Extraction temperature should be kept low for good color although higher temperatures result in better extraction efficiency. Heating the meats to a high temperature, while considered an advantage in pressure removal of the oil, causes both poor color and lowered extraction efficiency in trichloroethylene extraction of cottonseed oil.

The toxicity to cattle of certain batches of trichloroethylene-extracted soybean oil meal has raised the question of possible toxicity of other products extracted by trichloroethylene. Since the work presented in this paper was a study in extraction only, the use of trichloroethylene as an experimental solvent should not be construed as a recommendation by the authors that the product resulting from this extraction is or is not suitable as a feed.

Summary

Trichloroethylene cottonseed oil miscellas from prime meats heated during desolventization above 180°F. produced a refined oil darker than prime. When the miscellas were heated above 190°F., the bleached oils produced from them were darker than prime. Extracting prime meats with trichloroethylene above 118°F. produced an oil darker than prime. There is some evidence that heating the meats above about 170°F. also gives a dark oil. Dilute miscellas, when desolventized, produced a darker oil than more concentrated ones probably because of the longer time required for solvent removal. It is believed that the darkening is primarily a function of time and temperature, rather than the solvent used.

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Micelle Formation and Solubilization in Nonaqueous Solvents

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OIL-SOLUBLE SOAPS have been familiar industrial materials for many years, and the colloidal nature of their dispersions in oils was early recognized (4, 8, 12, 16, 25, 53). It is only within the past 10 years however that much information has become available concerning the exact state in which such substances exist in nonpolar solvents. This paper will discuss some aspects of micelle formation in nonpolar solvents in the light of the published data and of hitherto unpublished results from the Naval Research Laboratory.

For the purposes of this discussion the term micelle will be taken to mean any thermodynamically stable association colloid formed by three or more amphipathic molecules. One dimension of such a structure will usually, in a nonpolar solvent, be comparable with twice the length of the monomer unit. Because some soaps show a continuous transition from small spheres of less than 50 monomer units to polymer-like linear structures containing many hundreds of molecules, it will be convenient to extend the term micelle, and our consideration of the micellar state, to the chain-like structures exhibited by aluminum soaps and by the arylstearate soaps. The liquid crystalline systems formed in many concentrated soap-oil systems will not be considered although some elements of similarity exist. Emulsions also will not be considered although there may be cases in which micelles pass smoothly into emulsion droplets as the amount of water solubilized by the micelle becomes large as compared with the amount of soap present.

It will be convenient, although inexact, to use the term soap as a generic name for the ionic amphipaths which form micelles in oil. The term oil-soluble soap is also a misnomer but has been established by long usage; it will be used here to refer to a soap micellarly dispersible in a nonpolar solvent.

Micelle formation in nonpolar solvents has been demonstrated for the following classes of compounds:

a) alkali and alkaline earth soaps of naphthenic and sulfonic acids from petroleum and of related synthetic substances, such as the arylstearic and alkylnaphthalene sulfonic acids (2, 22, 28, 37, 36, 55);

b) oleates, naphthenates, and various C_8–C_{18} normal fatty acid soaps of the heavy metals, including copper, zinc, iron, nickel, and cobalt (8, 25, 35, 40, 53, 54);

c) aluminum soaps of oleic, 2-ethylhexanoic, naphthenic, and C_8–C_{18} normal fatty acids (18, 33, 34, 51);

d) quaternary ammonium salts of a suitable cation with an anion of relatively small volume (10, 14, 29, 48);

e) alkali and alkaline earth alkylphenolates, and alkylphosphates (44); and

f) nonionic surface active substances such as hexanolamine oleate, nonaethylene glycol monolaurate, mannitan mono-oleate, and certain alkyd resins (17, 43, 47, 50).

Micelle formation by soaps in aqueous solution has been studied so extensively and fruitfully that there is a natural tendency to reason about nonaqueous micelles by analogy from aqueous phenomena. The basic structures of the two types of micelle however are so diametrically opposite that such reasoning may be unsafe. In the nonaqueous micelles the polar portions of the amphipathic molecule are buried in the central core, rather than distributed over the outer surface as in aqueous systems. While the oil-soluble soaps are still strongly ionic, they are not appreciably dissociated in oil, and the micelle carries no net charge comparable with that of aqueous soap micelles. In aqueous systems soap micelle size is considered to be limited by the accumulation of charged ions in the micelle, which prevents the approach of further ions; in nonaqueous systems one must look elsewhere for the mechanism that stops micelle growth before precipitation can occur. The major energy available for micelle formation in a hydrocarbon solvent comes from the interaction of the polar heads, either as a generalized dipole attraction or by the formation of specific atom to atom coordination or hydrogen bonds, whereas in aqueous micelles the driving force may be considered to be the decrease in free energy possible by sequestering the hydrocarbon tails within a structure in which the polar heads are oriented toward the water. The major similarity between the two sorts of micelles is that both have marked solubilizing power for substances otherwise insoluble in the medium, but even here differences are to be expected because of different forces involved in maintaining the micelle structure.

