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DSC ANALYSIS OF THE STATE OF WATER IN SURFACTANT-BASED MICROSTRUCTURES

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Abstract

A review is made about the different kinds of water in surfactant-based microstructures (liquid crystals, microemulsions and micelles) and their study by DSC.

Keywords: DSC, microstructures, surfactants, water

Introduction

Differential scanning calorimetry (DSC) is widely used in the study of binary and multicomponent systems containing surfactants. Transition temperatures and enthalpies are often determined and used to draw the limits of existence of the different phases [1–6]. The state of the surfactant molecules in these phases is studied by means of thermal analysis [7, 8]. However, the study of the state of one of the principal components of the system, water, is often neglected, and only the melting point of this component in the system is reported. The behaviour of water is sensitive to the presence of adjacent interfaces of different nature, as biomembranes, proteines, and inorganic compounds [9]. Water molecules properties depart considerably from their average bulk values when there are solutes or interfaces in the neighbourhood. Focusing on the thermal analysis of water, many interesting and pertinent information may be obtained. Water in very small volumes plays a dominant role as the medium that controls structure, function, dynamics and thermodynamics near biological membranes or in other confined regions of space [10].

Several types of water have been detected in surfactant-based microstructures, such as microemulsions and liquid crystalline phases [11–18]. Water in microstructured systems may be roughly classified into four categories: free water, interstitial water, surface water (physically and/or chemically adsorbed) and internal water (chemically-bound water). The state of interstitial water may be similar to bulk free water. A reduction in the free energy would make the water remain unfrozen at a temperature well below the normal freezing point. These 'kinds of water' have different enthalpies and temperatures of melting, as well as anomalously low supercooling temperatures [13]. Supercooling and freezing be-

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haviour of water in nonbulk states is important for understanding the behaviour of water in microporous materials, gels, biological tissues, foods, and other microstructured fluids at subzero temperatures. Besides, water exists in various states with different properties in living beings. Much pertinent information about phase structures in surfactant-based systems and interactions among polar (ionic and nonionic) species and water may be obtained by studying the state of water in microstructured systems. Knowledge of the properties of water at interfaces of organized assemblies, at the microscopic level, is a prerequisite for understanding the effects of these species on chemical reactivity and equilibria. Interfacial water is involved in, inter alia, solvation of reactants and transition states, solvation of surfactant headgroups and counterions, and in proton [19]. Sludge dewatering is one of the most difficult problems in wastewater treatment, and the knowledge of the state of water in different sludges is of industrial and economical importance [20].

There are still questions about, for instance the distance the perturbations made by surfaces extend to, their influence on diffusion and other physical properlies, their effects on chemical reactions, such as acid-base equilibria, and phenomena taking place in biological microsystems [21]. These questions are of great interest because of the fundamental role that interfacial water plays in many physical, geophysical, chemical, biological and industrial processes.

The theoretical and practical interest of this information is evident. Hence, it is important to understand the nature of the different types of water in liquid crystalline systems.

The identification of water transitions

In some cases, water transitions may be misinterpreted as other type of transitions. This has been the case of the transition at ~0°C in the system Aerosol OT (AOT)–water, which was interpreted as the transition gel-liquid crystal. By substitution of water by deuterium oxyde, the transitions shifted 4°C . This undoubtly proved that these peaks belong to water melt [22, 23]. AOT does not form gel phase up to –150°C. Another form to identify the transition of water melting is by plotting the enthalpy per gram of sample *vs.* composition giving $\Delta H \approx 319.6$ J g^{-1}, at 100 % water.

Non-freezing water

In various surfactant-based systems, some water molecules may be non-freezable. The amount of this kind of water which is unable to freeze into ice is practically the same when it is determined by different methods [24]. This amount may be determined by plotting the total melting enthalpy of water by weight unit of sample against the sample composition, by extrapolation to zero enthalpy. Unfreezable water has a very small vapour pressure [25]. It has been interpreted as the water bound to solute in a first hydration shell, based in the close proximity of determined amounts with hydration numbers of ions measured at room temperature [26, 27]. However, this interpretation is not necessarily the only possible one [27].

