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Hydrotropy

STIG E. FRIBERG and IRENA BLUTE Institute for Formulation Science, University of Southern Mississippi, Hattiesburg, Mississippi and YKI, Institute for Surface Chemistry, Stockholm, Sweden

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I. INTRODUCTION

Hydrotropes are an essential ingredient of cleaning and laundry products, serving to reduce excessive thickening of the former and to improve the dirt-removing action of the latter.

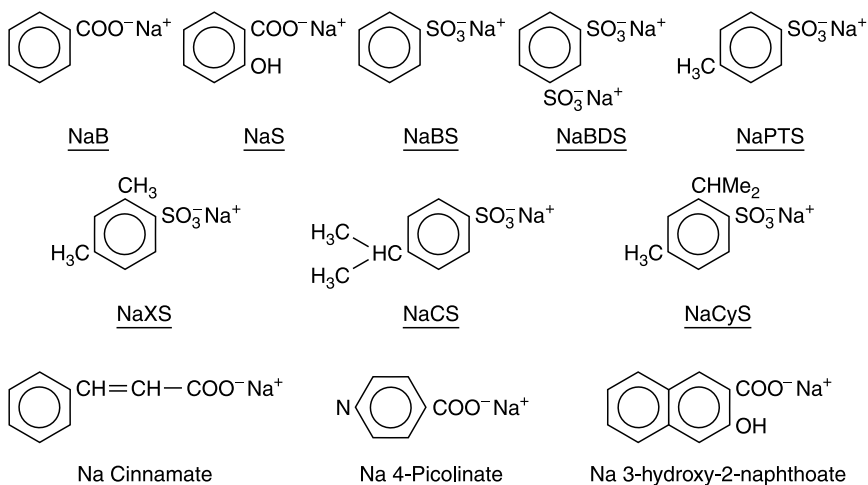
This chapter provides a short review of the early development in the knowledge of the function of these compounds. This is followed by a discussion of the fundamentals of their action and a section devoted to phenomena specific to their action in cleaners and detergents.

II. HISTORICAL REVIEW

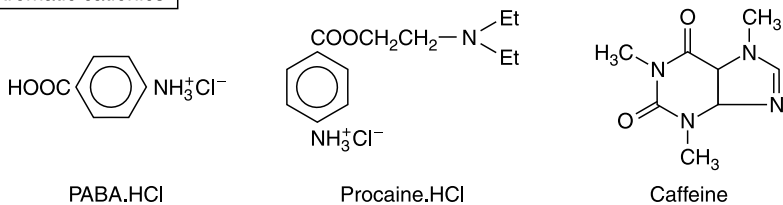
Hydrotropes are molecules traditionally with a structure of a short hydrocarbon chain, often aromatic, combined with a polar group that in the early days of their development was ionic. [Figure 2.1](#) shows a few typical structures of these kinds of molecules and in addition gives examples of more recent developments.

The historical development of the science of these molecules has been amply described [1–3] and the following treatment is, hence, condensed. The evolution of knowledge of these compounds and their action may be characterized as taking place in three distinct periods, the first of which was the introduction by Neuberg in 1916 [4,5]. Neuberg described the hydrotropes as compounds enhancing the solubility of organic compounds in water and investigated a large number of them.

Aromatic anionics



Aromatic cationics



Aromatic nonionics



Aliphatics and linear anionics

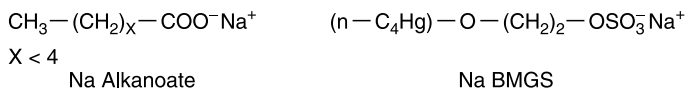


FIG. 2.1 Structure of some hydrotropes.

The next period came 30 years later with efforts geared toward chemical engineering focusing on applied aspects. McKee [6] noted that hydrotrope solutions during dilution have a tendency to separate the dissolved compound leaving the hydrotrope in the aqueous solution to be used anew for extraction purposes. In addition, during this period the structure of hydrotrope solutions and the specific mechanism of the enhanced solubility were the aim of an initial discussion with Lumb [7] advocating the view that the enhanced solubility is due to solubilization: a well-known colloidal phenomenon in surfactant solutions. Licht and Wiener [8] supported the view of McKee in describing the enhanced solubility as a “salting-in” effect.

The third period came when Lawrence [9], Friberg and Rydhag [10], and Pearson and Smith [11] presented phase diagrams for hydrotrope solutions. The interpretation of the results from the determination of phase diagrams [10] introduced a new view of the hydrotrope solubilizing action. Instead of the earlier attempts to relate the increased solubility to the association of the hydrotrope molecules *per se*, the results showed that the superior solubilization in a hydrotrope solution compared to that in a surfactant solution (Figure 2.2) is in fact an outcome of the hydrotrope action on the colloidal association structure of surfactants. The very large solubilization of a hydrophobic amphiphile, octanoic acid, in a hydrotrope solution is caused by the influence of the hydrotrope molecule on the packing conditions in colloidal association structures, especially a lamellar liquid crystal (Figure 2.3). In fact the hydrotrope molecule was seen as an entity that would not only be unsuited to form such a liquid crystal, but actually by its presence would prevent the formation. This result has had a bearing on the practical applications of hydrotropes, which will be briefly discussed in the following paragraphs.