Micelle formation may be detected and the size of micelles estimated by a wide range of physico-chemical techniques. In general, micellar systems do not show a gross turbidity but are optically clear although careful measurements may show Rayleigh scattering enhanced over that of the pure solvent. True micelles, with diameters of the order of twice the maximum length of the monomer, are not resolvable in the optical ultramicroscope although, in a suitably prepared mount, individual micelles may be resolved by the electron microscope (44). The presence and size of micelles in a hydrocarbon solvent, such as benzene, may be established by cryoscopic or ebullioscopic measurements, or from the osmotic pressure of the solution. These methods become less accurate as the size of the micelles becomes larger (10, 35, 52).

If the solvent is chosen so that its refractive index differs enough from that of the micellar material, rather complete information about both the size and shape of the particle may be gathered by the application of the light-scattering techniques that have been developed in the past 10 years (41). Very few data obtained by this method are available for association micelles in nonaqueous solvents (50). The ultracentrifuge has been used to evaluate micelle size for Aerosol OT in benzene (36).

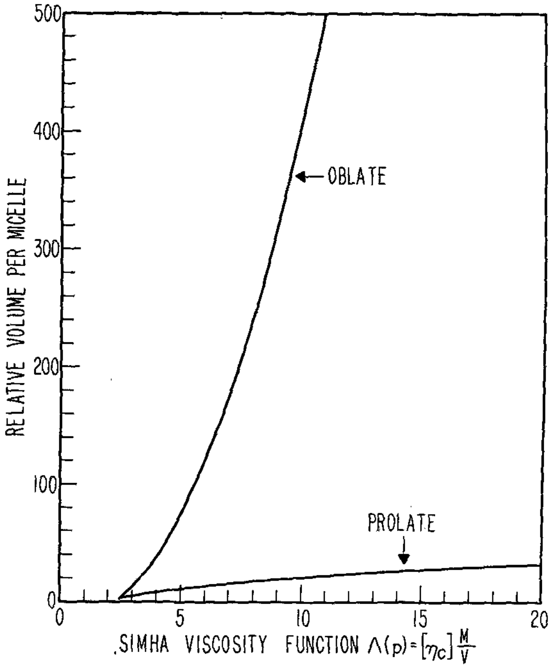

Fig. 1. Relative volumes of prolate and oblate ellipsoids having equivalent limiting viscosity numbers.

Workers at the Naval Research Laboratory have recently described a method for estimating micelle size for oil-soluble soaps in nonpolar solvents from measurements of the depolarization of the fluorescence of a suitable dye molecule which has been solubilized by the micelle (27, 52). The depolarization observed is a result of the Brownian rotation of the dye-bearing unit between the time of excitation and the time of emission; it depends upon the size of that unit. Given a dye, such as Rhodamine B, which is colorless in hydrocarbon solvents but colored when incorporated into a soap micelle, one excites the micelle-borne dye with plane-polarized light and measures the degree of polarization of the fluorescence emitted at 90° to the incident beam. The volume of the micelle can be computed from an equation due to Perrin (45).

$$V = (1/p_o - 1/3)\ \frac{\tau RT}{\eta}\left(\frac{pp_o}{p_o - p}\right)$$

Here p_o, the polarization of light emitted by an immobilized dye molecule, is a quantity near 0.5 which can be determined experimentally, and p is the observed polarization of light emitted by the dye in a micelle. η is the viscosity of the solution, and V is the volume of a sphere hydrodynamically equivalent to the micelle. The average excited life τ of the dye molecule can be estimated by comparing the efficiency of the fluorescence process in the system under study with the known efficiency in a situation for which τ has been measured. The excited life is proportional to the quantum efficiency of the fluorescence. The fluorescence efficiency in such systems is generally high but varies somewhat with the concentration of soap, or of polar substances such as organic acids or water, so that it must be experimentally determined for each system measured. Micelle volumes estimated from fluorescence depolarization have been found to agree well with those computed from measurements of the osmotic pressure of soap solutions. The major advantage of the fluorescence method is that 10^{-8} mole per liter of dye furnishes sufficient fluorescence intensity for useful measurements so that direct measurements of micelle volume can be carried out on soap solutions as dilute as 5×10^{-7} molar. There is no other technique applicable in this extremely dilute range, except possibly diffusion measurements with radioactive tracers in the micellar phase.