In some cases, water may be nonfreezable by probably two different constraints: water may exist in very small clusters centered on hydrophilic groups or ions. These clusters may be too small to form a nucleous for ice formation. In some cases, stretched water probably do not freeze as a result of its extreme viscosity at low temperatures, which results in vitrification instead of crystallization since diffusion becomes rate-limiting rather than nucleation [28–30]. In some biological microstructures, non-freezing water is in a metastable viscous state [31]. Stretched water has expanded and increased local partial molar volume by interaction with surfaces (Section: 'Interfacial' water).

The postulation of unfreezable water as the hydration layer in ionic surfactant microstructures was based in the coincidence with the hydration number of ions and polar head groups determined by different methods. The extent of hydrogen bonding in water is modified by the presence of ions [Ref. [32] and references therein]. Neutron scattering measurements have shown that the hydrogen bond is lost for every direct association of a water molecule with an ion, which disrupts the structure by energeticalliy favourable ion-water interactions [32]. Hydration water molecules are very close to the ion surface. As an example, the maximum distance between protons of water molecules in opposite sides of the hydrated Cl^- and Li^+ ions was 0.7 nm, and between neighbouring protons on an hydrated ion, 0.31 nm [32]. Hydration number is a function of concentration and ion nature. So, Li^+ ions have a coordination number which decreases from about 6 at concentrations of about 4 m to 3 at 10 m [32]. In contrast, Cl^- ions possesses ≤ 6 water molecules in the first hydration shell over a wide range of concentrations and a much weaker hydration structure [33].

Non-freezable water in surfactant-based systems

In Aerosol OT (AOT)–water systems, unfreezable water corresponds to 6 molecules of water per molecule of AOT [26]. The hydration number of Na^+ ion is about 5±1 , so the hydration number of the sulfosuccinate group must be 1±l, similar to that of phosphate groups of phospholipids (~1.5) [34]. The melting enthalpy of water vanished at 90 wt.% of surfactant in the system sodium dioctylphosphinate (SDOP)–water, corresponding to 2 hydration water molecules [35]. In the system didodecyldimethylammonium bromide (DDAB)–water, melting enthalpy of water per gram of sample vanishes at 93% w/w of surfactant, which corrresponds to 2 water molecules per surfactant molecule [36]. This figure corresponds to the first hydration layer of the bromine ion (~2). This means that the dimethylammonium group has negligible primary hydration capacity. The dioctadecyldimethylammonium bromide (DODAB)–water system led to the same conclusion. In systems of *n*-alkanephosphonic acids (RPA)–water, the global enthalpy of water melting per gram of sample vanished at 100 wt.% RPA, leading to the conclusion that there is no hydration water [37]. However, in monosodium *n*-alkanephosphonates there are four water molecules per surfactant molecule, which coincides with the crystallization water [38]. In some biological gels, as bovine corneas, up to 30% of water does not freeze [39]. The question about whether there is non-freezable water in polyoxyethylene-based non-ionic surfactant microstructures will be discussed below.

The disappearance of the melting enthalpy of water coincides with phase changes: in the AOT–water system, a transition occurs from lamellar mesophase to inverse hexagonal mesophase [40–42]. The vapour pressure of water falls when only hydration water exists in the system.

'Free' or 'bulk' water

When the system is enough diluted, 'free' or 'bulk' water is present in the system. Free water is assumed to have physicochemical properties not much different from those of pure water. Its presence is detected by the melting peak at about 0°C (with a slight dependence on water content). Its melting enthalpy is that of pure water (320 J g^{-1} of water). Free water heat capacities are nearly the same as ice below the melting point, and very close to those of water above this temperature [27]. The concentration at which the system has no free water may be determined by extrapolation to zero enthalpy per gram of sample (60% w/w of surfactant in AOT–water systems) [25]. Free water has the same vapour pressure as pure water (23.8 mm Hg at 25°C in AOT–water systems) [25]. In SDOP–water systems, free water exists up to 60 wt.% SDOP [35]. In some systems the melting point of free water is below 0°C (between –1 and –2°C), which suggests that this water is not entirely free or pure [18, 38]. It must be also reminded that in concentrated ionic surfactant microstructures the free water is a very concentrated ionic solution, which reduces the activity of water and its melting point.