Many studies of these applications have been reported reflecting the importance of these compounds in the commercial realm. Among the recent examples of new molecules with hydrotropic action may be mentioned vitamin C [12], useful for sunscreen formulations [13,14]. Other hydrotropes reported as new are diisopropylnaphthalene sulfonates [15], while the application of hydrotropes to solubilize pharmaceuticals continues to be extensive [16–24]. Long-chain amphiphiles [25] and polymers [26] have been shown to exert hydrotropic action under certain conditions. Among the most recent developments should be mentioned the alkyl polyglucosides as hydrotropes [27]. They have been shown to be useful in strongly alkaline systems [28].

Investigations using hydrotrope solutions in reaction kinetics have varied from the direct analysis of the influence on the kinetics by the solubilization *per se* [29] of aromatic esters to more elaborate reaction systems. Microwave heating was early shown as an efficient way to enhance organic reactions [30,31]. However, the use of common organic solvents causes environmental problems in connection with microwave heating and aqueous solutions offer safe and convenient

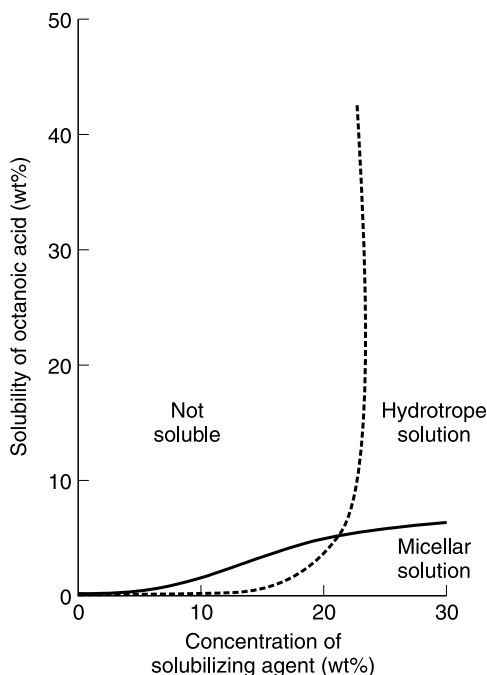


FIG. 2.2 Solubilization of octanoic acid into an aqueous micellar solution of a surfactant, sodium octanoate (—), is limited, while the solubilization into a corresponding hydrotrope (sodium xylenesulfonate) solution (---) is very large at high concentrations of the hydrotrope.

reaction media as demonstrated by the Hantzsch dihydropyridine ester synthesis [32]. Hydrotrope solutions also offer a useful medium in the scale-up process [33]. In addition, hydrotrope solutions have been involved in reactions concerning solid particles. As examples may be mentioned the template-free synthesis of microtubules [34], important materials in nano-technology, and the more sophisticated role of hydrotropes to concurrently optimize the interfacial tension and the colloidal stabilization of rhodium particles in biphasic liquid–liquid alkene hydrogenation catalysis [35]. Finally reaction kinetics has been used as a means to follow the association of hydrotrope molecules in aqueous solutions [36].

The use of hydrotrope solutions for extraction was introduced by McKee [6] (Figure 2.4). More recent studies have been concerned with optimization [37] and with the separation of *o*- and *p*-chlorobenzoic acids [38–40]. The latter separation is excellent even for eutectic mixtures of the two compounds [39]. Results such as these may at first lend support to an earlier suggestion [41] of complex formation

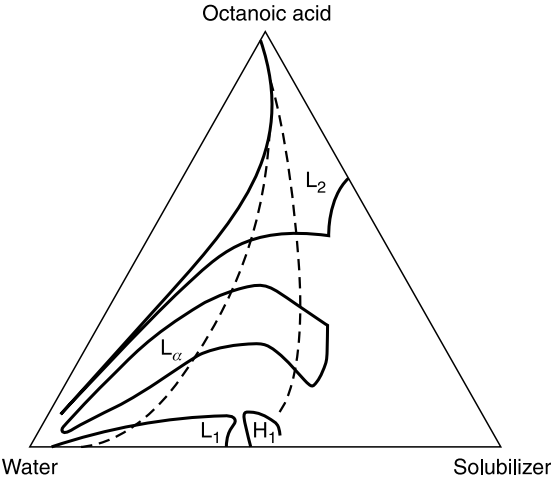


FIG. 2.3 Solubilization of octanoic acid into a surfactant micellar solution (L_1) is limited because the addition of the acid leads to the formation of a lamellar liquid crystal (L_α).

