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Nonaqueous Surfactant Systems

MARIE SJÖBERG and TORBJÖRN WÄRNHEIM* Institute for Surface Chemistry, Stockholm, Sweden

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I. INTRODUCTION

There has been much interest in studying surfactant aggregation in polar solvents other than water over the last few decades. In a large number of studies various surfactant systems have been mapped and evidence for self-assembly of surfactants in some nonaqueous polar solvents has been published. During the last few years more detailed information on the structure of the aggregates and on the characteristics of the aggregation processes have been provided.

The research on aggregation of surfactants in nonaqueous, polar solvent systems can be motivated, mainly, with two different arguments. First, are the basic considerations of amphiphile aggregation involving a description of the hydrophobic interaction leading to, for example, micelle and liquid crystal formation. What can be learned from comparing water with other polar solvents? Much work has been performed to elucidate those properties of the solvent that are essential in order to obtain a hydrophobic (or “solvophobic”) interaction. Comparisons of critical micelle concentrations in different solvents with parameters characterizing the solvent are numerous in the literature [1,2].

Second, there are technical applications where amphiphile aggregates and structures are needed to promote a specific effect, while circumstances may prevent the particular use of water due to certain reactions, corrosion, or other specific

*Current affiliation: ACO HUD AB Upplands Väsby, Sweden

interactions with water. Of particular interest in this context are, for example, alcohol-based systems for cleaning purposes [3]. Another highly relevant area is that of chemical reactions in an aprotic solvent such as formamide [4–6].

This review deals with the first, fundamental, point, in particular the formation of micelles and the mapping of phase equilibria. This is a logical starting point, since a prerequisite for most applied work in the field is some knowledge of aggregation processes and the relevant phase diagrams.

Methodological questions have often been raised when studying nonaqueous systems, since many early studies on micellization were performed using indirect methods for detecting aggregation [7–14]. This has caused considerable confusion due to apparently irreconcilable results. Also, several studies have pointed out the difference between a proper micellization process and ordinary aggregation. As is discussed in this chapter, depending on the combination of solvent and surfactant [15–18], it is possible to have a cooperative aggregation (micelle formation) as well as a more gradual aggregation process.

II. MICELLAR AGGREGATION

Micellization has been studied in a large number of nonaqueous polar solvents, such as different alcohols, formamide, fused salts [19–26], hydrazine, hydrogen fluoride [27], and *N*-methylsydnone [28,29]. However, most of the early investigations used indirect methods such as surface tension measurements or conductimetry for the detection of surfactant aggregation. More recently, direct methods have been used to prove the existence of aggregates in the solution phase of polar solvent other than water. For example, PGSE-NMR [17], fluorescence spectroscopy [30], and SANS [31] have proven to be powerful methods for probing micelle formation in aqueous and nonaqueous systems.

The nonaqueous polar solvent that has been studied most extensively in this context is probably formamide. Lattes and co-workers have studied the aggregation of surfactants in formamide [32–35]. They have investigated the SDS–formamide and the C₁₆TABr–formamide systems. A sharp rise in solubility of the surfactant with increasing temperature was noted in these systems and interpreted as the Krafft point, i.e., the temperature where the monomeric solubility of the surfactant exceeds the c.m.c. The c.m.c. as well as the Krafft point were found to be considerably higher in formamide than in water for both surfactants. Other studies of surfactant aggregation in formamide, where aggregates were not found, have been performed at temperatures below the Krafft point [36–38]. The C₁₆TABr–formamide system has been widely studied with a number of different techniques, such as NMR relaxation and self-diffusion [18,35,39,40], small-angle x-ray scattering [34], positron annihilation [38], or Raman spectroscopy [41]. Most studies agree that aggregates start to form at considerably higher surfactant concentration than in water and that they are considerably smaller than in water. An aggregate radius of 9 Å was found at a concentration close to the c.m.c. [34], while it was

TABLE 6.1 Interfacial Tension Between Solvent and Hydrocarbon, and Dielectric Constant for the Solvent

Solvent	Interfacial tension ^a (mN/m)	Dielectric constant
Water	50 ^b	78
Glycerol	29.7 ^c	42
Formamide	27.3 ^c	109
Ethylene glycol	17.2 ^c	37
<i>N</i> -methylformamide	12.5 ^c	182

^aAt 20°C.

^bAgainst hexadecane.

^cAgainst dodecane.

Source: From Wårnheim, T. and Jönsson, A., *J. Colloid Interface Sci.*, 125, 627, 1988.

found to be about 15 Å at five times the c.m.c. [18]. This corresponds to an aggregation number of approximately one third of that in water. Aggregate growth with concentration has been verified both in a study of the solvent binding to the aggregates [39] and in a study of the counterion binding [40]. An increase in the micellar size with increasing surfactant concentration was also found in the SDS-formamide system [42].

An investigation of counterion binding of a cationic surfactant, C₁₆TAF, in formamide, ethylene glycol, and water showed that the degree of counterion binding is very different in the different solvents, depending on the dielectric constant of the solvent [40]: high in water and ethylene glycol but lower in formamide. Calculations confirmed that the effects of the dielectric constant (Table 6.1) could account for this trend [40]. This observation supports the study of Binana-Limbele and Zana [15], who found the micelles to be small and highly ionized in formamide.

The aggregation process of cationic and anionic surfactants in formamide has also been studied by SANS [31,43]. For *N*-alkylpyridinium halides, it was found that at an alkyl chain length of 12 carbons, only small, unstructured aggregates are formed while at a chain length of 16 to 20 carbons micelles are sole species. The micelles are smaller and with a higher charge than in water. Moreover, in a study of SDS in formamide it was found that micelles are formed but the mechanism of self-association is in agreement with a multiple equilibrium model rather than a pseudophase model. That is, the aggregates increase in size with surfactant concentration over a large region. The authors of the study conclude that the aggregation process in formamide is analogous to that of short-chained surfactants in water.

Micelles of cationic surfactants have been found to form both in glycerol [44] and in ethylene glycol [18]. The micelle formation of C₁₆PyBr in ethylene glycol and glycerol was studied with surfactant-selective electrodes [45,46]. The monomer concentration could in this way be measured at different total surfactant concentrations, and it was concluded that there is some premicellar aggregation

and that the c.m.c. is not very well defined. The dissociation of C_{16} PyBr micelles in mixtures of water and ethylene glycol has been studied and it was concluded that the degree of counterion association decreases with increasing amount of ethylene glycol in the solvent [47]. This is consistent with earlier estimations of the counterion binding in the water–ethylene glycol system, where conductivity measurements suggested a decrease in counterion association when ethylene glycol was added to the water [48].