Garti *et al.* [18] computed the amount of free water in inverse microemulsions using the equation:

$$W_F = \frac{100\Delta H_F(\exp)}{\Delta H_F^0} \tag{1}$$

where W_F is the free water concentration (in wt.%), $\Delta H_F(\exp)$ is the measured enthalpy change for the 0°C peak, and ΔH_F^0 the fusion heat of pure water, measured at the same experimental conditions.

The enthalpy change associated with the melting of free water in poly(ethylene glycol) (PEG)–water systems is less than the enthalpy of free water, as with most aqueous solutions [43, 44]. The amount of free water per polymer repetitive unit, Φ , may be computed by [45, 46]:

$$\Phi = \frac{1}{w_1}\left(w_2 - \frac{\Delta H_f}{\Delta H_w}\right)\frac{M_p}{M_w} \tag{2}$$

where w_1 and w_2 are the weight fraction of polymer and water, ΔH_f is the heat of fusion from heating experiment and ΔH_w that of pure water at the transition temperature. M_p and M_w are the molecular weights of polymer repetitive unit and water, respectively.

When the depression of the melting point of free water is significant, the enthalpy of fusion of water must be corrected by:

$$\Delta H_w = \Delta H_w^o + (c_{p,w} - c_{p,i})(T_f - 273.16) \tag{3}$$

where ΔH_w^o is the melting enthalpy of pure water at 0°C, T_f the fusion temperature and $c_{p,w}$ and $c_{p,i}$ the specific heats of liquid water and ice, respectively [41]. The quantity $(c_{p,w} - c_{p,i})$ can be taken as 2.3 $\mathrm{Jg^{-1}K^{-1}}$ [46, 47]. A further correction for the heat of mixing is not needed because it is much smaller than the heat of fusion [46, 48].

The plot of the dependence of the heat of fusion of free water on surfactant concentration must be a straight line if the amount of bound water is independent of concentration. The intercept must be ΔH_w^o. However, this value may be sligthtly different to that of pure water (334 J $\mathrm{g^{-1}}$)[43]. Values as 280 and 246 J $\mathrm{g^{-1}}$ were found [43]. De Vringer *et al.* also found similar values [46). They attribute this to overlap between peaks of free and interfacial water in the heating thermogram. ΔH_f must be zero when all water present is bound.

At constant PEG concentration, the melting points of free water are the lowest at low polymer molecular weight, and rise toward the melting point of ice as the molecular weight rises. This can be attributed to the colligative effect, since at low molecular weights there are significantly more polymer molecules than in higher molecular weights. The magnitude of the freezing point depression is much greater than the predicted by ideal-solution behaviour, due to the highly nonideal character of PEG solutions [48, 49].

Bulk-like water can be supercooled to temperatures around –16 to –23°C. However , water in thin films or in emulsified microdroplets can be supercooled to temperatures as low as –40°C [50–52]. In surfactant systems, free water is in enough large domains to supercool at –16 to –22°C [25, 37, 50].

'Interfacial' water

In several systems, other kind of water may be present. It is named 'interfacial' water, which is associated to the hydrophilic surfaces (polar groups and counterions) of the surfactant microstructures. This kind of water was also named 'bound water', 'hydration shell', 'hydration water', 'solvent shell' [24] or 'vicinal water' [10]. This type of water may be defined by an operational definition, as water detected by a certain technique as it had been influenced by the surface of the substrate in contact with the water [18]. For some definitions in sludges, see Lee and Lee [20] and references therein. The presence of the microstructure surface may alter the thermodynamic properties of water (such as melting point, enthalpy and entropy of melt and heat capacity) and spectroscopic (such as IR absorption frequencies and band shapes) [25, 53]. The chemical potential of bound water should be different from the bulk water [67].

The existence of the boundary layers of water possessing modified properties was indicated by several different experiments (Derjaguin and Churaev [55] and references therein).