Observations of the viscosity (21) or of the streaming birefringence (13) of soap solutions may furnish valuable information concerning the shape of the units present but cannot give explicit information concerning the size of the particles. Information as to shape is important however because the micellar volumes obtained from ultracentrifugation, diffusion, or fluorescence depolarization data are the volumes of spheres hydrodynamically equivalent to the actual particles, whose true volume may be estimated only if their shape is known. If one makes the additional assumption that the minimum dimension of an anisotropic micelle in a nonpolar solvent is unlikely to be substantially less than twice the length of the monomer molecule involved, it is possible to assign a minimum micelle size on the basis of the shape factor derived from the viscosity or birefringence measurements. There may remain an uncertainty as to whether the eccentricity is associated with an oblate or a prolate ellipsoid but, as will be seen from Figure 1, the relative volumes that must be inferred for the two shapes are so disparate for eccentricities of 2 or greater that a reasonable choice is frequently obvious.

Size and Shape of Micelles

The data available on the size of micelles formed by polar solutes in nonaqueous solvents are summar-

TABLE I
Micelle Formation in Hydrocarbon Solvents

Solute	Solvent	Temp. °C.	Solute Conc.	Conc. Units	Aggreg. No.	Ref.
Tetraisoamylammonium thiocyanate	benzene	5.4	0.02 –0.42	molal	10–25	14
n-Octadecyltri-n-butylammonium formate	benzene	5.4	0.001–0.0033	molal	10–22	14
n-Amyltri-n-butylammonium iodide	benzene	5.4	0.001–0.50	molal	3–22	14
Tetra-n-butylammonium perchlorate	benzene	5.4	0.001–0.014	molal	3–6	48
Sodium bis(2-ethylhexyl)sulfosuccinate	dodecane	30.0	1	g./100 g.	(32)	36
Sodium bis(2-ethylhexyl)sulfosuccinate	dodecane	30.0	1 + 0.2 H_2O	g./100 g.	(28)	36
Sodium bis(2-ethylhexyl)sulfosuccinate	dodecane	30.0	1 + 1.0 H_2O	g./100 g.	(380)	36
Sodium dinonylnaphtalene sulfonate	benzene	25.0	10^{-5}–10^{-3}	molar	12	28
Barium dinonylnaphthalene sulfonate	benzene	25.0	10^{-5}–10^{-3}	molar	7	28
Barium petroleum sulfonate	benzene	25.0	0.001	molar	34	28
Calcium cetyl phosphate + calcium alkyl phenolate	lube oil	25.0	0.013	molal	(20–30)	44
Hexanolamine oleate	benzene	5.4	0.089–0.16	molal	3+	17
Hexanolamine caprylate	benzene	5.4	0.072	molal	4+	17
Dodecylamine oleate	cyclohexane	6.5	1.0	g./100 g.	5	43
Dodecylamine propionate	cyclohexane	6.5	1.0	g./100 g.	10	43
Nonaethyleneglycol monolaurate	cyclohexane + water	6.5	0.101	molal	4+	17
Alkyd resin	heptane	25.0	0.35–3	g./100 ml.	(ca. 100)	50

TABLE II
Micelle Formation by Metal Carboxylates in Hydrocarbon Solvents

Solute	Solvent	Temp. °C.	Solute Conc.	Units Conc.	Aggreg. No.	Ref.
Zinc laurate	toluene	111	0.6 –1.9	g./100 ml.	5–6	40
Magnesium laurate	toluene	111	0.5 –2.3	g./100 ml.	6–33	40
Copper laurate	toluene	111	0.5 –1.5	g./100 ml.	5–18	40
Ferric trilaurate	toluene	111	0.005–0.05	molar	2	40
Zinc octanoate	toluene	111	Extrapolated to ∞ dilution		6.3	40
Zinc decanoate	toluene	111	Extrapolated to ∞ dilution		5.4	40
Zinc laurate	toluene	111	Extrapolated to ∞ dilution		4.8	40
Zinc myristate	toluene	111	Extrapolated to ∞ dilution		4.2	40
Zinc stearate	toluene	111	Extrapolated to ∞ dilution		3.2	40
Sodium phenylstearate + 0.2 mole phenylstearic acid per mole soap	benzene	25	1.73	g./100 ml.	200	22
Sodium phenylstearate + trace of water	benzene	25	0.68	g./100 ml.	(5000)	22
Calcium xenylstearate + 2 moles water per mole of soap	benzene	25	10^{-6}–10^{-3}	molar	24	52
Calcium xenylstearate + trace water	benzene	25	3.4	g./100 ml.	(1000)	3
Aluminum dicaprylate	benzene	30	0.12	g./100 ml.	(640)	51
Aluminum dicaprylate	benzene	30	0.30	g./100 ml.	(880)	51
Aluminum dilaurate	benzene	30	0.10	g./100 ml.	(840)	51
Aluminum dilaurate	benzene	30	0.40	g./100 ml.	(1330)	51
Aluminum dimyristate	benzene	30	0.075	g./100 ml.	(520)	51
Aluminum dimyristate	benzene	30	0.30	g./100 ml.	(980)	51
Aluminum dipalmitate	benzene	30	0.10	g./100 ml.	(600)	51
Aluminum dipalmitate	benzene	30	0.30		(700)	51
Aluminum distearate	benzene	30	0.20		(670)	51
Aluminum distearate	benzene	30	0.30		(970)	51