For micelles of C_{14} TABr in mixtures of water and ethylene glycol the solvent penetration in the micelles was investigated [30] through the fluorescence anisotropy of different probe molecules residing in different regions of the micelles. When the ethylene glycol–water ratio is increased the microviscosity in the hydrophobic regions of the micelles is constant while the microviscosity at the micellar surface increases. This indicates that the micellar interior does not change but the solvent penetration at the micellar surface increases upon addition of the ethylene glycol cosolvent.

Aggregation of nonionic surfactants in these nonaqueous solvents could, in principle, be more energetically favorable than that of ionic surfactants since, at least in water, the repulsive interaction between the polar head groups is smaller. The values of c.m.c. of different polyethylene glycol alkyl ethers (C_iE_j) have been determined in different nonaqueous solvents [17,49–55]. Different C_iE_j –formamide systems have been investigated using NMR self-diffusion [17]. Micelles are formed but are smaller than in water. In contrast to what is found in water, no micellar growth occurs at high temperatures, high surfactant concentration, or when approaching the lower consolute temperature. The same systems were later examined in a calorimetric study [16], and it was found that the enthalpies of micelle formation of C_iE_j in formamide are much smaller and not as temperature dependent as in water. The aggregation numbers were found to be smaller, and for the $C_{12}E_j$ surfactants the smoothly bended titration curves indicate that the micelle formation extends over a significant concentration region.

Ruiz *et al.* have investigated the micellization of the nonionic surfactant Triton X-100 (*p*-*tert*-octyl-phenoxy(9.5)polyethylene ether) in mixed solvents of water and ethylene glycol [56], or water and formamide [57]. They found that for both solvent combinations there is a decrease in the micellar size, due to a decrease in the micellar aggregation number, with increasing cosolvent concentration. Moreover, the cloud point for the nonionic surfactant was found to increase with addition of formamide or ethylene glycol. This increase in the cloud point can be explained by the increased solubility of the EO chain in the solvent at high temperatures with increasing cosolvent content. A fluorescence study suggested that there is a considerable contact of the cosolvent with the inner region of the micelles for the Triton X-100 surfactant in water–formamide mixtures.

The effect of three alcohols (glycerol, propylene glycol, and 1-propanol) on the surfactant aggregation of $C_{12}E_8$ in water has been studied by Kunieda *et al.* [58].

They observed that addition of propylene glycol or 1-propanol results in smaller micelles and more solvent penetration into the palisade layer of the aggregates. In contrast, in the corresponding system with glycerol the micelles grow in size with increasing glycerol content. Moreover, the cloud point for the nonionic surfactant was found to decrease with increasing glycerol concentration. Both these observations are opposite to what has been found for the nonionic surfactant in formamide or ethylene glycol (higher cloud point and smaller micelles with more cosolvent). Both SAXS and PGSE-NMR results reveal that the addition of glycerol induces dehydration of the EO chain of the surfactant. The consequence of this dehydration is that the surfactant becomes increasingly hydrophobic the higher the glycerol content, which is consistent with larger micelles and lower cloud point upon glycerol addition. This is compared with a “salting-out” effect, i.e., when the added species are depleted from the surfactant film [59].

In a SANS study of the aggregation of nonionic surfactants in water mixed with glycerol or ethylene glycol, Penfold *et al.* [60] found similar differences comparing the two alcohols. With addition of ethylene glycol the cloud point of the surfactant increases, while addition of glycerol causes a reduction of the cloud point. They have also shown that the micellar aggregation number increases for $C_{12}E_8$ when the glycerol concentration increases. This increase in the micellar size is associated with the dehydration of the EO head group, similar to the observations made by Kunieda *et al.* [58].

The aggregation of amphiphilic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymers is in many ways similar to the aggregation of nonionic C_iE_j surfactants. The phase behavior of these block copolymers in nonaqueous polar solvents was first reported by Samii *et al.* [61]. More recently, these systems have been investigated thoroughly by the group of Alexandridis [62–64]. This group has studied the micelle formation of the block copolymer Pluronic P105 ($EO_{37}PO_{58}EO_{37}$) both in pure formamide and in mixed solvents of water and formamide, ethanol, or glycerol. They conclude that micelles are formed in pure formamide but at higher concentration and temperature than in water [62]. Moreover, the enthalpy of micellization is lower in formamide and both the micelle radii and the association numbers are lower in formamide than in water. For the block copolymer in a mixed water and formamide solvent, it was concluded that the polymer volume fractions in both the micelle core and the micelle corona decreased with increasing formamide-to-water ratio [62]. Thus, addition of formamide causes an increased solvation of the micelle core and corona, thereby favoring the formation of smaller micelles.

Comparing micellization behavior in the cosolvents formamide, ethanol, and glycerol, some interesting trends were observed [64]. With formamide or ethanol as cosolvent the micelle formation of Pluronic P105 occurs at higher concentrations and temperatures compared to water without cosolvent. However, for glycerol the results show an opposite trend. The addition of glycerol promotes the formation of

micelles and micellization starts at lower concentrations and temperatures. Also, the micelle association number increases and the polymer volume fraction in the corona increases when the glycerol content is increased (see Figure 6.1). This is similar to the differences found for nonionic surfactants comparing, for example,

