vary continuously from very low to quite high values. All compositions chosen by us for the DSC investigation described in this paper lie along this line.

The phase diagrams for the oligomeric systems were constructed by a similar procedure [25].

Calorimetric measurements

A Mettler TA 4000 Thermal Analysis system, equipped with TC 11 TA processor and DSC 30 low-temperature cell, was used. The DSC measurements were carried out as follows: microemulsion samples (5–15 mg) were weighed, using a Mettler M3 microbalance, in standard 40 μl aluminium pans and immediately sealed by a press. All DSC measurements were performed in the endothermic scanning mode (i.e. the controlled heating of previously frozen samples) thus circumventing possible complications from supercooling when measurements are performed in cooling (exothermic) mode. The samples were rapidly cooled by liquid nitrogen at a pre-determined rate from ambient to -100°C (sometimes to -30°C) and then heated at a constant scanning rate (usually $3^{\circ}\text{C min}^{-1}$) back to ambient temperatures. The same results were obtained when the samples were kept at the minimum temperature for 1 h. An empty pan was used as a reference. The calorimeter measured and recorded the heat flow rate of the sample as a function of temperature, while the sample underwent the aforementioned cooling and heating procedure. The instrument also determined the total heat transferred in the observed thermal processes. The enthalpy changes associated with thermal transitions were evaluated by integrating the area of each pertinent DSC peak. DSC temperatures reported here were reproducible to $\pm 0.5^{\circ}\text{C}$ and have absolute values calibrated to $\pm 1^{\circ}\text{C}$.

Thermal analysis

We followed the method utilized by Senatra *et al.* [1, 15, 16, 26–31], in which the endothermic scanning mode was applied and the peaks representing various states of water were identified and analyzed. Senatra *et al.* differentiate between three types of water [28]:

'Free' water, that is water whose properties are similar to those of bulk water. It melts at 0°C .

'Interphasal' water, which is the water confined within the region separating the aqueous core from the oleic dispersing phase. This region is considered to be finite in extent and not just an imaginary line which serves as a border between the two phases. The interphasal water melts at ca. -10°C . This complicates the study of dodecane-containing systems, such as our monomeric model system, as dodecane itself also melts at -10°C , and thus its fusion peak overlaps the peak of interphasal water. However, the existence of this type of water was clearly shown for our system, using the following considerations: (a) The heat of fusion, measured at -10°C was higher than that required for the known amount of dodecane in the system. By subtracting the enthalpy change due to the dodecane, the contribution of the interphasal water is readily calculated. (b) The endothermic peak at -10°C remained in the absence of dodecane, or when hexadecane was substituted for dodecane. (c) Analysis of microemulsions in which D_2O was used in-

stead of water, and with all other components and compositions being the same, showed a typical shift of the D₂O relevant endothermic peaks toward higher temperatures.

'Bound' water means water which is bound to hydrophilic groups and cations, and melts at temperatures lower than -10°C .

Results and discussion

Microemulsions based on monomeric amphiphiles

Thermal behavior

Figure 2 shows a typical DSC curve for the monomeric model system. The peak at -78.1°C was identified as belonging to pentanol and the identification was corroborated by comparing this peak with that of pure pentanol. The peak at -2.7°C is assigned to free water. The peak at -10.4°C is related to both dodecane and 'interphasal' water.

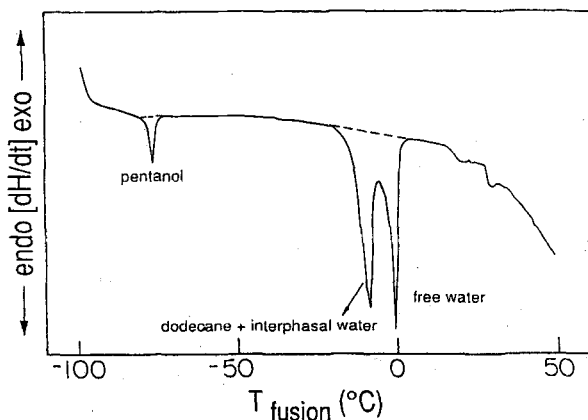


Fig. 2 DSC curve for the system dodecane (13.7%)/pentanol (13.7%)/C₁₂(EO)₈ (27.6%)/water (45.0%). The non-constant baseline above about 30°C is probably due to water evaporation

From the intensities of the DSC peaks, the content of interphasal and free water in the microemulsions the compositions of which lie along the 50% dilution line (fixed mass ratio C₁₂(EO)₈/pentanol/dodecane of 2:1:1, respectively), can be plotted. The results are shown in Fig. 3.