ized in Tables 1 and 2. Representative entries have in some cases been chosen from more extensive data. It should be noted that the entries in these tables refer to a variety of solvents and temperatures which must be taken into account when generalizations are attempted. The aggregation numbers given in parentheses have been estimated from the published data and may not represent the conclusions of the original author. Table 1 includes examples of micelle formation by quaternary ammonium salts, metal sulfonates, metal alkylphenolates plus metal alkylphosphates, amine carboxylates, and nonionic surface-active compounds. With the exception of the last six entries these substances are all ionic salts containing one or more large amphipathic ions and a relatively small counter ion. The aggregation numbers reported or estimated are all less than 100 molecules per micelle except for Aerosol OT in the presence of an equal weight of water; in the concentration range in which micelle formation is well established, most of the micellar units contain between 10 and 40 large amphipathic ions. Such a number is compatible with the concept of the micelle as an approximately spherical structure in which the hydrocarbon portions of the molecules surround a central polar core, screening it from interaction with the similar cores of other micelles.

Kraus and co-workers have considered the aggregation of quaternary ammonium salts to be the result of dipole-dipole interaction between ion pairs, and such interaction seems also a plausible explanation for the formation of the sulfonate and phosphate-phenolate micelles. In the cases of hexanolamine oleate, nonaethyleneglycol monolaurate, and the low molecular weight alkyd resin, hydrogen bonding is probably the interaction responsible for holding the core of the micelle together. An investigation of tertiary amine carboxylates has indicated that such amine carboxylates in dry benzene are association complexes rather than typical ionic salts (26) and and that they do not form micelles.

The carboxylate soaps listed in Table 2 form micelles ranging in size from five molecules or less for the heavy metal soaps studied by Pink in boiling toluene to a thousand or more molecules for the aluminum soaps whose micellar weights Sheffer determined by osmotic pressure measurements in benzene at 30°C. The continuity between these divergent types is furnished by the alkali and alkaline earth arylstearates which have been studied at the Naval Research Laboratory (3, 22). Solutions of these soaps have been shown to pass from a highly viscous state resembling that of the aluminum soaps to low relative viscosities characteristic of small micelles simply by the addition of small amounts of acids, or of substances like water, alcohol, or phenol which might react with the soap to form an acid. The behavior of calcium xenylstearate is shown in Figure 2 and the more complex response of sodium phenylstearate in Figure 3. With the sodium soap the addition of excess water or glycol results in reaggregation of the soap into more extensive structures. The effect of acids, alcohols, or phenols is not reversed at higher concentrations of the additive. The viscosity decrease

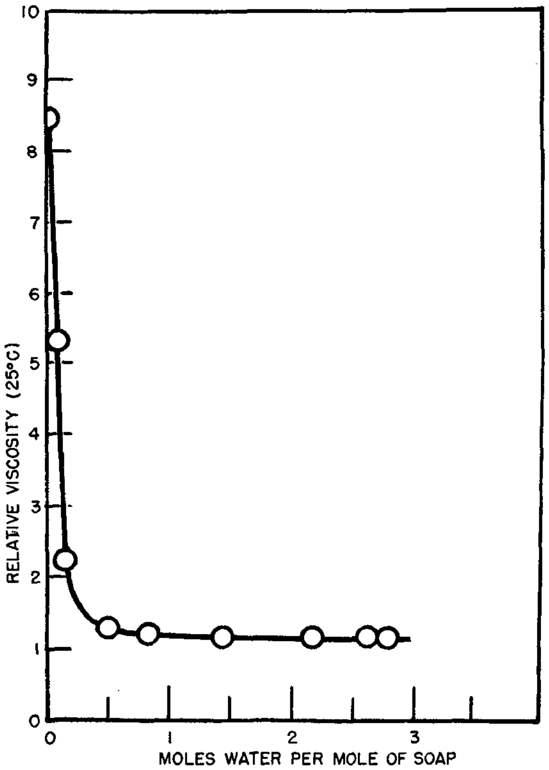

Fig. 2. Effect of water content on the relative viscosity of a solution of calcium xenylstearate in benzene (3.48 g. soap/100 cc.).

depends upon the presence in the polar additive of acidic or hydrogen bonding groups; ketones and amines are ineffective. The initial high viscosity of the dry arylstearate soap solutions is considered to result from the aggregation of the soap molecules into polymer-like chains somewhat analogous to those proposed for the aluminum soaps in hydrocarbon solvents (18, 51). The reversion of the sodium phenylstearate to high and markedly non Newtonian viscosity in the presence of a larger amount of water or glycol results from a secondary reaggregation of small micelles into large, shear-sensitive structures. The water appears to hold the secondary aggregates together by a bridging action involving hydrogen bonding.