In many ways, bound water is the most interesting type of water related to surfactant-based microstructures. Differences in the structure of interfacial water (relative to that of bulk water) have large effects on micellar catalysis by affecting both the enthalpy and entropy of activation [56]. The properties of water at the interfaces between surfactant microstructures and solution affects the absorption spectra of solubilizates, which is used in enhancement of analytical methods [57]. Almost all water in the inner part of cells is close to a membrane, which is an amphiphile aggregate. This means that almost all reactions in living beings occur in an interfacial water medium.

Up to three different kinds of 'interfacial' water may be detected in some systems. These kinds of water may be detected as small melting peaks as may be seen in Fig. 1. In the system AOT–water, two kinds of interfacial water may be detected, whose melting points are –5 and –9°C [25]. These peaks were not detected by DSC in pure water at any sensitivity. When water melting enthalpy per gram of surfactant is plotted *vs*. concentration, it remains constant, which gives a strong evidence of its association with surfactant. The vapour pressure of this kind of water drops abruptly when no free water is present [25].

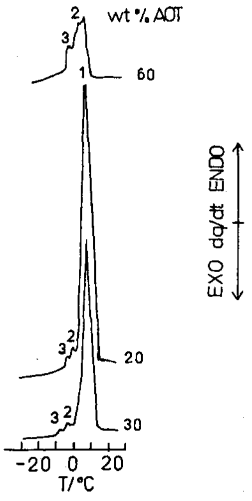

Fig. 1 DSC curves of AOT–water liquid crystalline samples as a function of AOT concentration, showing the peaks of 1: free water, 2 and 3, interfacial water [25]

DSC determination of interfacial water

Various methods for measuring bound water content have been proposed (see Lee and Lee [20], and references therein). A considerable amount of work on the properties of intefacial water of organized assemblies has been made using probes or reactions whose rates are sensitive to their microenvironment [58–60]. These methods often involve hydrophobic solutes whose (average) solubilization site in the micellar pseudophase is a matter of discussion, and they may perturb aggregate structure [61, 62]. This is not the case in thermal analysis.

The amount of 'interfacial' water may be found by the difference between the concentration at which the enthalpy of melting of total water vanishes, and that of the free water. In some cases, the melting peak of one kind of water may be superimposed to that of another component of the system, as dodecane in an inverse microemulsion [18]. In this situation, the amount of interfacial water was computed by the equation [18]:

$$W_\mathrm{I}=\frac{100\Delta H_\mathrm{I}(\mathrm{exp})-\Delta H_\mathrm{D}f_\mathrm{D}}{\Delta H_\mathrm{I}} \tag{4}$$

where W_I is the interfacial water content in wt.%, ΔH_I(exp) the measured enthalpy for the transition, which includes the contribution of the dodecane, ΔH_D is the heat of fusion of pure dodecane (191.6 J g^{-1}), f_D the dodecane weight fraction and ΔH_I the heat of melt of interfacial water. This enthalpy dependes on which of the polyrnorphic forms of ice the interfacial water forms. Some authors used the crystallization enthalpy of water without introducing an appreciable error [63], whereas others used a corrected value (312.38 J g^{-1}) [18, 64].

The overlapping of close peaks on heating may be avoided using cooling curves. On this basis, de Vringer *et al.* [46] used cooling curves to calculate bound water. However, it is difficult experimentally to get reliable values for ΔH_f , even making corrections for supercooling [43]. In the same experiment with different polyoxyethylene glycol molecular weights, Antonsen and Hoffman [43] found between 3 and 3.8 bound water molecules per oxyethylene group by heating, and between 2.3 and 2.8 by cooling. The two methods gave the same results at low polymer molecular weights.

The lowering of the melting point

The lowering of the melting point is related to the size and shape of the water domains [18, 65, 66]. For water in cylindrical pores with radius a, the reduction in melting temperature ΔT(°C) is $\Delta T \approx -52/a$. The following modified Kelvin equation was also proposed [67]:

$$\Delta T(\mathrm{K}) = (49.5\pm2.0)\,/\,(a-0.349\pm0.036\ \mathrm{nm}) \tag{5}$$

However, only a fraction $[(a-0.55\pm0.04\ \mathrm{nm})/a]^2$ of the water within the cylindrical pore of radius a freezes out at this temperature. For pores with radius close to 0.55 nm, the fraction of water that freezes out within the pore will be very small. The remaining part of the water undergoes a phase transition at a lower temperature, within the range –73 to –66 °C. This later phase transition is not a normal thermodynamic bulk water transition in the sense that no hysteresis effect is observed.