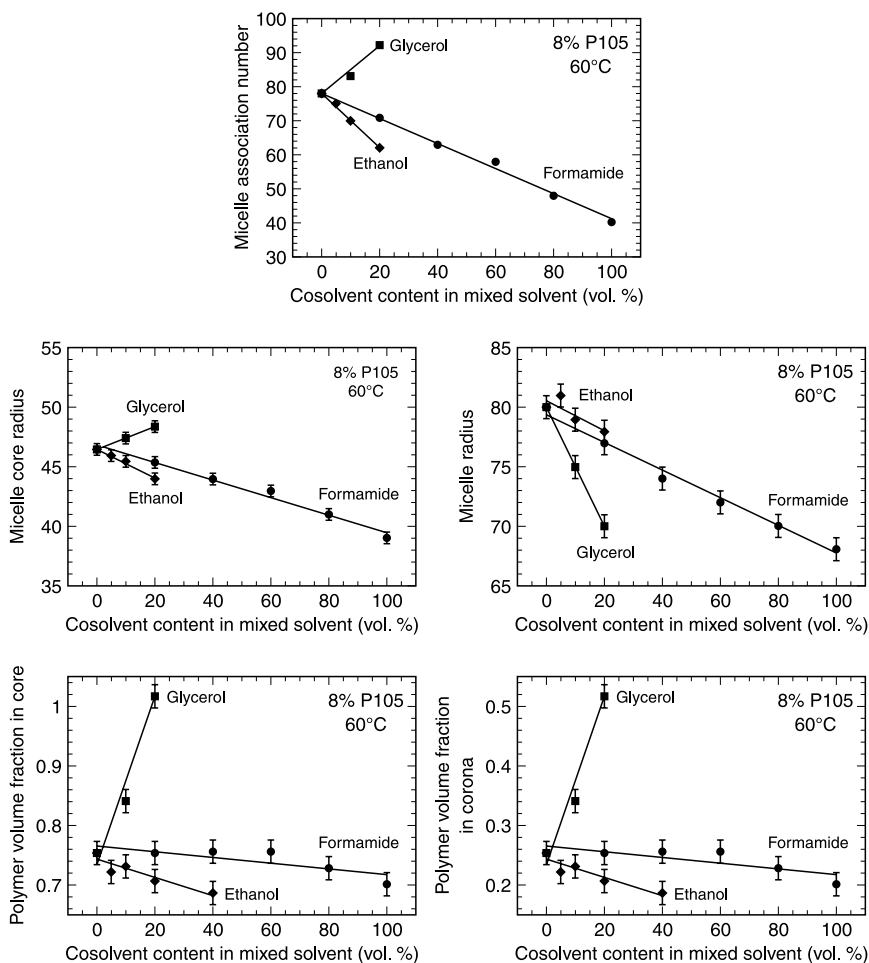


FIG. 6.1 Structural information obtained from SANS for an 8 wt% EO₃₇PO₅₈EO₃₇ solution at 60°C plotted as a function of the cosolvent (glycerol, formamide, or ethanol) content in the mixed solvent. First row: micellar association number ($N_{\text{association}}$); second row: radii of core and core + corona (R_{core} and R_{micelle}); third row: polymer volume fraction of core and corona (α_{core} and α_{corona}). (From Alexandridis, P. and Yang, L., *Macromolecules*, 33, 5574, 2000.)

formamide and glycerol. Consequently, it is probable that the observed differences are due to the dehydration of the EO head groups.

The aggregation of fluorinated surfactants in nonaqueous solvents has also been studied. These surfactants form aggregates at lower concentrations than ordinary hydrogenated surfactants in water. Chrisment *et al.* have studied nonionic fluoro-alkyllipopeptides in DMSO and found progressive and very limited aggregation in this solvent as expected from the low polarity of the solvent [65]. In addition, the lithium salt of nonadecafluorodecanoic acid has been studied with ^{19}F NMR in formamide, *N*-methylformamide, and ethylene glycol [66].

The thermodynamics of micellization in nonaqueous polar solvents have been studied by a number of authors. Important work has been published by Evans *et al.* using hydrazine as solvent [67,68] and later by Ruiz using ethylene glycol as solvent [69]. Both groups conclude that even though both the enthalpic and entropic contributions to the micellization differ substantially comparing water and the other solvent, these effects cancel out in the standard molar Gibbs free energy of micellization. Evans *et al.* could from their work challenge the conventional view that the structural properties of water would be necessary to obtain a driving force for aggregation [67,68].

The experimental work published so far on micelle formation in polar solvents other than water is clearly very extensive. Efforts to use theoretical models to predict the aggregation behavior have been more scarce. However, the group of Nagarajan has reported on theoretical thermodynamic treatment of these systems [70–72]. They could predict some trends that previously have been observed experimentally. For example, they predict an increase in the c.m.c., a decrease in the average micelle size, an increase in the aggregate polydispersity, and a stronger dependence of the aggregation number on the total surfactant concentration for nonaqueous solvents compared with water (see Figure 6.2). Also, they conclude that:

1. The high c.m.c. values in nonaqueous solvents are mainly due to the smaller magnitude of the surfactant tail transfer free energy to the nonaqueous solvent compared to water.
2. The small aggregation numbers in nonaqueous solvents originate mainly from the smaller magnitude of the hydrocarbon–solvent interfacial tension compared to water.
3. Neither the c.m.c. nor the micellar size is affected to any great extent by the lower dielectric constant of the nonaqueous solvent compared to water.

It is evident from all these experimental and theoretical investigations that micelles are formed in a selection of nonaqueous, polar solvents but that the aggregates, comparing the same surfactant, are generally smaller than in water. There is consequently a larger contact between the inner regions of the micelles and the solvent in these small aggregates. In the nonaqueous solvents investigated

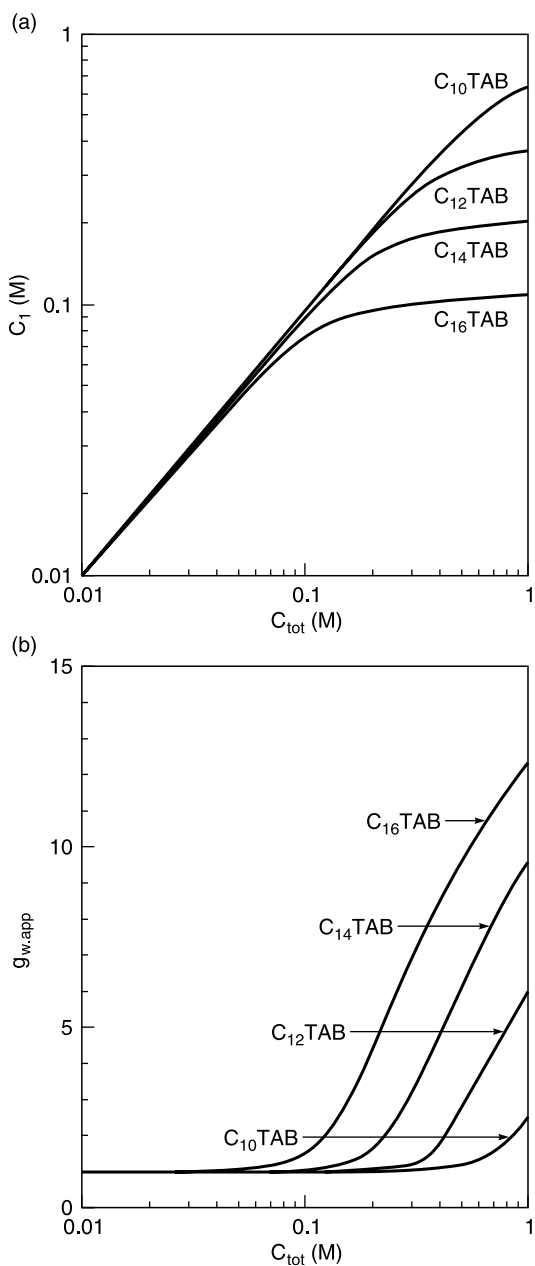


FIG. 6.2 Calculated dependence of (a) the monomer concentration C_1 and (b) the weight average aggregation number g_w on the total surfactant concentration C_{tot} for decyl, dodecyl, tetradecyl, and cetyl trimethylammonium bromides in ethylene glycol solutions. (From Nagarajan, R. and Wang, C.-C., *J. Colloid Interface Sci.*, 178, 471, 1996.)

the interfacial tension between solvent and hydrocarbon is smaller (Table 6.1) and smaller aggregates are thus less energetically unfavorable from this point of view. Also, the micelles are generally formed at higher surfactant concentrations and the micelle formation extends over a significant concentration region. However, there is one exception to this trend, i.e., the aggregation of nonionic C_jE_j surfactants or nonionic block copolymers ($EO_iPO_jEO_i$) in glycerol. In mixtures of glycerol and water the micellization starts at lower concentrations and temperatures, the aggregates grow in size, and the cloud point decreases with increasing glycerol content of the solvent. This has been explained by the dehydration of the EO groups with increasing glycerol content.