Both chemical and infrared studies (5, 24) show that hydrolysis of the soap to give free acid is the major mechanism responsible for destruction of the high polymer structure in the arylstearate soaps; the presence of a small excess of free alkali in the sodium soap completely prevents the reduction in viscosity ordinarily caused by the addition of water. The presence of carbon dioxide is a powerful promoter both of hydrolysis and of the reduction in micelle size by water.

Nelson and Pink have concluded that dipole forces alone are probably inadequate to account for the association behavior of the zinc and copper soaps they have studied in toluene and suggest that coordination forces are important. Coordination bonding appears to be the major mechanism responsible for the linear aluminum soap polymers, and it is probable that coordination also plays a part in forming the linear structures in the dry anhydrous arylstearates of the alkali and alkaline earth metals.

The formation of thermodynamically stable micelles requires not only an adequate driving energy but some self-limiting mechanism which prevents the indefinite growth of the micelle with ultimate separation of a second phase. In aqueous soap systems Debye and others (15, 19) have discussed the accumulation of charge as the factor finally preventing the entry of further ions into the micelle. Such a mechanism does not apply to the undissociated molecules which form micelles in nonpolar solvents. Geometrical considerations are the most obvious factor limiting the growth of small approximately isodimensional micelles of the type illustrated in Table 1, in which the binding forces are considered to be nonspecific, rather than definite interatomic bonds of the type proposed for the aluminum soaps (11, 18). The ionic micelle formers characteristically contain bulky hydrocarbon radicals having cross sections substantially larger than the polar heads with which they are associated so that close packing in lamellar sheets, such as occurs in the crystalline phase of normal fatty acid soaps, is energetically less attractive than the compact clustering of polar heads possible in the small and approximately spherical micelle. The number of molecules per micelle is then sterically limited by the relative cross-sections and volumes of the polar head and nonpolar tails, respectively. (This geometrical model for soaps is not appropriate for discussion of nonionic detergents, such as the polyoxyethylene esters, which have bulky polar portions.)

Micelles containing 50 or fewer acid residues must

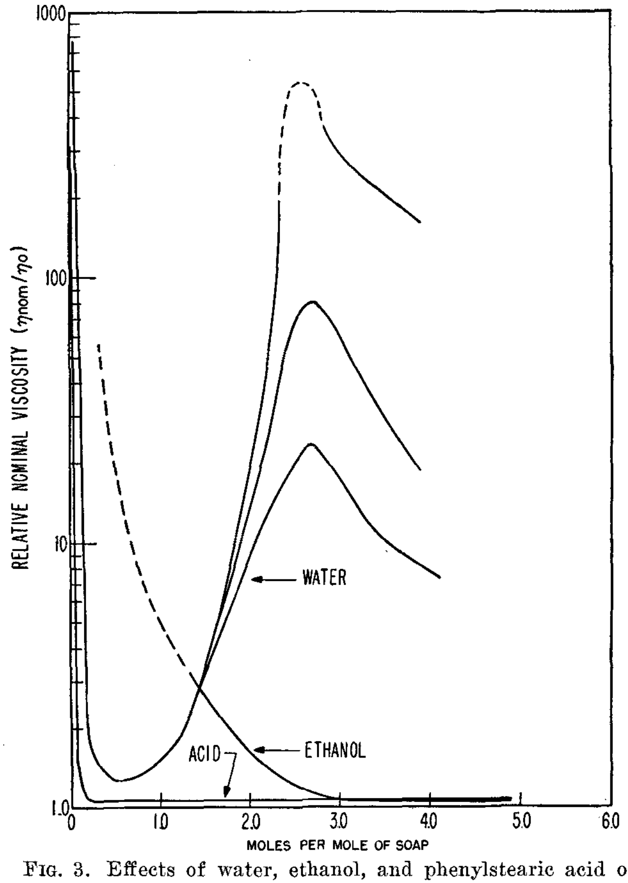

Fig. 3. Effects of water, ethanol, and phenylstearic acid on the relative viscosity of solutions of sodium phenylstearate in benzene (ca. 1.75 g. soap/100 cc.). Upper, middle, and lower branches of water curve refer to low, medium, and high shearing stresses respectively.

be approximately isodimensional because of the molecular arrangement required to shield the polar cores from mutual interaction to form larger aggregates. This will be true whether the idealized pattern of the core is assumed to be a sphere, a cylinder, or a lamella. Given a representative amphipathic molecule with a molar volume of 450 cc. and an effective length of 20 Å, the largest spherical micelle that can be formed by simple radial packing will contain 45 molecules. If the cross-section of the tail is much greater than that of the polar head, the maximum size for a spherical micelle may be less. If the core forces are great enough to pull in a larger number of molecules, the shape of the micelle must be altered to accommodate the added units by deformation to a prolate or an oblate spheroid. If the forces are great enough, and the geometry permits, molecules continue to enter indefinitely, and the micelle becomes a cylinder or a lamella.