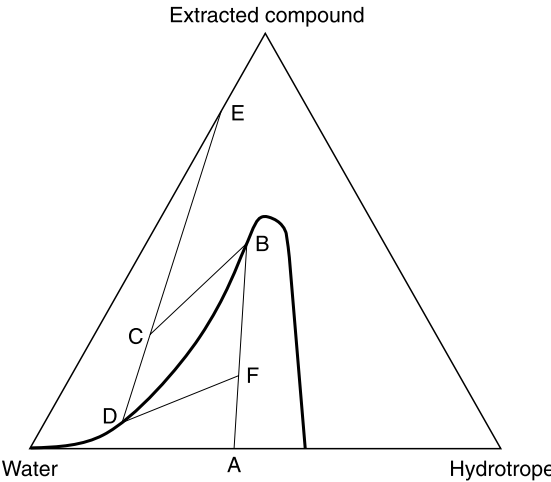


FIG. 2.4 Extraction is initiated with the aqueous hydrotrope solution at A, saturation extraction at B. The total composition along BC when water is added. The extracted compound, saturated with water, is separated E, while the aqueous solution changes along BD. Evaporation of water gives DF and the process is repeated.

between the hydrotrope and the solubilizate. However, vapor pressure values of the solubilizate [42] do not support such an interpretation, but instead show the solubilizate to be located in a colloid association structure. Hydrotrope solutions have also been used to study the solubility and mass transfer coefficient for butyl acetate [43] and methyl salicylate [44]. In the production of semisynthetic antibiotics, intermediates may be difficult to separate. A good example is the production of 6-aminopenicillanic acid, the separation of which from phenoxyacetic acid is difficult with traditional systems. However, the use of aqueous solutions of sodium monoglycol sulfate has been shown to be efficient for the process [45].

Finally, hydrotrope solutions have been involved in natural product separation, e.g., in lipase purification and the evaluation of its thermal stability [46], as well as in the extraction of piperine from black pepper [47].

III. FUNDAMENTALS

The structure of hydrotrope molecules, as mentioned earlier, is characteristic (Figure 2.1). One finds a short, predominantly aromatic hydrophobic chain and in most cases an ionized polar group. With this structure in mind, it is not surprising that the association structures of the hydrotrope molecules in water have attracted some interest over the years, even if these may not be the decisive feature in the practical applications of these compounds.

It is of interest to note that the focus of research on the self-association of hydrotrope molecules was due, in part, to the early discussions about the fundamental nature of the solubility-enhancing capacity of hydrotrope molecules in aqueous solutions. These early attempts at clarification argued for the phenomena of colloidal solubilization versus molecular dispersion [6–8]. This dispute was resolved by the results from traditional surface chemistry analysis of interfacial tension, etc., which favored a colloidal association of molecules at high concentrations [48,49], and from vapor pressure measurements [42].

On a more detailed scale, osmotic vapor pressure measurements and light scattering determinations [50] gave results that were interpreted as arising from the formation of dimers and trimers at the initial association of nicotineamide in water while at higher concentrations an aggregation number of 4.37 was found. As expected, the trimerization constant was significantly greater, about two orders of magnitude, than the dimerization constant. It was tacitly assumed that the association takes place through stacking of the molecules, an expected conclusion considering the molecular structure of these compounds. However, this assumption was to some extent cast in doubt by Balasubramanian and coworkers [51], who determined the crystalline structure of sodium *p*-*tert*-butylbenzenesulfonate dihydrate, sodium cumenesulfonate semihydrate, sodium toluenesulfonate hemihydrate, and sodium 3,4-dimethylbenzenesulfonate. In none of these crystalline

structures was a stacking of the molecules found and it was concluded that the notion of stacking of the molecules during association in aqueous solutions should not be assumed *a priori*. As for the conditions in a solubilized system at high concentrations, the determination of vapor pressure of the solubilize phenethyl alcohol in sodium xylenesulfonate solutions [42] showed a constant vapor pressure at hydrotrope concentrations above the association concentration, indicating a colloid association without structure changes, once the association and solubilization take place. These results, once more, justify the emphasis on the influence of the hydrotrope molecule on colloidal association structures as a meaningful exercise.

The comparison with surfactant associations is a relevant theme and Srinivas and Balasubramanian [52] have evaluated this difference by observing the surface tension of and solubilization by a series of sodium alkylbenzenesulfonates. Varying the alkyl chain length gives a range of compounds with properties changing from those of a hydrotrope to those of a traditional surfactant. The results were interpreted to indicate that the transition is gradual.

In this context it is appropriate to caution against routine interpretation of such results. Mechanical analysis of the variation of surface tension versus the logarithm of the amphiphile concentration may be misleading, as exemplified by the results for a series of alcohols, which were interpreted as indicating micellar association [53]. The correct visualization in the form of a plot of surface tension versus the activity of the amphiphile [54] shows no indication of a sudden association (Figure 2.5). Hence, while a plot of the surface tension values from Srinivas and Balasubramanian [52] against the logarithm of the concentration certainly gives the knick-points characteristic of micellar association behavior (Figure 2.6), a correct interpretation must await information about the activity of the amphiphiles taking into consideration the very high concentrations of hydrotrope for association to take place.

Unfortunately, information about the activity of hydrotrope molecules in the concentration range of interest is not available. The only determination in existence, to our knowledge, is concerned with a more complex associated system [55]. This is in contrast to the case for traditional long-chain surfactants, which have been thoroughly investigated [56–59], the results of which justified the approach to use concentrations instead of activities in the common plot of surface tension to determine critical micellization concentrations. The closest to hydrotrope molecules should be bile salts, which have been investigated [60].