The thickness of an unfrozen water layer on a mineral surface d_u, is related to the fusion temperature with the equation $\Delta T \approx -50/d_u$. For planar bilayers, the following equation holds [35]:

$$\frac{\Delta T_{\min}}{\Delta T_{\max}} = 2^{\alpha+1}(l_o/L)^{\alpha} \tag{6}$$

where L is the total layer thickness, l_o is the thickness of the interfacial water, α is an adjustable parameter (usually taken as 2), $\Delta T_{\min}$ is the highest melting point of ice (the position of the endothermic peak of free water) and $\Delta T_{\max}$ is the maximum depression of the freezing point of water in the presence of the bilayers (that of interfacial water). The application of the preceding equations gave 0.5 nm as the thickness of the interfacial water in polyoxyethylene chains [18].

In samples with no free water, interfacial) water freezed at about –40°C [25]. Lee and Lee [20] found a thermodynamic dependence between the decrease of freezing point of bound water and the binding strength between water molecules and the surface of microstructures in sludges and the colligative effects of solutes in the aqueous phase:

$$\Delta T = \left(Rx_B + \frac{E_B}{T_{fo}}\right)\frac{T_{fo}^2}{\Delta H_f} \tag{7}$$

where x_B is the mole fraction of solutes in the interaggregates solution, R the constant of ideal gases, E_B the specific energy of interaction of water with surfaces, T_{fo} the standard temperature of fusion of water (273.16 K) and ΔH_f the enthalpy of fusion of water. This equation leads to estimate the value of E_B, giving 25 to 37 kJ kg^{-1} of sludge for $\Delta T = -20$ to -30 K, a value much larger than the usually supposed (1 kJ kg^{-1}) [68].

When a AOT-water sample containing interfacial and free water was cooled from room temperature, a single peak at ~ –16°C appeared due to supercooling of bulk-like water. However, when the sample was heated to –1 or –6°C to melt only bound water, the free water remained frozen and the interfacial water freezed without supercooling, because the two kinds of interfacial water could not remain supercooled in contact with frozen water. The melt of the two kinds of interfacial water might be followed by ^{1}H-NMR. One of them melted between –11 and –8°C, the other between –3 and –1°C [25].

In some lyotropic liquid crystals, the temperature of fusion of interfacial water remained almost constant with concentration [25, 69], but in some cases, as in inverse microemulsions [18], there is a dependence of the temperature of fusion with water content: from about –12.3°C at very low water contents to a plateau at about –9.5°C when free water appeared.

In microemulsions, the dependence of the amount of interfacial water on total water content shows the changes in phase structure. It rises up to the concentration at which free water begins to appear, then forms a plateau in a concentration range in which all added water behaves as free, and then the amount of interfacial water diminishes when the inverted microemulsion changes to a direct one [18].

Interfacial water in surfactant-based systems

In AOT–water systems, the disappearance of interfacial water peaks at 80 wt.% AOT is accompanied with a change in liquid crystalline structure: the lamellar mesophase is replaced by an inverse hexagonal mesophase [40–42].

The presence of different types of water in AOT–water systems at room temperature was corroborated by FT-IR spectroscopy. By deconvolution analysis of the OH stretching region (3700–3100 cm^{-1}) [25], three peaks at 3290 cm^{-1} ('free' water), 3490 cm^{-1} ('interfacial' water), and 3690 cm^{-1} (matrix isolated trapped water) appeared [70–72]. The amounts of these three kinds of water showed changes in their dependence with concentration when the structure of the liquid crystalline phases changed. The amount of bulk-like water is very small above 80 wt.% AOT, but below this concentration it started to rise rapidly and about 55 wt.% AOT the amount of 'free' water was larger than the 'interfacial' water. 'Interfacial' water dominated at intermediate (60 wt.% AOT) to high concentrations, in agreement with DSC measurements [25]. The maximum value of 'trapped' water was at 80 wt.% AOT, where the melting enthalpy of water became zero. In SDOP–water systems, the 'interfacial' water enthalpy vanished at 90 wt.% SDOP, whereas that of 'free' water vanished at 60%. This means that 9.6 water molecules per surfactant molecule are bound in some way to the polar heads and counterions [35].