The cross-sectional area of the hydrocarbon portion of most oil-soluble amphipaths exceeds that of the polar head. For such molecules the spherical micelle allows the loosest packing of tails about a core of given volume, and the prolate ellipsoid the next, while an oblate ellipsoid of equal eccentricity requires the closest packing. The prolate ellipsoid is thus a more probable form than the oblate ellipsoid as the micelle departs from a spherical shape. The lamella is even less likely, although it might occur if the cross-section of head and tail were equal, as in the normal alkali fatty acid soaps. Here however the lamellae grow into crystals too large to be considered micelles.

Sodium phenylstearate, under suitable conditions, has been shown to form micelles containing approximately 200 molecules (22). Viscosity measurements indicate an eccentricity of 4.8. Accepting twice the length of the soap molecule as the minor axes of the ellipsoid, the volume and eccentricity given are compatible only with a prolate form. The viscometric and osmotic data of Sheffer for various aluminum soaps (51) are consistent with a model of the aluminum soap polymer as a rather rigid rod of eccentricity 40-80; they could not be reconciled with the model of an oblate ellipsoid of equal intrinsic viscosity.

Schulman *et al.* (49) studied concentrated solutions of long-chain hydrocarbon-polyethylene oxides in hydrocarbon solvents. They concluded that the x-ray and optical evidence indicated the appearance of spherical, cylindrical, and lamellar structures; the spherical form is favored at higher temperatures.

Van der Waarden (55) has interpreted his rheological data for sodium petroleum sulfonate in terms of an oblate ellipsoid. If a minimum thickness of 40 Å for the ellipsoid is assumed, the reported eccentricities of 1/5.5 to 1/30 (by the Simha equation) imply micellar volumes of 600,000 to 18,000,000 cc., containing from 1,500 to 45,000 molecules. These values are high in comparison with the directly measured sizes reported in Tables 1 and 2. If, on the other hand, the prolate model is assumed, an estimate from the same rheological data indicates that the micelles contain from 220 to 680 molecules, well within the range of established micelle sizes. The data pertain to rather concentrated solutions (5 to 25%); it is possible that in more dilute systems the estimated size might be still further reduced. Kaufman and Singleterry (28) found 34 molecules (68 acid residues) per micelle for barium petroleum sulfonate in dilute benzene solutions.

It should be noted that if large amounts of water enter the polar core, as in the case of the Aerosol OT micelles studied by Mathews and Hirschhorn, the radius of the micelle may exceed the length of the amphipathic molecule by a large factor and the geometrical considerations applicable to relatively anhydrous systems no longer apply.

Critical Concentration

The idea of a critical concentration below which micelle formation in a soap solution is negligible (1, 23, 39) was proposed by Jones and Bury on the basis of mass law considerations. It has been a productive concept in the study of aqueous soap systems. The effects resulting in an nonaqueous system from an equilibrium,

$$n\,S \rightleftarrows S_n$$

or

$$K = (S_n)/(S)^n,$$

where S_n and S signify the micellar and monomer soap species, respectively, are presented graphically in Figure 4. Here the solid curves correspond to the case in which the micelles formed contain 20 molecules each. It is a peculiarity of such an equilibrium that the formation of micelles becomes appreciable within a narrow concentration range which depends upon the magnitude of the constant K. Above the CMC the fact that the monomer concentration enters the equation to the n^{th} power means that this concentration need change very little as the total soap concentration increases; nearly all further soap added will appear in micellar form. Thus the concentration of molecularly dissolved soap, and hence the activity of the soap in solution, increases only slightly with a many-fold increase in soap content. One deals in