The main concern of the investigations discussed so far was the self-association of the hydrotrope molecules. Although such a subject constitutes an interesting area of research, it must be kept in mind that the hydrotrope molecule functions as a modifier of surfactant association structures in the majority of its applications. It is, hence, of interest to review available material on the alteration of surfactant association structures by addition of a hydrotrope.

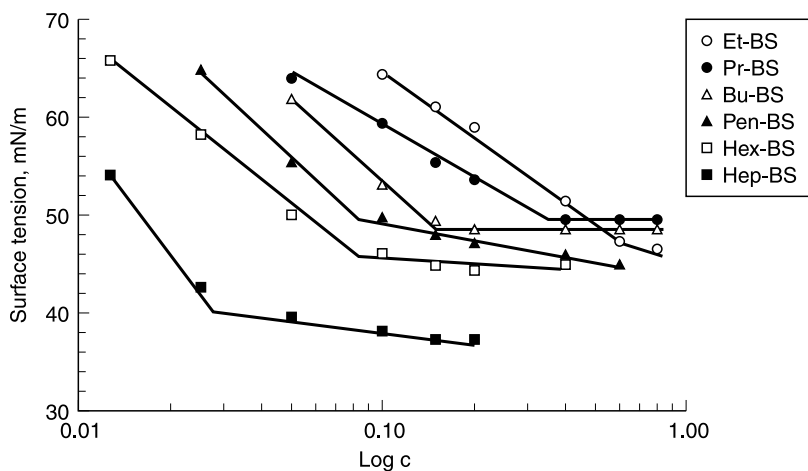


FIG. 2.5 Curve of surface tension vs. logarithm of mole fraction of amphiphiles at first indicates micellization. (Adapted from Srinivas, V. and Balasubramanian, D., *Langmuir*, 14, 6658–6661, 1998.)

The initial publications did not emphasize the specific action of the hydrotrope molecules in different applications. Instead they considered the structural modification of aqueous micelles by the addition of hydrotrope. Assessing the results from this point of view [61–64] the conclusion was that the reduction of electrostatic repulsion is the main cause of the modification of surfactant micelles from spherical to cylindrical shape after addition of a hydrotrope with opposite charge.

It should be noted that the effect is present at hydrotrope concentrations well below the self-association concentration. A more elaborate and sophisticated investigation of this phenomenon has recently been presented by Kaler and collaborators [65,66]. They analyzed the influence of added salt and added hydrotrope on a solution of worm-like micelles and were able to reveal the alteration of relevant length scales of the micellar system (contour length, entanglement length, mesh size, persistence length, and cross-sectional radius) by a combination of rheological, flow birefringence, and small-angle neutron scattering measurements, (Figure 2.7). The interpretation is similar to that of more simple systems [61–64], with the important difference that information now was obtained also for the number of branches, which increase due to the change in relative energy of branching versus that of the formation of end caps.

Although this research on ionic surfactant micelles is of high quality and fundamentally relevant, the research on nonionic micellar systems has a more direct bearing on the application of hydrotropes. One essential function of hydrotropic

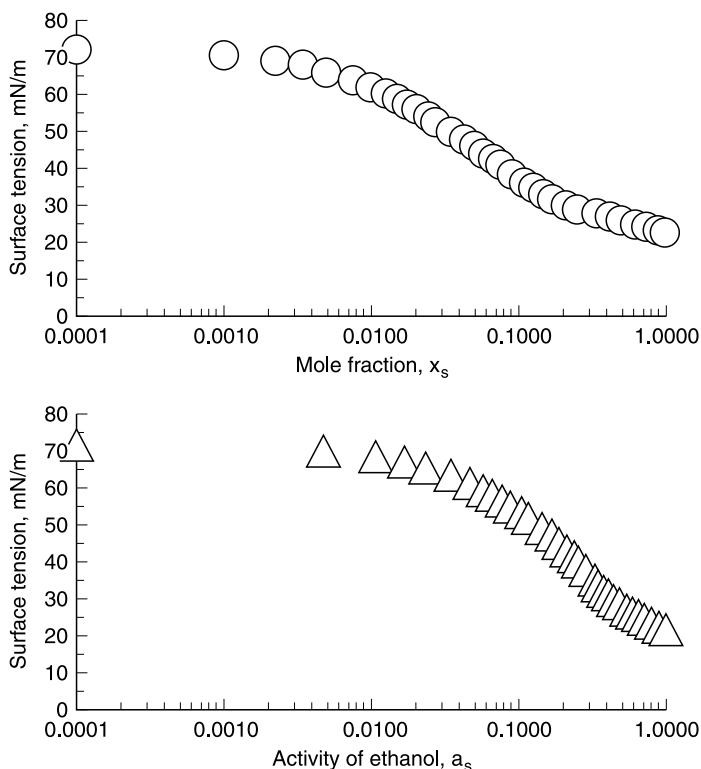


FIG. 2.6 Curve of surface tension vs. logarithm of mole fraction shows a pattern indicating micellization (top), while the curve vs. the logarithm of activity shows no such features (bottom).