III. CONCENTRATED SURFACTANT SYSTEMS

A. Liquid Crystals

The first report on a nonaqueous lyotropic liquid crystal in a polar solvent appeared in 1979, where Friberg and co-workers revealed the existence of a lamellar (D) phase in the lecithin (dialkylphosphatidylcholine)–ethylene glycol system [73]. In a series of papers a large number of lecithin–diol systems have been characterized, and detailed structural properties of the systems have been elucidated [74–81]. The interlayer distance in the D-phase with ethylene glycol is shorter than in water, indicating an enhanced disorder in the lipid layers [73]. It was suggested that the primary solvation shell of the phosphatidylcholine group contains one bound solvent molecule per polar head group, with several more loosely associated, as determined by 2H NMR measurements [74,76]. Extensive phase studies reveal that lecithin readily forms D-phases with the homologous series of α,ω -diols, from ethylene glycol up to 1,7-heptanediol, although the swelling decreases with increasing molecular size of the solvent [75]. Oligomers and polymers of EO [79] and polyethylene glycol alkyl ether also form D-phases with lecithin, the latter as mixed lamellae containing the acyl part of the lecithin and the alkyl chain of the ethers [81].

The existence of a lamellar phase with lecithin has also been demonstrated for ethylammonium nitrate [82]. For lecithin and formamide, *N*-methylformamide, or *N,N*-dimethylformamide, the full phase diagrams have been determined [83] showing a gradual disappearance of liquid crystalline phases with increasing methylation of the solvent (Figure 6.3). The lamellar phase is stable with *N*-methylformamide, but disappears with *N,N*-dimethylformamide.

To summarize, the lecithin studies provide a qualitative picture of how the solvent affects the phase behavior for a zwitterionic surfactant with a large hydrophobic moiety. Lecithin forms lamellar lyotropic liquid crystals with a wide variety of solvents; a sufficiently hydrophilic solvent — and indeed even amphiphilic compounds with a hydrophilic moiety — stabilizes lamellar phases.

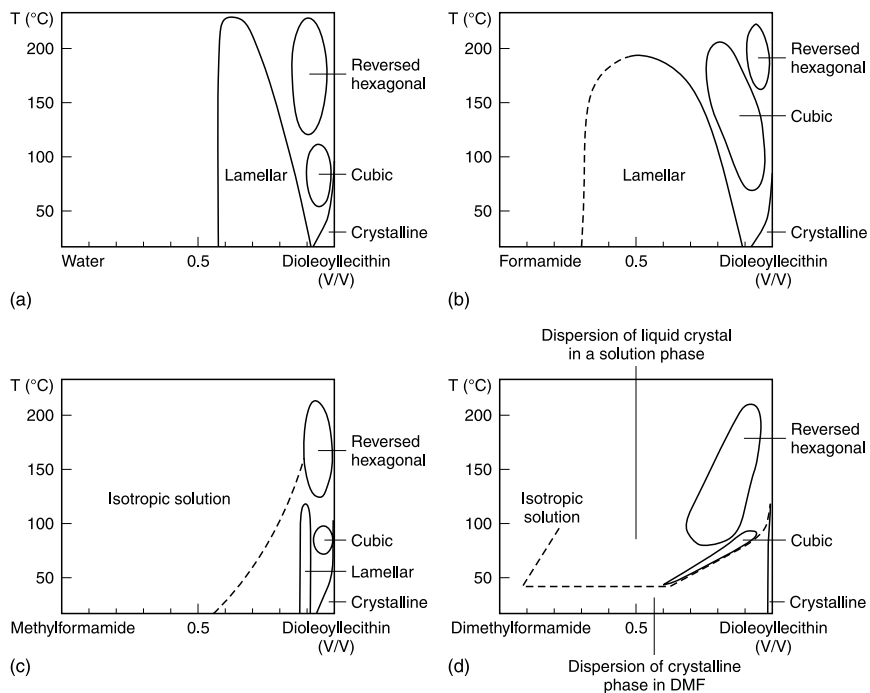


FIG. 6.3 Phase diagrams of dioleoyllecithin and (a) water, (b) formamide, (c) methylformamide, and (d) dimethylformamide. For notation, see Section V. (From Bergenstål, B.A. and Stenius, P., *J. Phys. Chem.*, 91, 5944, 1987.)

Full and partial phase equilibria have also been determined for a large number of systems with ionic surfactants, and there are numerous reported combinations of surfactant and solvent that form liquid crystals. The first reported liquid crystal formed in a binary system containing a single-alkyl-chain ionic surfactant was for the $C_{16}TABr$ –formamide system. $C_{16}TABr$ forms hexagonal, cubic, and lamellar phases in formamide, in analogy with the aqueous system [84–88]. The liquid crystals form at higher temperatures and melt at lower temperatures than in water. The melting point of solvated crystals can be lowered by addition of alcohol cosurfactants, as in the aqueous systems, which would be of importance in different technical applications [89]. $C_{16}TABr$ and the homologous series of alkyltrimethylammonium bromides have been extensively characterized, and there are reports of liquid crystals formed in glycerol [86], ethylene glycol [86], mixtures of ethylene glycol and water [90], and *N*-methylsydnone [91,92] (Figure 6.4).

An extensive comparison between the aggregation of $C_{16}TABr$ and $C_{16}PyBr$ in a series of solvents, formamide, *N*-methylformamide, *N,N*-dimethylformamide,