In the system sodium 4-(1′-heptylnonyl) benzenesulphonate (SHBS)–water, three different kinds of 'interfacial' water were detected by DSC, whose melting points were –50, –40 and –31°C, plus 'free' water melting at 0°C [69]. Incidentally, the hydrocarbon domains of this system 'melt' at –70°C, so the gel structure exists with fluid hydrocarbon chains and solid water. Unfortunately, the amount and domain of existence of these different kinds of water were not investigated in the paper.

No 'interfacial' water was detected in DDAB–water systems [36].

In RPA–water systems, 'interfacial' water freezed at –20°C with an average freezing enthalpy of 47.2 J g^{-1} of surfactant. However, when heated, only one melting peak occurred. This indicated that this type of water was associated with the acid head groups when liquid, but this association did not exist when the system as a whole was solid [37]. FT-IR spectra demonstrate that there were not interactions among phosphonate headgroups and water in frozen samples.

In systems with Brijs (polyoxyethylene-based nonionic surfactants), the disappearance of the melting peak of free water occurred when there was 3 water molecules per oxygen atom in the polyethylene oxide chain bound in some way to the interface. The same value was found by Garti *et al.* [18] in inverse microemulsions with octaethylene glycol mono-*n*-dodecyl ether ($C_{12}(OE)_8$). The interfacial water melting enthalpy vanished at 1.40 water molecules per oxygen atom [23, 25]. This gave an average of 4.47 water molecules bound to the polyoxy-ethylene chain per oxygen atom, in good agreement with the value of 5.05 found by Tokiwa and Ohki [74]. Antonsen and Hoffman [43] found that the amount of bound water varies between 2.3 and 3.8 per oxyethylene group. Tilcock and Fisher [73] found between 1.8 and 2.7 by finding the polymer concentration at which the peak of free water disappears. Earlier results gave between two and three water molecules bound per oxygen atom in the polyoxyethylene chains [45, 46, 73, 75–77]. There was a gradual rise between this range with molecular weight. However, Elias [78] reported values ranging from 8.23 to 10.06, in dependence on the chain length, which suggested that those water molecules in excess of five that are strongly bound to the oxygen atoms, may be trapped in the helicoidal structure of the hydrophilic chain of the surfactant ethers [79], and may be participating in the kinetic entity, without being part of the true hydration of the surfactant molecules. Garti *et al.* had not found nonfreezable water in relation with $C_{12}(OE)_8$ and concluded that its existence may be related with the helicoidal structure adopted by large polyoxyethylene chains, where the trapped water may be in a very restricted space giving an interaction between water and oxygen strong enough to prevent the water from freezing [I8].

In poly(ethylene glycol) (PEG)–water systems, an exothermic peak was found at about –50°C on heating, which is associated with changes in ice structure [80]. Two endothermic peaks, one at ~ –14°C and the other at 0°C appeared. The latter was caused by the melting of ice, whereas the lower temperature peak was interpreted as caused by the melting of a polymer hydrate containing approximately two water molecules per polymer repetitive unit [43, 45, 75]. Antonsen and Hoffman [43] found that between the two water fusion peaks, the system was composed by ice and a concentrated polymer solution. The melting point of interfacial water (which is about the 50% of the polymer hydrate) [75] increased rapidly with polymer molecular weight before leveling off at approximately –10°C, at a molecular weight of 1200 (about 26 oxyethylene units). The melting point of interfacial water was not detected at polymer molecular weights lower than 400 (8 oxyethylene units) at temperatures as low as –80°C. This behaviour is related to the helicoidal structure adopted by large polyoxyethylene chains, in which loosely-bound water molecules can be more easily shared between adjacent segments of a single chain. The PEG hydrate generally solidifies slowly [46], thus, during cooling only one exotherm is exhibited, correspondig to the freezing of free water.