It can be seen from Fig. 3 that the concentration of the interphasal water increases until it reaches a constant value, which we have evaluated from the experimental data to be $28.4 \pm 1.0\%$ (wt.). We may say that when the total concentration of water equals 28% (wt.), virtually all the water in the microemulsion system is of the interphasal type. At 30% water (based on total sample mass) free

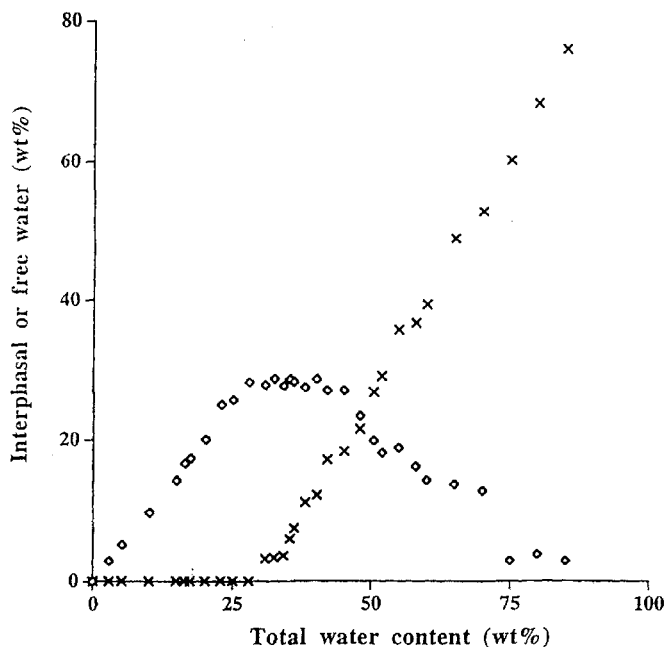


Fig. 3 Variation of free and interphasal water content with the total concentration of water. Concentrations are calculated in mass percentage, relative to the masses of the microemulsion samples. x stands for free water and ◇ stands for interphasal water

water begins to appear and its fraction increases steadily, while the concentration of the interphasal water remains constant at $28.4 \pm 1.0\%$ (wt.) until somewhere between 45 and 48 wt.% water. At this point the decrease in concentration of the interphasal water is clearly seen. We have shown, independently, by NMR techniques that an inversion to an O/W microemulsion occurs at 50–55 wt.% water [22].

The molar ratio of total water/surfactant (referred to hereafter as W_0) was evaluated at the beginning of free water formation in two ways. First, the beginning of the plateau of Fig. 3 coincides approximately with the first appearance of free water. The total concentration of water is then $28.4 \pm 1.0\%$ (wt.) and thus W_0 is 23.8 ± 1.2 . A similar molar ratio is obtained from the intersection of the free water curve with the abscissa in Fig. 3. This curve is a straight line ($r^2=0.998$) and the intersection occurs at total water concentration of 30.4 ± 1.0 wt.%, which corresponds to $W_0 = 26.2 \pm 1.2$. The agreement between these two values of W_0 is good, as they were calculated from independent data. Taking into consideration all the measured values of W_0 , it may be shown that on the average ~ 25 water molecules are bound per surfactant molecule before free water begins to form. This means $25/8 \approx 3$ molecules of water are then bound per EO group.

As far as we know, no other non-ionic quaternary microemulsion systems have been investigated by such a technique. However, it will be instructive to

compare these systems with similar binary systems. Our results are in good agreement with those of Carlström and Halle [32], obtained by oxygen-17 magnetic relaxation study. They concluded that the head-group shell of $C_{12}(EO)_8$ aggregates in water contains less than 5 and possibly only 2–3 water molecules per EO group. Schulz and Puig [33] have shown by low-temperature DSC that for aqueous dispersions of $C_{12}(EO)_{23}$ and $C_{16}(EO)_{20}$ there are 3.07 molecules of interfacial water per EO group, in excellent agreement with our results. It may *prima facie* be inferred that the water-surfactant interaction is independent of the length of the hydrophilic head-group of the ethoxylated surfactant and that the presence of pentanol (and dodecane) does not affect the interaction between water and the EO groups of non-ionic surfactants. These conclusions are, however, preliminary [34].