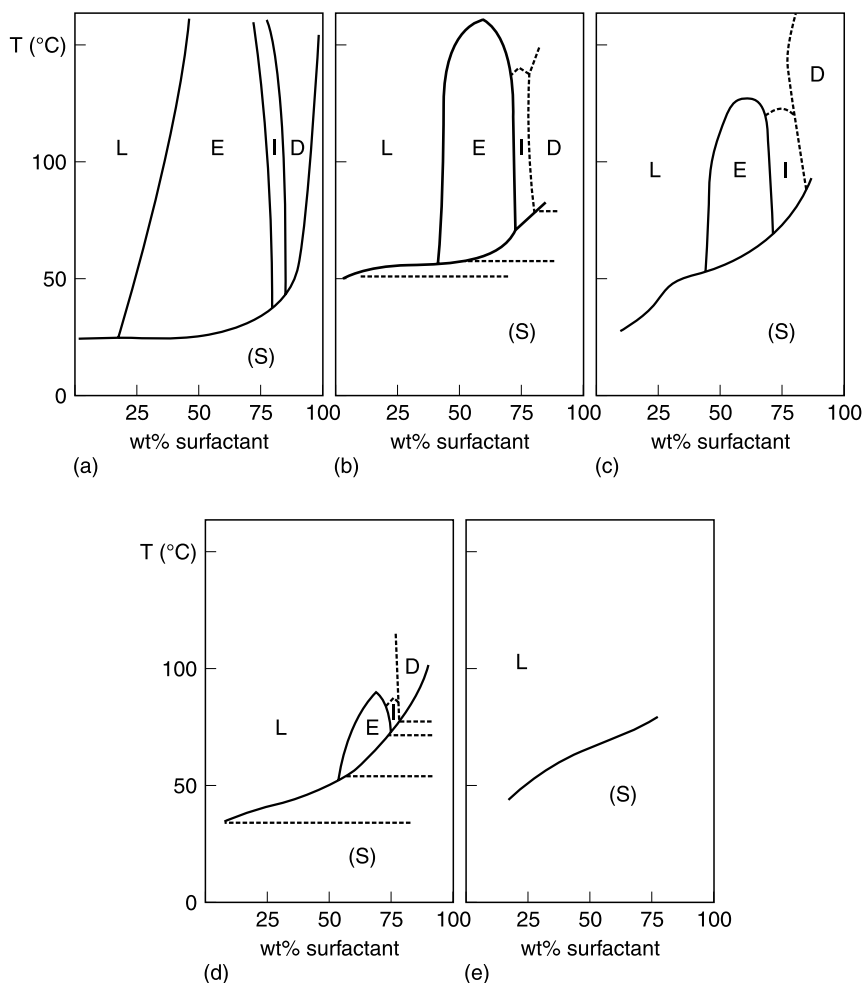


FIG. 6.4 Phase diagrams of $C_{16}TABr$ and different solvents: (a) water, (b) glycerol, (c) formamide, (d) ethylene glycol, and (e) methylformamide. For notation, see [Section V](#). (From Auvray, X., Anthore, P., Petipas, C., Rico, I., and Lattes, A., *C. R. Acad. Sci. Paris*, 306, 695, 1988; Wörnheim, T. and Jönsson, A., *J. Colloid Interface Sci.*, 125, 627, 1988.)

glycerol, ethylene glycol, or *N*-methylsydnone, revealed some interesting differences between the surfactants. With formamide, ethylene glycol, and glycerol, the phase sequence was $E \rightarrow I \rightarrow D$ for both surfactants, and with *N,N*-dimethylformamide, the least polar solvent, only D-phases formed. However, only $C_{16}PyBr$ showed the sequence $E \rightarrow I \rightarrow D$ with *N*-methylformamide and *N*-methylsydnone [91,92].

Considering solely the phase diagram, the main effect of exchanging water for a more weakly polar solvent in these systems is to decrease their existence regions. In addition to that, more subtle phenomena may occur in the nonaqueous systems. It has been demonstrated that for alkylpyridinium chlorides and bromides in glycerol and formamide, cubic phases can occur intermediate to the L_1 - and E-phase region, where they are not stable in water [93].

E-, I-, and D-phases have been observed in the SDS-formamide system. In other solvents, ethylene glycol, glycerol, *N*-methylformamide, only a D-phase is formed at high surfactant concentrations with SDS [94].

Binary phase diagrams of the homologous series of potassium soaps (with alkyl chain length C_{12} – C_{22}) and ethylene glycol, butylene glycol, or glycerol have been determined [95]. Extensive structural investigations of the different phases using x-ray diffraction have been performed [96].

The nonaqueous systems also form liquid crystals analogous to aqueous systems in ternary systems with an added weakly hydrophilic component. SDS has been extensively employed in studies of ternary and quaternary systems with glycerol or formamide, a long-chain alcohol, and, sometimes, hydrocarbon [97–101]. In the SDS-glycerol-decanol system the lamellar phase swells extensively, even more so than in water [97]. While no liquid crystals form at room temperature in the binary systems, a D-phase occurs when decanol is added.

Aerosol OT (sodium diethylhexylsulfosuccinate) is another extensively studied ionic surfactant. This surfactant forms a lamellar and cubic phase with formamide [103] and glycerol [104], just as with water. With ethylene glycol and *N*-methylformamide, no liquid crystals except the inverse hexagonal occur [103].

In contrast, for a solvent such as propylene glycol, which has a less polar character, no liquid crystals are formed even for ionic surfactants with a reasonably large hydrophobic moiety such as didodecyldimethylammonium bromide [105].

The formation of liquid crystals by nonionic surfactants of the polyethylene glycol alkyl ether type, C_iE_j , has been much less considered. Phase diagrams of $C_{12}E_3$, $C_{12}E_4$, $C_{16}E_4$, $C_{16}E_6$, and $C_{16}E_8$ with formamide as solvent have been determined [17]. No liquid crystals are stable for the $C_{12}E_j$ surfactants; however, there is a clouding, a lower consolute temperature, in the $C_{12}E_3$ system [17]. The $C_{16}E_j$ series follow the same trend as the aqueous systems [107]: $C_{16}E_4$ gives a D-phase, $C_{16}E_6$ an E-phase, and $C_{16}E_8$ an I-phase, most likely of the I_1 type. As with ionic surfactants, the existence regions of the liquid crystalline phase are smaller, and there are fewer phases present, comparing formamide with water as solvent [17,107]. For $C_{12}E_8$, the phase diagrams with glycerol, propylene glycol, and propanol as solvents together with water show that no liquid crystalline phases are stable at volume fractions of polar cosolvent above 0.5 [108].

More recently, investigations of the solution behavior of block copolymers of the poly(ethylene oxide) (PEO)–poly(propylene oxide) (PPO) type have been extended to nonaqueous, polar solvent systems. The block copolymer Pluronic

P105 ($\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$) forms a variety of liquid crystalline phases (micellar cubic, hexagonal, bicontinuous cubic, and lamellar phase with increasing polymer concentration) in formamide [109] (Figure 6.5). Investigations on the aggregation behavior of Pluronic 105 in other solvents or solutes (ethanol, glycerol, propylene glycol) show that the formation of liquid crystals is limited to formamide.