molecules in practice is to clarify slightly turbid systems of high water content: an important problem as regards applications. This phenomenon has been described as a “coupling” or “linking” of organic and aqueous regions in a liquid vehicle. In this context a recent publication [67] is of interest, relating the action of hydrotropes to a general scheme of interactions with the oil and aqueous regions in emulsions and microemulsions [68,69]. There is no doubt that this manner of describing the phenomena is valuable, but it must be emphasized that a purely molecular modeling approach may significantly contribute to a better understanding of the clouding phenomenon. The approach by Shinoda and Arai [70] interpreting the cloud point behavior as a consequence of the curvature of the surfactant layer, defined the cloud point as an increase of the layer radius toward the hydrophobic region to a degree such that a normal micelle could not be formed because of packing considerations.

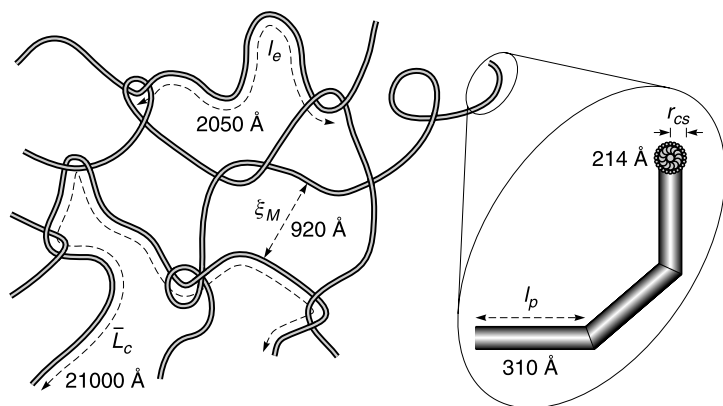


FIG. 2.7 Relevant length scales for the colloidal structure of worm-like micelles: contour length, \bar{L}_c , entanglement length, l_e , mesh size, ξ_m , persistence length, l_p and cross-sectional radius, r_{cs} . Values shown are those measured for a solution with 1.5% total surfactant at a cetyltrimethylammonium tosylate (CTAT)/sodium dodecylbenzenesulfonate (SDBS) ratio of 97/3 with 0.10% added sodium tosylate. (Reproduced from Schubert, B.A., Kaler, E.W., and Wagner, N.J., *Langmuir*, 19, 4079–4089, 2003. With permission.)

The recent investigation [71] of a nonionic system, hexaoxyethylene dodecyl ether and water, showed a hydrotrope molecule to be introduced into the micelle first at concentrations at which the hydrotrope self-associates. This increase of the minimum concentration at which the hydrotrope molecule enters the micelle from the values in ionic systems [61–66] is in all probability due to electrostatic effects. One essential result of the investigations into nonionic systems [71] is that the presence of the hydrotrope reduces the size of the micelle; i.e., the radius of the curvature toward the hydrophobic region is reduced and, hence, the cloud point is enhanced in accordance with the views of Shinoda and Arai [70]. Investigations of block copolymer systems [72–76] may now be interpreted in a similar manner and the coupling or linking action of a hydrotrope in a nonionic system is given a simple explanation in the form of a modified micellar structure.

The clarifying action of a hydrotrope in an aqueous system of ionic surfactants, which is generally described as a coupling action of the hydrotrope between the organic and aqueous regions, has recently been given a simple explanation [77,78]. It was shown that in a number of systems the cloudiness at high water content is due to the formation of a lamellar liquid crystalline phase and that the addition of a hydrotrope destabilizes the lamellar structure in accordance with the original interpretation of this phenomenon [10], (Figure 2.8).

These results have added to the understanding of the action of hydrotropes in the clouding in aqueous solutions, but have also had a significant influence on other