Evaluation of the thickness of the interphasal water layer

The DSC results, which show that there are 3 water molecules per EO group, may be used to assess the thickness of the interphasal water. The exact location of the water molecules around the head-group chain is not known. Using molecular modelling, we may postulate a tetrahedrally coordinated structure where each oxygen atom of an ethylene oxide group is hydrogen-bonded to two water molecules, and a third water molecule is hydrogen bonded to both of the two other water molecules, forming an octagonal ring. A similar network of structured water for the polyethylene oxide-water system was suggested [35]. Of the several possibilities analyzed by the researchers, regarding the binding of water to EO, one was the possibility that on the average, three water molecules can bind per one EO group [35]. However, it should be remembered that such an ice-like structure may be distorted due to the stereochemical constraint imposed by the presence of the surfactant.

Our model (Fig. 4) leads to an effective thickness of the two monolayers of interphasal water of ca. 4.5 Å.

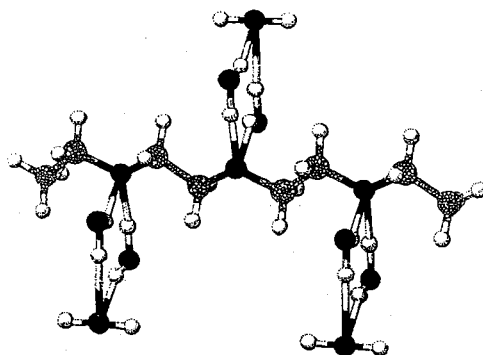


Fig. 4 A possible configuration of hydrated EO groups. Filled spheres, O atoms; blank spheres, H atoms; grey spheres, C atoms

It was also possible to derive a $\sim 5\text{\AA}$ thick water bilayer around the surfactant from the freezing point data as well [34].

Formation of free water and structural polymorphism

Figure 3 clearly shows that up to a total concentration of 30 wt.%, all water interacts with the EO surfactant groups and thus is considered as interphasal water. In contrast, NMR results [22], FTIR [9] and ESR [30] techniques demonstrate the presence of free water in equilibrium with bound water even with the smallest amounts of total water content. This is due to the fact that DSC 'regards' the binding of water molecules (which is conceived as a restriction imposed on their mobility) in terms of an interference with their freezing at 0°C .

The high water content within the monophasic area, along the 50% water dilution line (Fig. 1), may be interpreted as follows: up to 30 wt.% water the surfactant (which presumably aggregates in elongated channels) [36] becomes saturated with interfacial water. Upon adding more water an internal core of free water is being formed and it continuously swells with increasing water content. It should be emphasized that this aqueous core is not the common spherical one encountered in regular inverted W/O microemulsions. We have shown, using cryo TEM, SAXS, SANS, NMR and electrical conductivity techniques (20,36) that at water content (20–60 wt.%) the system assumes a local lamellar structure, i.e. alternate layers of water and [dodecane + pentanol + $\text{C}_{12}(\text{EO})_8$]. Upon adding water the aqueous layer swells one-dimensionally, while the thickness of the nonwater components' layers remains constant. At ca. 60 wt.% water the local lamellar structure collapses, and clusters of normal micelles are formed [36]. At approximately 85 wt.% water discrete O/W micelles are detected [20].

The microstructure of the oligomeric systems was examined using the SAXS technique. It was found that in these systems the structure is local lamellar [25], so we decided to compare the water state within both monomeric and oligomeric surfactant systems.

Microemulsions with oligomeric grafted amphiphiles

Thermal behavior

Figure 5 demonstrates the isotropic areas in the phase diagram of dodecanol, water and the oligomeric amphiphiles Silwet L-7607 (A); Silwet L-7600 (B) and Silwet L-7605 (C). Two surfactant/oil mass ratios have been examined (1 and 3/7) in a dodecanol/water microemulsion in presence of 6, 10 and 15 wt.%, and 10, 20 and 30 wt.%, respectively, of solubilized water. Figures 6 and 7 demonstrate the thermal behavior of the two selected systems of PHMS-POE, Silwet L-7607 (MW 1000 and 74% EO), respectively.