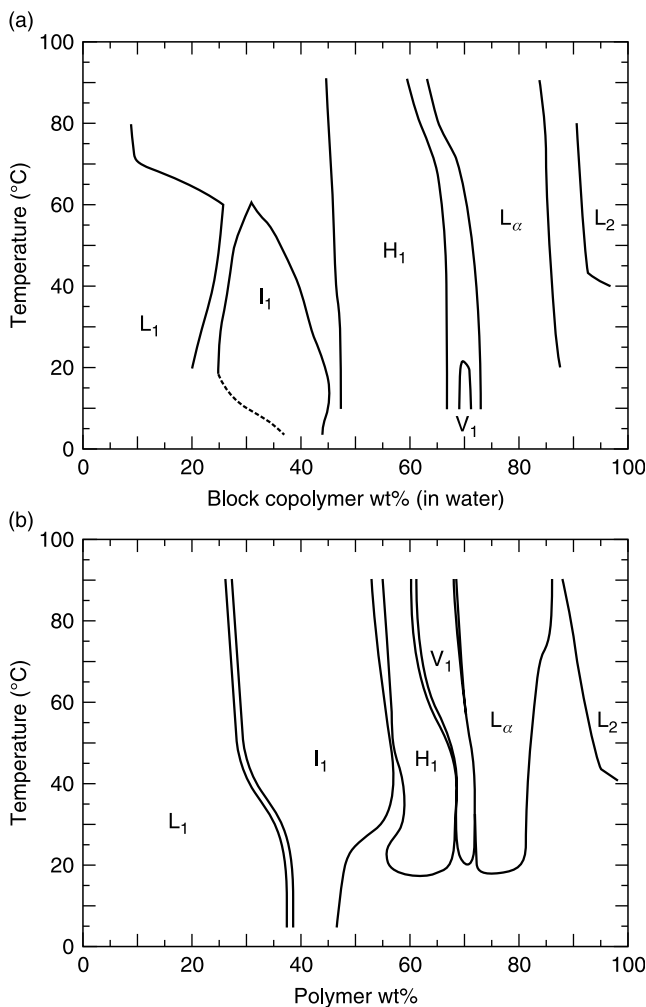


FIG. 6.5 Binary phase diagrams of (a) Pluronic 105 ($\text{EO}_{37}\text{PO}_{58}\text{EO}_{37}$)–water and (b) Pluronic 105–formamide. For notation, see Section V. (From Alexandridis, P., *Macromolecules*, 31, 6935, 1998; Ivanova, R., Lindman, B., and Alexandridis, P., *Adv. Coll. Interface Sci.*, 89–90, 351, 2001.)

Some interesting features are found for the lattice parameters and aggregate dimensions derived from SAXS for the liquid crystalline phases when gradually exchanging water for another polar solvent. Cosolvents that are shown to have a smaller effect on the lattice parameters (e.g., propylene glycol) will maintain the microstructure and stability of the phase up to high cosolvent-to-water ratios [110]. The block copolymers could be of particular practical relevance for different applications, e.g., within the pharmaceutical area. This prompts investigations of cosolvent–water systems that are acceptable in this context [110,111].

Monoglycerides form an inverse hexagonal phase with glycerol, as in water [112]. Mixtures of triethanolamine and oleic acid form a nonaqueous lamellar liquid crystal with a surfactant bilayer of soap and acid with intercalated ionized and unionized alkanolamine as solvent [113,114]. Lamellar liquid crystals form analogously with dodecylbenzenesulfonic acid and triethanolamine [115].

These and other systems reported to contain a nonaqueous liquid crystalline phase are summarized in [Table 6.2](#).

B. Microemulsions

The first reports on nonaqueous microemulsions, isotropic solutions containing a hydrophilic and a lipophilic component, stabilized by a surfactant, were made by Palit and McBain in 1946 [116] and by Winsor in 1948 [117]. They both used glycols as polar solvents. The microemulsion regions were only observed visually so no structural information could be obtained.

Three groups reported independently the observation of microemulsions with nonaqueous polar solvents in 1984. The group of Lattes found microemulsions in the $C_{16}TABr$ –formamide–cyclohexane system with butanol as cosurfactant [118–120] while Friberg and Podzimek detected a narrow microemulsion region in the lecithin–ethylene glycol–decane system [121] ([Figure 6.6](#)). The third group investigated glycerol in heptane microemulsions, with AOT as surfactant [122], using dynamic light scattering to study the aggregation.

Lattes and co-workers have investigated the $C_{16}TABr$ –formamide–butanol system with cyclohexane or isooctane as an oil component [118–120]. In both of these systems, conductivity measurements with varying composition were interpreted as indicative of percolation. When an x-ray scattering study was conducted on the latter system, no discrete droplets could be detected. When increasing the hydrocarbon volume of the surfactant by using didodecyldimethylammonium bromide ($(C_{12})_2DABr$), microemulsions form without cosurfactant in formamide and in ethylene glycol using dodecane and toluene as oil [102].

Fletcher *et al.* have investigated the glycerol-in-oil microemulsion stabilized by $C_{16}TABr$ using a mixture of *n*-heptane and chloroform as oil with dynamic light scattering, giving a hydrodynamic radius of reverse micellar aggregate, glycerol droplets, and an area per surfactant head group [123].

TABLE 6.2 Nonaqueous Lyotropic Liquid Crystalline Phases Reported in the Literature

Surfactant	Solvent	Additive	Phases detected ^a	Ref.
Lecithin	EG		D	73
Lecithin	1,3-Propanediol		D	75
Lecithin	1,4-Butandiol		D	75
Lecithin	1,5-Pentanediol		D	75
Lecithin	1,6-Hexanediol		D	75
Lecithin	1,7-Heptanediol		D	75
Lecithin	(EG) ₁₋₄		D	79
Lecithin	PEG		D	79
Lecithin	C ₁₂ E _j		D	81
Lecithin	EAN		D	82
Lecithin	FA		D, I, F	83
Lecithin	MFA		D, I, F	83
Lecithin	DMF		I, F	83
Lecithin	EG	Methanol	D	80
Lecithin	EG	Decanol	D	80
Lecithin	EG	Decane	D	80
C ₁₆ TABr	FA		E, I, D	84-87
C ₁₆ TABr	G		E, I, D	86, 87
C ₁₆ TABr	EG		E, I, D	86
C ₁₆ TABr	MFA		D	91, 92
C ₁₆ TABr	NMS		D	91, 92
C ₁₆ TABr	EG	Decanol	D	102
C ₁₆ TACl	FA		I, E...	91, 92
C ₁₆ TASO ₄	EG		E, D	86
C ₁₄ TABr	G		E, I, D	86
C ₁₄ TABr	EG		E, D	86
C ₂₀ PyBr	FA		...I...	93
C ₁₈ PyBr	FA		...I...	93
C ₁₆ PyCl	FA		I, E, I...	91-93
C ₁₆ PyCl	G		E, I, D	93
C ₁₆ PyCl	MFA		E, I, D	91, 92
C ₁₆ PyCl	DMF		D	91, 92
C ₁₆ PyCl	EG		E, I, D	91, 92
C ₁₆ PyCl	NMS		E, I, D	91, 92
SDS	FA		E, I, D	94
SDS	FA	Decanol	D	97
SDS	FA-H ₂ O	Decanol	D (E)	124
SDS	FA	Decanol + toluene	D	97
SDS	G		D	94
SDS	EG		D	94
SDS	MFA		D	94
SDS	G	Decanol	D	97

(continued)

TABLE 6.2 (Contd.)