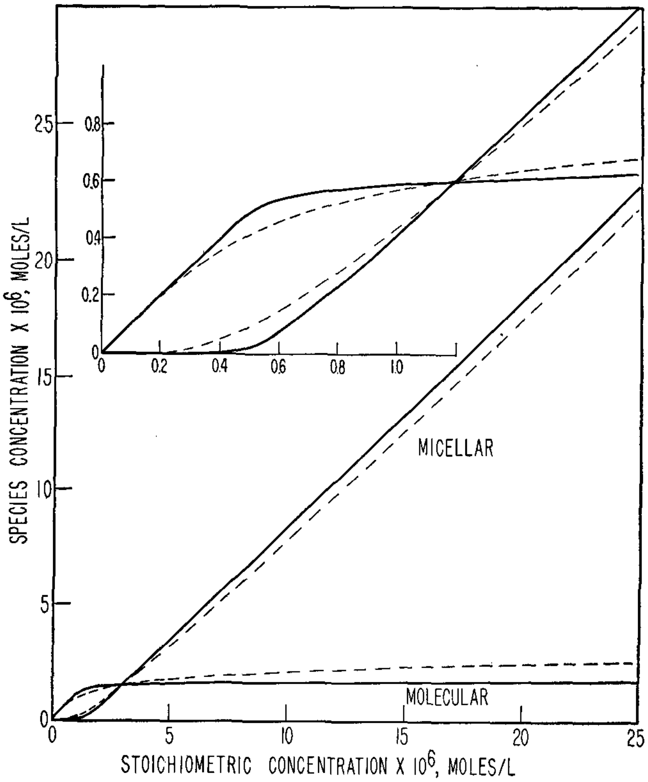

Fig. 4. Concentrations of soap in monomer and in micelles, according to the equilibrium $n\,S \rightleftarrows S_n$. Solid lines, $n = 20$; dotted lines $n = 5$.

effect with a saturated solution in which there is an instantaneously available reserve of micellar soap to make up any loss of monomer by adsorption or chemical reaction. The effect of a lower value of n is to decrease the sharpness of the transition and allow a greater increase in monomer concentration above the CMC; it is illustrated by the dotted curves for the case $n = 5$.

This approximate constancy of the monomer concentration above the CMC explains the plateau that is found in the surface tension curves for aqueous soap systems; it explains also the strong adsorption of a rust inhibitor onto metal surfaces from oil solutions in which the soap might be considered, on superficial examination, to show unlimited solubility. The degree of adsorption of a solute tends to be inversely related to its solubility in a solvent, and maximum adsorption occurs only from a saturated solution (4, 7). In a micellar system all concentrations above the CMC are virtually saturated.

Unfortunately our knowledge of the CMC in nonaqueous micelle systems is still very meager. In the case of the tetra-alkylammonium salts studied by Kraus and co-workers, micelle formation appears to set in at experimentally accessible concentrations in the range between 0.001 and 0.1 molal. This is comparable with the range of the CMC values found for common soaps in aqueous systems. Gonick's data for hexanolamine oleate and caprylate (17) show only that micelle formation is appreciable in the range 0.05 to 0.15 molal. Shaw and Johnson (50) concluded that micelle formation by an alkyd resin in heptane began rather sharply at 0.3 g. per 100-ml. concentration. Ross (47) has reported a CMC for mannitan monooleate in mineral oil at 0.05% concentration of this nonionic surfactant. Pink and co-workers found micelle formation by zinc soaps to be dominant at the lowest concentration at which they were able to make ebullioscopic measurements (about 0.01 molar). Calcium xenylstearate has been shown by Singleterry *et al.* (27, 52) to form micelles in benzene 15% saturated with water at concentrations as low as 10^{-6} molar. The CMC estimated for this system was 6×10^{-7} molar, but the experimental difficulties from adsorption and other wall reactions at this concentration are such that the value can be considered only approximate. Kaufman and Singleterry (28) have recently studied micelle formation by sodium and barium dinonylnaphthalene sulfonates, for both of which the CMC again seems to lie between 10^{-6} and 10^{-7} molar.

The experimental difficulties of working with rigorously anhydrous solutions at very low concentrations have thus far discouraged the investigation of possible CMC phenomena with the polymer-like linear aggregates formed by arylstearate soaps in the absence of water or other acidic solutes. The molecules in these linear structures are considered to be much more strongly bound than those in the small spherical association micelles so that their CMC may be an order of magnitude or more smaller than that of the spherical type. The same considerations apply with equal force to the linear structures formed by aluminum soaps.

One must conclude that in hydrocarbon solutions of ionic micelle-forming salts the concentration of single soap molecules, though important, is exceedingly small.

Solubilization

Beyond the fact that micelle formation provides a mechanism by which an otherwise insoluble polar additive or reagent can be maintained in a non-polar solvent in a stable but instantaneously available form, the largest practical importance of micelles in such systems arises from their ability to solubilize substances in the oil which are themselves not oil-soluble. Water is strongly solubilized by micelles in oil. Aerosol OT has been shown (36) to take up water to the extent of 50 molecules per molecule of soap. The size of the micelles is adjusted, Mathews concludes, so that the detergent present is just sufficient to cover the micro droplets of water with a monolayer of the sodium bis(2-ethylhexyl)sulfosuccinate. Calcium and sodium arylstearates have been found (3, 22) to take up from two to five moles of water per mole of soap but are precipitated from the system by larger amounts. Sodium dinonylnaphthalene sulfonate in benzene solubilizes 10 moles of water per mole of soap; it is not precipitated even in the presence of a separate water phase (22). In this case the amount of water which the soap can hold decreases sharply with increasing temperature, which suggests that the water is largely held by hydrogen bonding rather than as a simple core of liquid water at the center of the micelle. Palit (43) has noted increased solubilization of water in nonpolar solvents by mixed dodecylamine carboxylates, one of which is formed from a short-chain and one from a long-chain fatty acid.