The DSC curves consist of set of endothermic peaks. The biggest one is of the dodecanol (peak a) melting at 17.2°C and enthalpy of melting of $160\text{--}200\text{ J g}^{-1}$ depending on the system composition (24°C and 190 J g^{-1} respectively for pure

decanol as in the literature). No endothermic peak was found at 0°C, indicating that all water is bound. In fact, close examination of the L₂-phase reveals to much of our surprise that although the microstructure is local lamellar in both systems (monomeric and oligomeric) there is no free water in the Silwet surfactant aggregates at any water contents!

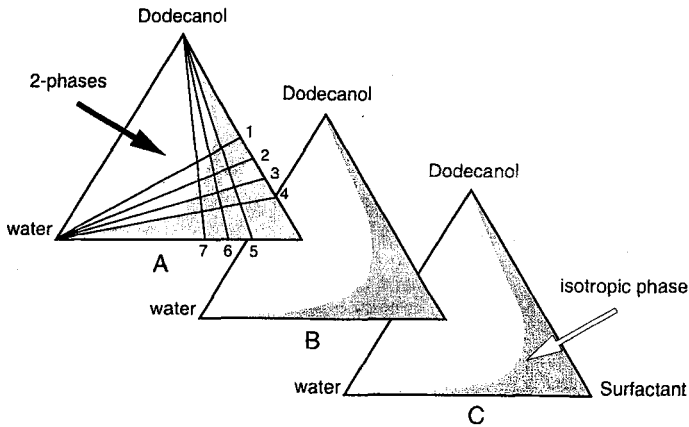


Fig. 5 Phase diagrams of water, dodecanol and various types of polymeric siloxanic emulsifiers (Silwets). (A) Silwet L-7607, MW 1000 and 75% EO; (B) Silwet L-7600, MW 4000, 75% EO, (C) Silwet L-7605, MW 6000, 75% EO

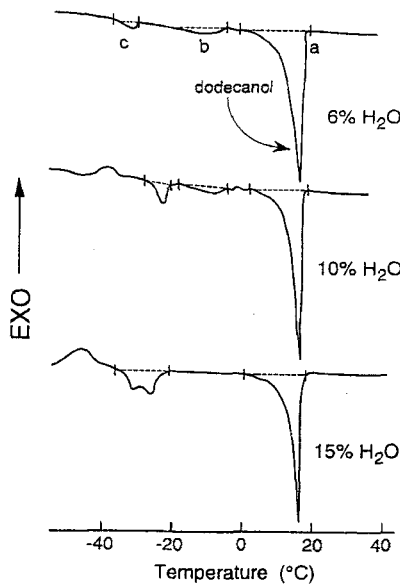


Fig. 6 Thermal behavior of microemulsions prepared with dodecanol, Silwet L-7607 surfactant/oil mass ratio of 1, in the presence of 6, 10 and 15 wt.% of solubilized water (heating rate 3°C min⁻¹)

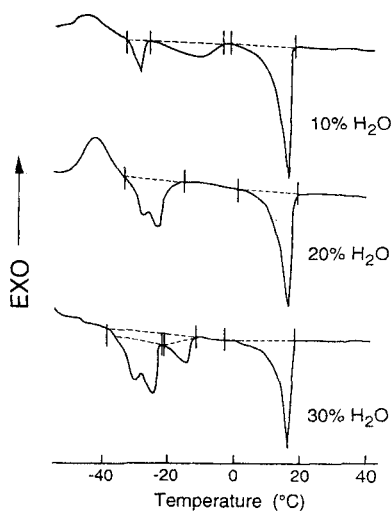


Fig. 7 Thermal behavior of microemulsions prepared with dodecanol, Silwet L-7607 at surfactant/oil mass ratio of 3/7 and in the presence of 10, 20 and 30 wt.% of water (heating rate $3^{\circ}\text{C min}^{-1}$)

The endotherms at the sub-zero temperatures (peaks b and c) were attributed to interfacial and bound water. A confirmation to these assumptions was taken from an experiment in which the solubilized water was replaced by D_2O revealing a shift of 3.4°C in each of the endothermic peaks. The b peaks in the DSC curves are attributed to bound water weakly interacting with the surfactant or the hydroxyl group of the oil. The c-type peaks are attributed to more strongly bound water. It was surprisingly found that with the increase in the solubilized water content, the 'endotherm' of the b-type 'water peak moves' to a less negative temperature (lower melting point) and becomes more pronounced. The effect is stronger in the second set of systems (oil-to-surfactant ratio of 3/7), in which more water was solubilized (Fig. 7). Detailed analysis for the nature of these endotherms will be reported separately.