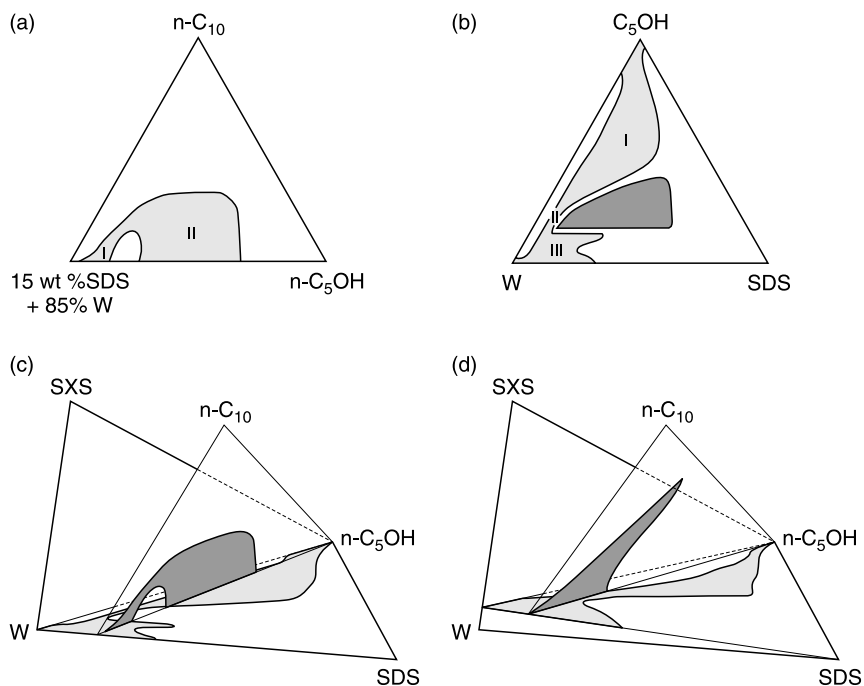


FIG. 2.8 Microemulsion regions for the system containing (a) water (W), sodium dodecylsulfate (SDS), pentanol (C_5OH), decane ($n\text{-C}_{10}$), and sodium xylenesulfonate (SXS). The composition of the aqueous solution of the surfactant and the hydrotrope is given in the left-hand corner. (b) The system containing water (W), sodium dodecylsulfate (SDS), and pentanol (C_5OH) shows an isotropic liquid solubility region with three kinds of amphiphilic association structures. I: inverse micellar region; II: bicontinuous micellar region; III: aqueous micellar solution; LLC: lyotropic liquid crystal. (c, d) Combination of the diagrams in (a) and (b). (Reproduced from Friberg, S.E., Brancewicz, C., and Morrison, D.S., *Langmuir*, 10, 2945–2949, 1994. With permission.)

applications of hydrotropes. At first, the influence on the method of preparation of oil-in-water microemulsions should be mentioned. The early phase diagrams showing the oil-in-water microemulsion areas [79] could not be interpreted, but did indicate significant problems in practical formulation efforts, because the areas were narrow and there were serious difficulties establishing the areas of thermodynamically stable formulations. These problems were resolved once the influence of a hydrotrope was established [77]. Addition of hydrotrope in small amounts (of the order of 5% by weight) gives wide areas of microemulsion formulations, which is very useful for practical applications (Figure 2.8).

The early realization that the tremendous solubilization of octanoic acid into an aqueous solution of sodium xylenesulfonate [10], as distinct from the modest solubilization into a surfactant solution, is in fact, due to the inability of the hydrotrope molecule to form liquid crystals with the hydrophobic straight-chain amphipile, led to the later insight that hydrotropes would be useful to prepare vesicles at high concentrations in a simple one-step process [80,81]. In this context it is useful to refer to the early studies of bile salts and their relation to lecithin liquid crystals [82,83] and the resulting vesicles. Although lecithin and other double-tail surfactants were popular compounds to prepare vesicles, it is obvious that the traditional oxyethylene adducts with sufficiently short hydrophobic chains to make them “insoluble” in water also should be useful to prepare vesicle solutions [84]. Actually such surfactants were the medium in the determinations of the vesicle formation kinetics [85,86]. The realization of these phenomena led to a renewed interest in the phase diagrams of systems with hydrotropes and liquid crystal-forming surfactants [87] and to an interesting study of the change in the rheological properties of a lamellar liquid crystal due to the addition of a hydrotrope [88].

IV. CLEANING AND WASHING

Cleaning and washing processes are mainly concerned with the removal of “oily dirt,” depending to a high degree on the complex phase equilibria encountered in the surfactant–water–oily dirt system [89].

In addition to the progress in the area of traditional hydrotropes [90,91] one finds two treatments [92,93] on the action of a nontraditional hydrotrope structure in cleaning and laundry systems. Instead of the short and bulky molecule (Figure 2.8), this compound [94] is a dicarboxylic acid of considerable chain length (Figure 2.9).

The fundamental action of this hydrotrope in a liquid cleaner has been investigated. In such an application, the hydrotrope functions in the formulation concentrate by preventing gelation. In addition, under the dilute conditions in the washing process, the hydrotrope facilitates the removal of oily dirt from the fabric. In the following discussion these two functions are related to the phase equilibria of water–amphiphile systems.

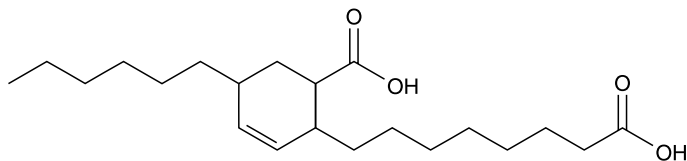


FIG. 2.9 Dicarboxylic acid hydrotrope with an elongated structure.