Surfactant	Solvent	Additive	Phases detected ^a	Ref.
KC ₂₂	G		E, D	95
KC ₁₈	G		E, I, D	95
KC ₁₆	G		E, D	95
KC ₁₄	G		E, I, D	95
KC ₁₂	G		E, D	95
KC ₂₂	EG		E, D	95
KC ₁₈	EG		E, I, D	95
KC ₂₂	BG		D	95
KC ₁₈	BG		I, D	95
AOT	FA		D, I, F	103
AOT	G	Decanol	D...	104
AOT	G	Decane	D...	104
AOT	G	<i>p</i> -Xylene	D...	104
TEAOI	TEA	G, EG	D	113, 114
DBSA	TEA	G, EG, TEG	D	115
C ₁₆ E ₄	FA		D	17
C ₁₆ E ₆	FA		E	17
C ₁₆ E ₈	FA		I, E	17

Note: For notation, see [Section V](#).

^aEllipses indicate that the entire phase diagram has not been investigated.

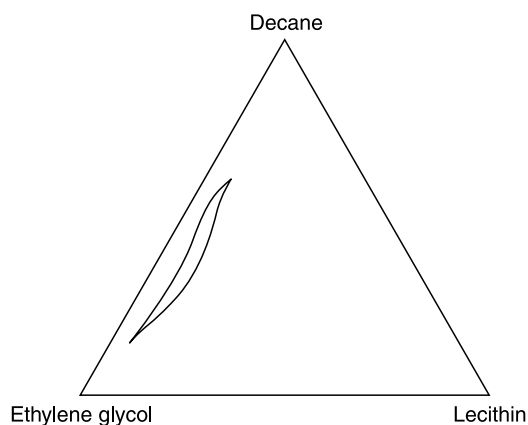


FIG. 6.6 Phase diagram of the lecithin-ethylene glycol-decane system at 25°C, showing a narrow microemulsion region. (From Friberg, S.E. and Podzimek, M., *Colloid Polym. Sci.*, 262, 252, 1984.)

Friberg and co-workers have studied a number of SDS-stabilized formamide microemulsions using different hydrocarbons and cosurfactants [124–126]. The system containing toluene and hexanol showed a microemulsion region but from light scattering studies it was concluded to be a nonstructured solution [125]. However, when increasing the alkyl chain length of the alcohol to decanol two isotropic solutions could be observed; the formamide solution gave no indication of an organized structure, but in the decanol solution the results were interpreted in terms of inverse micelles [126].

Ceglie and co-workers examined different microemulsions using SDS and formamide but changing the oil to *p*-xylene and using alcohols of different alkyl chain length, going from pentanol to octanol [37,127–129]. Both ternary and quaternary systems were investigated with two different NMR techniques: self-diffusion and frequency variable relaxation measurements. The self-diffusion study gave no indications of any organized structures, but from relaxation measurements a fraction of the SDS molecules was observed to aggregate into some interfacial domains when octanol was used as cosurfactant. Solution regions were observed with methylformamide and dimethylformamide as polar component and octanol as cosurfactant, but the phases were found to be nonaggregated solutions [37,127].

Another polar solvent that has been used in SDS-stabilized microemulsions is glycerol. Hexanol or decanol have been used as cosurfactants and systems both with and without oil have been studied. The ternary system with hexanol as cosurfactant was examined with SANS and NMR self-diffusion measurements by two different groups and both found the microemulsions to be structureless solutions [130,131]. Similar behavior was found from a self-diffusion study of the quaternary systems with *p*-xylene or decane as the oil component [131,132].

AOT-glycerol microemulsions have been carefully studied by two different groups: that of Friberg and that of Robinson. The former group studied ternary phase diagrams with decanol, decane, or *p*-xylene as the third component and isotropic solution phases were detected in all systems [104]. The latter group studied two other ternary systems with heptane or octane as the third component [122,133]. Reverse micelles with glycerol were found in both systems using dynamic light scattering for the heptane system and quasielastic neutron scattering for the octane system. AOT microemulsions have been the subject for additional investigations with formamide as polar solvent and isooctane or decane as an oil component [134–137]. Light scattering and steady-state adsorption spectra of the molecular probe Coumarin 343 were interpreted in terms of the formation of reverse micelles not only in formamide but also in a variety of less polar solvents such as methanol and acetonitrile [134]. The effects due to the molecular size of the probe have also been considered [135], effects that will be of importance in restricted systems [136].

Nonaqueous microemulsions with nonionic surfactants have been studied. The $C_{12}E_4$ surfactant was found to stabilize microemulsions of formamide and dodecane [138]. The ternary phase diagrams were studied at different temperatures and the solubilization of hydrocarbon was shown to be very temperature dependent (Figure 6.7). It was also observed that the temperature intervals of the three-phase regions are dependent on the hydrocarbon used; larger aliphatic hydrocarbons