Solubilization power of the amphiphile (binary systems)

In order to estimate the number of water molecules that the surfactant can bind, binary mixtures of surfactants and water have been tested by DSC. It was found that whereas at surfactant to water ratio of 9 to 1 all the water is bound to the surfactant, at 1 to 1 ratio a major part of the water is free and only minor proportions of the water are bound. Equation (1) was used to calculate the number of molecules of water bound to an ethylene oxide unit.

$$N_{\text{W/EO}} = \frac{XY/M_w(1 - \Delta H_S/\Delta H_F)M_S}{N_{\text{EO}}X(1 - Y)} \quad (1)$$

where X is the weight of the sample (g), Y is the water mass fraction, M_w is the molecular weight of the water, M_S is the molecular mass of the surfactant, ΔH_S is the measured enthalpy change of the free water (in Joules), ΔH_F is the heat of fusion of pure water, measured by us, and equals 323.7 J g^{-1} , $N_{W/EO}$ is the number of water molecules per EO group, and N_{EO} is the number of EO units in the surfactant molecule.

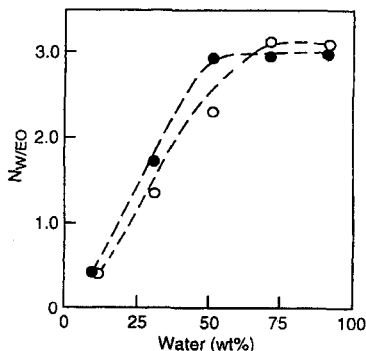


Fig. 8 The number of water molecules bound to each EO group $N_{W/EO}$, as a function of wt.% of solubilized water for two binary systems based on (●) Silwet L-7607 and (○) L-7600

The calculated $N_{W/EO}$ is presented for two sets of surfactants, at 10–90% of solubilized water. The graphic presentation of the results is illustrated in Fig. 8. The maximum number of molecules of water per EO groups is ca. 3 (in both cases) only when the amount of the solubilized water is over 90%. Similar binding capacity of EO groups in binary systems (minimum 3 molecules of water per EO group and up to 5.7 molecules of water per EO group) was found in our previous work with nonionic monomeric emulsifiers [34].

Binding capacity of the EO groups in the ternary systems

In Fig. 9 we plot $N_{W/EO}$, at the maximum solubilization point, of three sets of surfactants, at several surfactant to oil ratios (Figs 6 and 7). The Silwet L-7607 is capable of solubilizing three molecules of water per EO unit at 8/2 ratio of surfactant to oil at the maximum solubilization point. The maximum binding is obtained only when large excess of surfactant is present with regard to the oil. At lower ratios of surfactant to oil, the surfactant is probably interacting with the hydroxyl group of the oil (decanol) and cannot bind considerable amounts of water. A maximum of three molecules of water per EO group is obtained only with the surfactant that is dispersed in the oil, so that maximum water molecules can accommodate EO groups within its core similarly to the binding capacity of the amphiphile in the binary systems. The other two surfactants have lower solubilization capacity and do not reach the saturation point at any given surfactant to oil ratio. In all three cases there is no free water in the core of the structure.

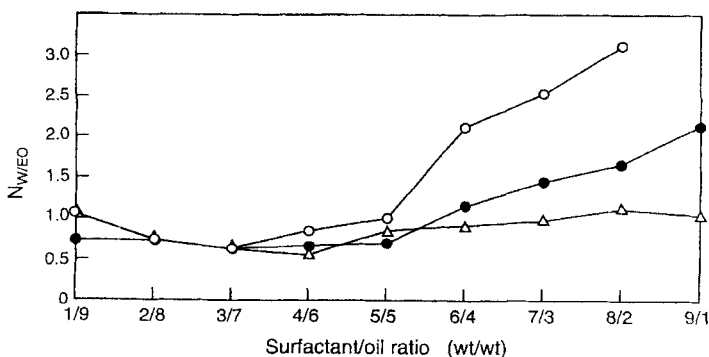


Fig. 9 The number of water molecules bound to each EO group $N_{W/EO}$ in three surfactant systems at various surfactant-to-dodecanol ratios (Δ - Silwet L-7605; \bullet - Silwet L-7600; \circ - Silwet L-7607, at the maximum solubilization point)

Even above 20% of solubilized water within the surfactant head-groups, one can observe only minor lamellae swelling. From the DSC curves it is clear that the additional water binds more loosely and packs probably in second and third peripheral layers. It should be noted that, as expected, the local lamellar structures have thinner nonwater layers with octanol in comparison to dodecanol.