Lee and Lee [20] measured free and bound water in natural and artificial sludges by DSC. They found that there was about 6–7 kg of bound water per kg of dry solid mass. After a freeze/thaw treatement, the bound water content had been reduced by approximately 50%.

What is interfacial water?

The structure of the boundary layers of water depends on the nature of the surface. Near a hydrophilic surface the structure must be essentially different from that on a hydrophobic substrate, because of the abscence of hydrogen bonds between water and the surface in the latter case. If the surface is chemically and physically inert, the inabilily of the water molecules to extend their hydrogen bond structure into such a surface could have the same effect as a thermal increase. If the surface interacts with water, the inability of those molecules forcibly oriented near the surface, to maintain normal hydrogen bounding with their neighbours creates the same type of perturbation [9].

Neutron-scattering experiments demonstrated that electrostriction effects are small in the secondary hydration shell of ions and beyond [81], and this conclusion is probably true in the hydration layer on the hydrophilic surfaces of surfactant microstructures.

Several estimations were made of the thickness of the interfacial layer. Derjaguin *et al.* estimated the thickness of the boundary layers of water with peculiar structure to be close to 10 nm [55]. This thickness diminishes with increasing temperature, and reduces to a monolayer at 65–70°C [82]. The distance of 10 nm (36 water molecules) has been proposed as the distance over which the co-operativity of hydrogen-bonding extends [28], on the basis of several experiments [83–85]. Some experiments indicate that the upper limit is between 3 and 5 nm [86–92], at which the differences in properties between bound and bulk water are significant. As it was discussed above, the thickness of the interfacial water was estimated to be 0.54±0.10 nm, in cylindrical pores [93]. In micellized sodium soaps, the distance between the carboxylate carbon and the nearest water proton lies around 0.3–0.4 nm [94]. This means that the lower limit of the thickness of the interfacial layer is about one water molecule.

Interfacial water exists in biopolymers in two states: stretched water, which has expanded and increased its local partial molar volume, and compacted water which has decreased its local partial molar volume. Compacted water is in the closest proximity of surfaces. These changes in density are accompanied by changes in water–water hydrogen-bond strength and therefore in all physical and chemical properties of the liquid.

Some results showed that hydrophobic headgroups (phenyl or *n*-butyl) enhance the structure of interfacial water; the main factors are electrostriction by the charged interface and hydrophobic hydration of the bulk group.

Table 1 Degree of structuration of interfacial water by surfactant headgroups [19]

Head group	φ_M
$N^+(C_4H_9)_3Br^-$	1.14
COO^-Na^+	1.08
$N^+(CH_3)_2(C_6H_6)Br^-$	1.06
$N^+(CH_3)_3Cl^-$	1.06
$N^+(CH_3)_3Br^-$	1.06
$SO_4^-Na^+$	1.06
$N^+(CH_3)_2(CH_2)_3\text{–}SO_4^-$	1.02
$N^+(C_2H_4OH)_3Cl$	~ 1
$\text{–}O(C_2H_4O)_{9.5}\text{–}H$	0.95

The fractionation factors φ_M measured by NMR give information about the structuration of interfacial water. If $\varphi_M > 1$, interfacial water is more structured than bulk water. Interactions that decrease surface charge density decrease φ_M because of lower electrostriction by the charged interface. The interaction between the head group and counterion affects the structure of interfacial water. Some examples of decreasing degree of structuration of interfacial water measured by φ_M are given in Table 1.

Based on these data, it may be concluded that ionic and zwitterionic head groups generally increase structuring of interfacial water. Some groups do not change the structure of water, as the tris (2-hydroxyethyl), and with polyoxyethylene groups interfacial water is less structurated than bulk water. The water of hydration of the nonionic surfactant Triton X-100 is less structured than bulk water [95–97]. The same conclusion was attained about the hydration layer of nionionic and zwitterionic micelles by NMR studies [98].

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