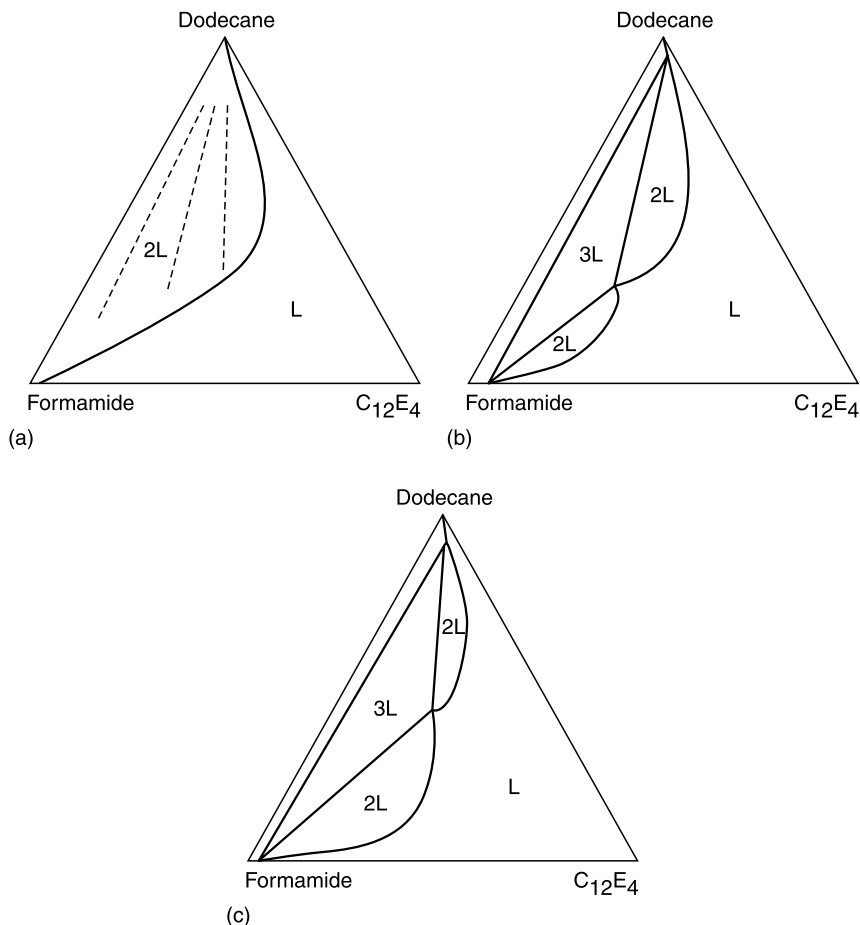


FIG. 6.7 Phase diagrams of the $C_{12}E_4$ -formamide-dodecane system at (a) 30°C, (b) 40°C, and (c) 50°C, showing the growth of the three-phase region where a solution phase is formed at minimum surfactant concentration. (From Wärnheim, T. and Sjöberg, M., *J. Colloid Interface Sci.*, 131, 402, 1989.)

give three-phase regions at higher temperatures, observations completely analogous to the corresponding aqueous systems. In a SANS study Schubert and Strey [139] investigated the order/disorder transition in microemulsions of nonionic surfactants, water-formamide mixtures, and oil. As the water content of the systems was decreased a more disordered microstructure was observed. However, even with pure formamide as polar solvent, the existence of internal interfaces, although uncorrelated, could be detected. Studies using NMR self-diffusion measurements and SANS in microemulsions formed with C₁₂E₅-propylene glycol and/or glycerol-alkane are interpreted in terms of droplet structures at low oil contents which through a percolation form an oil continuous structure [140].

As a brief conclusion it can be noted that many nonaqueous microemulsions reported do not seem to contain an organized structure, being simply molecular solutions. Since the degree of organization already in many aqueous microemulsion is low, in particular for quaternary systems containing ionic surfactant and cosurfactant, this is not really surprising.

IV. CONCLUDING REMARKS

Evidently, the mapping of surfactant aggregation in nonaqueous polar solvents has grown to be very extensive, and investigations of many different combinations of surfactants and solvents are available in the literature. Furthermore, a wide range of experimental techniques have been used. The results from different studies are quite consistent and most of the authors agree on some basic trends.

Qualitatively, the general aggregation behavior is similar to water. That is, surfactant aggregation in the form of micelles, liquid crystals, or microemulsions is possible in polar solvents other than water. However, the Krafft temperatures of ionic surfactants and c.m.c. values are higher and the aggregation numbers of the micelles are lower in these nonaqueous solvents. The existence regions for liquid crystal phases in nonaqueous solvents are reduced and the phase diagrams are less complex than in water. Also, the microemulsions formed in nonaqueous solvents have often a more disordered microstructure than in water. It is tempting, in a qualitative manner, to ascribe these differences to the less extensive solvophobic interaction in the polar solvents used compared to water.

There are other ways of expressing and discussing this solvophobic interaction than, for example, comparing the interfacial tensions between solvent and hydrocarbon as in Table 6.1. The nonaqueous solvents that have been reported to promote aggregation of surfactant molecules have one property in common: they all have high cohesive energy. That is, the net attractive interactions between the solvent molecules are strong. Hildebrand *et al.* [141] have derived a cohesive energy parameter from the heat of vaporization of the solvent. Another measure of the cohesive energy is the Gordon parameter [142], $\gamma/V^{1/3}$ (γ = surface tension,

V = molar volume). This parameter has the advantage that it can be used for both liquids and fused salts.

Different authors [15,143] have tried to determine a limiting value for the cohesive energy of the solvent above which a certain solvent should be able to promote surfactant aggregation. However, it is curiously often overlooked that the hydrophobicity of the surfactant must also be taken into account in this context. A surfactant with a long hydrocarbon chain or a fluorinated hydrocarbon chain will be able to aggregate in solvents where a less hydrophobic surfactant will remain in monomeric form, just as in water.

V. NOTATION

AOT	Aerosol OT (sodium diethylhexylsulfosuccinate)
(C ₁₂) ₂ DAB	Didodecyldimethylammonium bromide
C _{<i>i</i>} E _{<i>j</i>}	Nonionic surfactant of the polyethylene glycol alkyl ether type; the alkyl chain contains <i>i</i> carbon atoms and the polar group <i>j</i> ethylene glycol units
c.m.c.	Critical micelle concentration
C _{<i>x</i>} NH ₃ Br	Cationic surfactant of the alkylammonium bromide type; the alkyl chain contains <i>x</i> carbon atoms
C _{<i>x</i>} PyBr	Cationic surfactant of the alkylpyridinium bromide type; the alkyl chain contains <i>x</i> carbon atoms
C _{<i>x</i>} TABr	Cationic surfactant of the alkyltrimethylammonium bromide type; the alkyl chain contains <i>x</i> carbon atoms
C _{<i>x</i>} TASO ₄	Cationic surfactant of the alkyltrimethylammonium sulfate type; the alkyl chain contains <i>x</i> carbon atoms
CTbPB	Cetyltributylphosphonium bromide
D	Lyotropic liquid crystalline phase with lamellar structure
DBSA	Dodecylbenzene sulfonic acid
DMF	<i>N,N</i> -dimethylformamide
DMSO	Dimethylsulfoxide
E	Lyotropic liquid crystalline phase with hexagonal structure
EAN	Ethylammonium nitrate
EG	Ethylene glycol
EO	Ethylene oxide
F	Lyotropic liquid crystalline phase with reverse hexagonal structure
FA	Formamide
G	Glycerol
H	Lyotropic liquid crystalline phase with hexagonal structure (cf. E)
I	Isotropic liquid crystalline phase (used for structures with discrete aggregates) (cf. V)

KC _x	Potassium soap with <i>x</i> carbon atoms in the alkyl chain
L _α	Lyotropic liquid crystalline phase lamella structure (cf. D)
MFA	<i>N</i> -methylformamide
NaOl	Sodium oleate
NMS	<i>N</i> -methylsydnone
PEG	Polyethylene glycol
PG	Propylene glycol
PGSE NMR	Pulsed gradient spin echo NMR for self-diffusion measurements
PO	Propylene oxide
SANS	Small-angle neutron scattering
SAXS	Small-angle x-ray scattering
SDS	Sodium dodecyl sulfate
TEA	Triethanolamine
TEAOI	Triethanolammonium oleate
TEG	Triethylene glycol
V	Isotropic liquid crystalline phase (used for bicontinuous structures)

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