Microstructural considerations

It is our understanding that since the water layers in the monomeric and oligomeric systems swell in one dimension only, as evidenced by SAXS measurements [20, 25, 36] the structure will basically have the shape of lamellar multilayers. Those might be considered ill-defined, bicontinuous phases, or distorted local lamellar structures. Previous studies demonstrated that the elongated channels which characterize the structure of low-water systems based on the non-ionic ethoxylated surfactant, tend to swell in one dimension array, forming undulated, swollen layered structure, which we have named 'local-lamellar' [20]. The same picture emerges from SAXS measurements done on the oligomeric systems [25]. These lamellae, in our view, may be conceived as illdefined, distorted, short-domained, highly obstructed bicontinuous structures [36]. Figure 10 is a schematic illustration of what we believe these structures to be.

The water molecules form complex, cyclic structures around the POE head-groups. However, in the case of the oligomeric systems, they do not form an interior reservoir in the surfactant aggregates' core [38–43]. What is the reason for such a fundamental difference between these two types of systems? We suggest the following explanation.

In the monomeric system two main factors favor the formation of a free water core: the molecular structure of the surfactant $C_{12}(EO)_8$ and the presence of medium chain alcohol, which makes the interface flexible and enhances water solu-

bilization [36]. It is remarkable that although the pentanol plays such an important role in promoting water solubilization, its interaction with the water (and surfactant) could not, nevertheless, be revealed by DSC measurements [34].

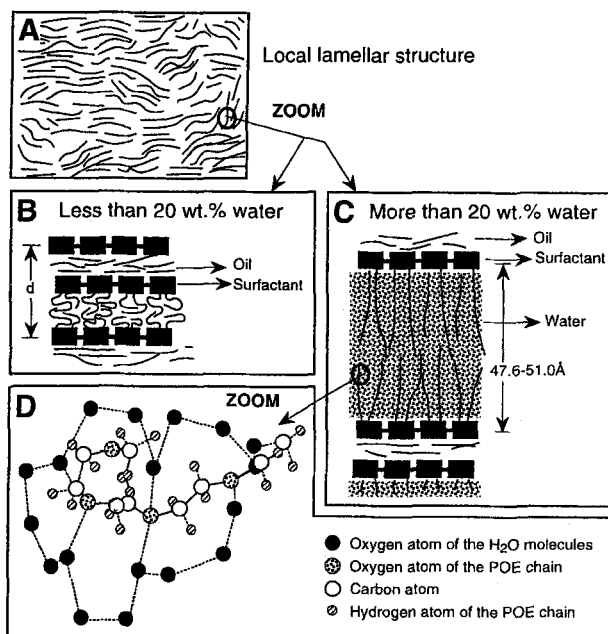


Fig. 10 Schematic illustration of possible structures of the quasi-lamellar isotropic phase of the systems composed of oligomeric amphiphiles L-7607 and oil

On the other hand, in the oligomeric system, the siliconic surfactant molecules cannot cooperatively aggregate with each other. The dodecanol is too long to make flexible interface and so the amount of water, which can be accommodated in such systems, is rather limited. As the Silwets become saturated with interfacial water, adding more water causes phase separation.

Conclusions

The DSC measurements proved to be a good technique to better understand the state of water in monomeric and oligomeric systems. The monomeric amphiphiles self-aggregate even in the presence of small amounts of water, swell continuously with increasing the total water content, and the structure changes from elongated channels [36] via ill-defined, local lamellar structures to O/W micelles (20, 36). The water binds strongly to the head-groups (3 molecules per EO group) and only after saturation forms reservoir of free (bulk) water, which becomes the outer phase at ca. 55–60 wt.% (total) water (20, 22, 36).

Oligomeric surfactants with long hydrophilic head-groups which strongly interact with the oil, and have lipophilic backbone, will self-organize at any water concentration in a structure of ill-defined, bicontinuous domains [25], in which the water is bound to the hydrophilic heads and does not form an interior reservoir. The oligomeric aggregates swell in one dimension only, implying a local lamellar structure.

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