The formula for the dicarboxylic acid (Figure 2.9) has a hydrophilic/lipophilic balance similar to that of octanoic acid, but the influence of the two acids on amphiphilic association structures is entirely different, as shown in Figure 2.10 [93]. The octanoic acid causes the formation of a liquid crystal when added to a solution of water in hexylamine. The size of the lamellar liquid crystalline region is large (Figure 2.10a). Addition of the dicarboxylic acid, in contrast, gives no liquid crystal, and it may be concluded that its action in concentrated systems is similar

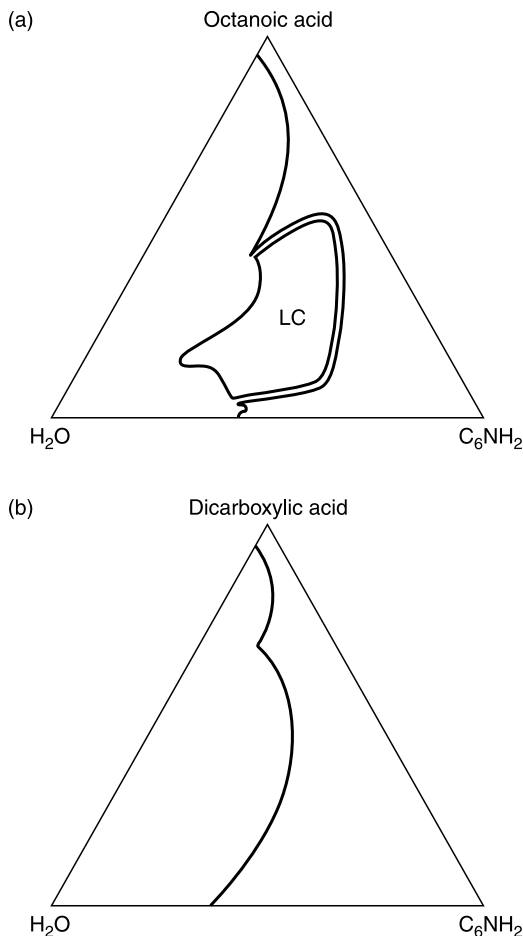


FIG. 2.10 (a) Combination of water and hexylamine with octanoic acid (a) gives a very large area of a lamellar liquid crystal (LC). (b) Combination with the dicarboxylic acid of Figure 2.9 results in an isotropic liquid solution only.

to that of the common short-chain hydrotropes despite its long hydrocarbon chain (Figure 2.10b).

Activity in dilute systems was investigated using a model system from Unilever [96] in which octanol mimicks the oily dirt. A lamellar liquid crystal is present at low concentration of the oily dirt [93], in the absence of the hydrotrope, because the formation of a lamellar liquid crystal on the addition of the octanol is the limiting factor in its solubilization into the micelles. After addition of the hydrotrope, the amount of model oily dirt solubilized into the aqueous micellar solution is greatly enhanced (Figure 2.11). Clearly, this hydrotrope functions not only as a destabilizer of liquid crystals in the formulation concentrate but also as a destabilizer of liquid crystals under the dilute conditions of the washing process [95].

The molecular mechanism behind the destabilization of liquid crystals was subsequently clarified [25]. The specific disordering promoted by the hydrotrope in the water–surfactant–oily liquid crystal was first determined, followed by an investigation into the conformation of the diacid molecule itself [92].

The order of the individual groups in the hydrocarbon chains in a liquid crystal is directly obtained from nuclear magnetic resonance (NMR) spectra using amphiphiles with deuterated chains. Each methylene group and the terminal methyl group give a NMR signal doublet, and the difference in frequency between the two signals is proportional to the order parameter [25]. Using a lamellar liquid crystal model system of “oily dirt,” [96] surfactant, and water, the influence of the hydrotrope on the structure can be directly determined. Addition of the hydrotrope molecule results in a narrowing of the difference between the NMR signals due to

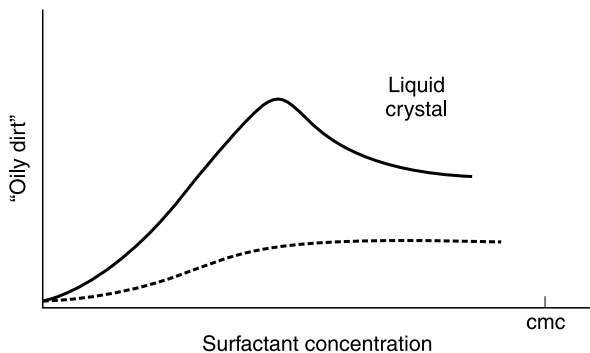


FIG. 2.11 Solubilization of a model compound for oily dirt is small in a surfactant solution at concentrations below the critical micelle concentration (----) because of the formation of a liquid crystal. A combination of hydrotrope and surfactant gives an increased solubilization (—) caused by the hydrotrope destabilizing the liquid crystal.

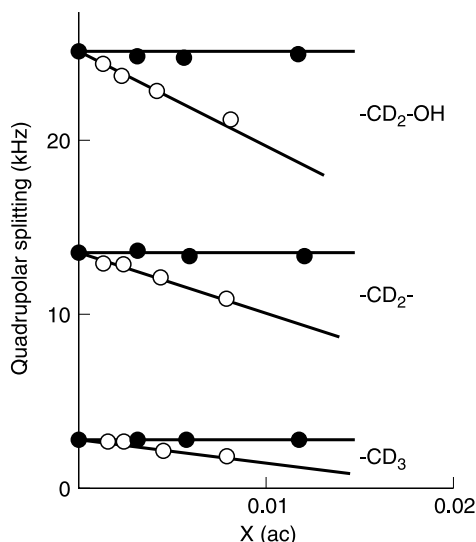


FIG. 2.12 Addition of a hydrotrope (that of Figure 2.9) to a lamellar liquid crystal gives a reduction of the order parameter of the surfactant hydrocarbon chain (o); addition of a surfactant gives no change in order (●).

a disordering of the liquid crystal, as shown in Figure 2.12 [25]. It was assumed that this is the primary factor in the destabilization of the liquid crystal.