The micellar solubilization of oil-insoluble dyes is a readily observed and almost universal phenomenon (2, 31, 32, 42, 47). Water-soluble dyes characteristically contain at least one ionic group and so are amphipathic molecules which fit readily into the architecture of the micelle in either aqueous or nonpolar systems. If dyes are to be used as qualitative indicators of micelle formation in oils, it is necessary to bear in mind that some dyes can form 1-1 association products with amphipathic molecules and that the resulting complex may be oil-soluble even in the absence of micelles (38). With proper precautions however the solubilization of dyes by micelles in oil furnishes a sensitive tool for the investigation of even extremely dilute micellar systems.

Acids, especially organic acids of high molecular weight, are readily taken up by micelles, even when the acid is otherwise soluble in the solvent in the monomer-dimer form. Baker *et al.* (6) have shown that the sequestration of acetic acid by the barium dinonylnaphthalene sulfonate micelle may reduce the effective concentration of the acid so greatly as to provide an important mechanism for the inhibition of rusting by such sulfonate additives. Glycols, alcohols, and phenols have also been shown to be solubilized by arylstearate soaps (22). This suggests a method for maintaining in an oil a higher concentration of a difficultly soluble oxidation inhibitor than might be otherwise possible (9), but it also implies that in the presence of an oil-soluble soap the effective concentration of free inhibitor at any instant may be much lower than the total amount present.

Soap micelles in oil also solubilize soaps, such as sodium or calcium stearate or sodium benzoate, which are otherwise insoluble in hydrocarbon solvents at room temperature (46). Honig has found that sodium phenylstearate will carry as much as 15% by weight of sodium stearate into micellar dispersion in benzene, with very little apparent change in the colloidal properties of the system. It is well known that oil-soluble petroleum sulfonates may contain on the order of 5% of carboxylate soaps. These examples might be viewed as cooperative micelle formation rather than solubilization. The phenomenon is analogous however to the mechanism proposed by Harkins and others for the solubilization of long-chain alcohols in aqueous micelles (20, 30). It is probable that in non-aqueous systems nearly all solubilization (except for water and similar small polar molecules) involves such cooperative micelle formation.

The field of solubilization by micelles of oil-soluble soaps has been little studied and will repay a larger amount of research attention that it has yet received.

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Report of the Spectroscopy Committee, 1954-1955

THE SPECTROSCOPY COMMITTEE in its report for 1952–1953 [Journal, *30*, 352 (1953)] concluded that "reasonably reproducible results, using A.O.C.S. Tentative Method Cd 7-48, revised May 1951, can be obtained in the hands of experienced operators."

In the report for 1953-1954, at the spring meeting in San Antonio, the committee confirmed this statement but concluded that "while the method gave satisfactory results within its scope, this scope was too restrictive." Many types of samples cannot be analyzed by the tentative method, several others are analyzed by unnecessarily complicated procedures. No further collaborative work is required to test the method, but further work is desirable to investigate possible means of extending its scope. Further investigation, with the view to simplifying the procedure in the analysis of specific types of samples, is also needed.

Present Work

Accordingly during the past year your committee has conducted a series of collaborative tests to determine whether

1. the method can be simplified in the analysis of samples which do not contain constituents more unsaturated than linoleic acid. Specifically can the method be revised to restrict measurements and calculations to the dienoic region in the analysis of cottonseed oil, peanut oil, sesame oil, and similar vegetable oils? The present A.O.C.S. method Cd 7-48 permits only elimination of measurements in the tetraene region.
2. a satisfactory modification can be devised which will permit the measurement of polyunsaturated nonconjugated constituents in the presence of large quantities of conjugated polyunsaturated constituents. Specifically can the linoleic acid content of tung oil be determined by any modification of the method? The present A.O.C.S. method Cd 7-48 is limited to materials containing only traces of preformed conjugation.
3. the method can be extended to include the determination of pentaenoic acids with the use of 21% alkali reagent. Is this reagent preferable for the determination of arachidonic acid? What recommendations can be made regarding the selection of % alkali in the reagent? The present A.O.C.S. method Cd 7-48 permits only the use of 6.6% alkali and does not provide for the analysis of pentaenoic acids.

Results of these collaborative tests are summarized briefly in Tables I, II, III, and IV.