The diacid conformation was determined after it was added to the oily dirt liquid crystalline phase. Figure 2.13 shows two possibilities for the conformation of the hydrotrope in the liquid crystal. In one form of the diacid (Figure 2.13, right), both polar groups are located at the interface between the amphiphile polar groups and the water; the other possibility is that only the terminal carboxylic group is found at this site (Figure 2.13, left). The two conformations would result in different interlayer spacing (Figure 2.14) and a determination of this dimension can be used to distinguish between the two alternatives. Low-angle x-ray diffraction gives the interlayer spacing directly from the maxima in the diffraction pattern.

Interpretation of the results is straightforward. If addition of the diacid to a lamellar liquid crystal model dirt system does not increase the interlayer spacing, the conformation on the right in Figure 2.13 is correct; if an increase does take place, the situation on the left in Figure 2.13 would describe the structural organization of the diacid molecule.

The interlayer spacing with the diacid added [25] is very close to that of the host liquid crystal (Figure 2.14), and the conformation shown on the right in

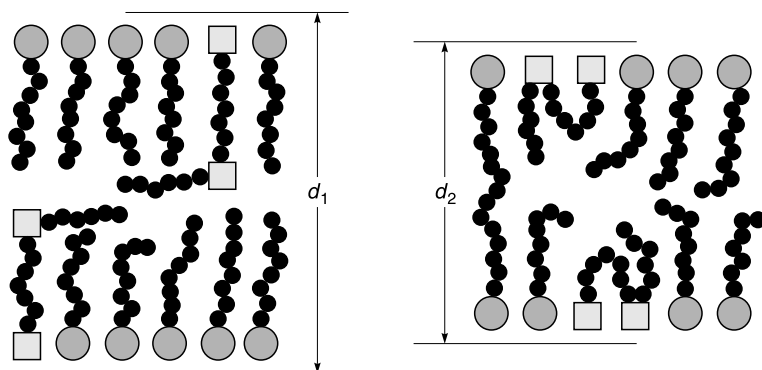


FIG. 2.13 A hydrotrope (that of Figure 2.9) conformation with only one polar group at the water–amphiphile interface (left) results in an enhanced interlayer spacing, d_1 , compared with the value, d_2 , for a conformation with both polar groups at the interface (right).

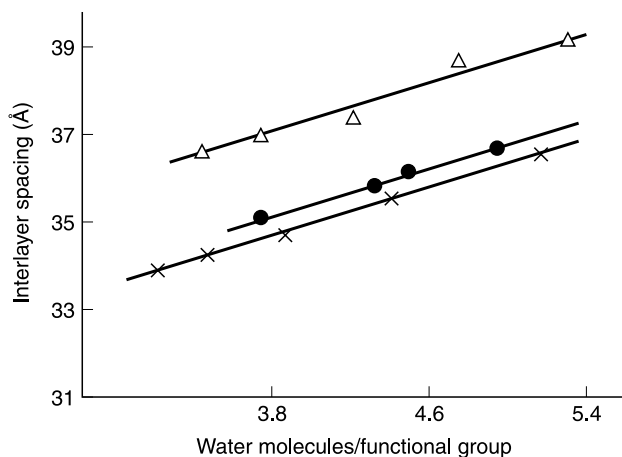


FIG. 2.14 Low-angle x-ray values for interlayer spacing in a lamellar liquid crystal (X) show the spacing is unchanged with the addition of the hydrotrope (●) of Figure 2.9. Addition of a long-chain compound, oleic acid, gives the expected increase (Δ).

Figure 2.13 is obviously the one encountered in the liquid crystal. As a comparison, the addition of oleic acid with one polar group located at the interface gives the expected increase in interlayer spacing, as shown in Figure 2.14. Destabilization of the lamellar liquid crystal is not only affected by the diacid: it appears to be a general property shared by other hydrotropes, such as alkanols, short-chain

quaternary ammonium salts, xylenesulfonates, and glycols, as shown by Pearson and Smith (11) and by Darwish *et al.* [97].

In some cases, the oily dirt is less polar than the model system of Kielman and Van Steen [96]. For less polar fatty oils the concept of hydrotropic breakdown of a liquid crystal is also useful [98].

V. SUMMARY

The function of hydrotropes in detergency has been discussed as regards their interaction with surfactant colloidal association structures, especially lyotropic liquid crystals. The main activity of the hydrotrope as a part of a liquid detergent is to avoid gelation in both the concentrated package system and under the dilute conditions in the actual laundry process.

Both these activities are directly related to a detergent's phase equilibria with hydrophobic amphiphiles. These phase equilibria illustrate and explain the two basic characteristics of hydrotropes: their high association concentration and their pronounced solubilizing power.

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