SOLUBILIZATION

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I. INTRODUCTION

A considerable amount of literature has been devoted to the various phenomena associated with surface-active agents. The problems of hydrotropy, solubilization, emulsification, and blending have made up an appreciable fraction of these reports, but unfortunately by far the greater part of this work has been done with soaps and detergents which have not been well characterized, since they were essentially commercial preparations. That these data are important from the point of view of application is clearly accepted, but no information can be obtained from them as to the various factors which influence solubilization. During the past few years, attempts have been made in a few laboratories

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to distinguish between these factors and to determine various types and mechanisms of solubilization.

To restrict somewhat the scope of the term "solubilization," it is necessary to define the companion terms "hydrotropy," "blending," and "emulsification." Neuberg (178) used the term "hydrotropy" to designate the increase in solubility in water of various substances due to the presence of large amounts of additives. Thus the presence of 25–50 per cent of sodium benzoate, benzenesulfonate, or others of this class increases the solubility in water of aniline, amyl alcohol, toluene, benzoic acid, and others. The solubility of benzoic acid is increased from 2.9 to 8.7 g. per 1000 g. when 2 N (about 50 per cent) sodium benzenesulfonate solution is used as the solvent in place of water (57). These phenomena must be due to a change in solvent, for essentially large proportions of this good solvent (additive) are necessary to bring about these increases in solubility. McKee (166) pictures this process as a salting-in effect in contrast to the well-known phenomenon of salting-out. However, it is necessary to understand that the classification of hydrotropy and solubilization as separate phenomena (144, 178) is not necessarily valid. There is a continuous gradation in the behavior of the sodium salts of fatty acids as solubilizers as the chain length increases (44a, 50, 178, 254). In ascending an homologous series, as from C_1 to C_{11} normal fatty acid soaps, there is a gradual change in solubilizing (= hydrotropic) properties (44a), just as there is found a twofold decrease in critical micelle concentration with each addition of one carbon atom to the normal alkyl chain (82, 109). For the lower members of this series, the solubilizing properties become evident at high concentrations (30–50 per cent); for the higher members, this concentration is much lower, but the general character of the processes involved is characteristically the same throughout (254).

A similar type of salting-in phenomenon is observed in the increase in solubility of polycyclic hydrocarbons, such as benzanthracene, in solutions of purine and pyrimidine bases as compared with water as a solvent (249). This enhanced solubility, a type of hydrotropy, has been shown to involve complex formation between added solvent and solute molecule, as evidenced by a decrease in fluorescence of the polycyclic hydrocarbons (250). It is possible that the salting-in phenomena, observed in those cases where the added solvent molecule is structurally similar to that of the solute molecule, would also involve the formation of complexes. Another method which would indicate hydrotropy is the phenomenon involved in those cases where there are spectral changes observed with the use of different solvents. Thus, the spectrum of 1,2,5,6-dibenzanthracene is observed to change when n-heptane is replaced by benzene or by 1-methylnaphthalene as a solvent (120).

Blending (182, 184) is a broad term which has been distinguished from solubilization by recourse to phase diagrams (8, 184, 248). This process involves the blending or mutual solubility of two normally immiscible solvents by the addition of a colloidal electrolyte. Thus, dodecylamine hydrochloride added to chloroform even in low percentages enables the chloroform to dissolve large quantities of water, up to 45 moles of water per mole of detergent. Conversely, the presence of water enables the chloroform to dissolve about one-fourth of its weight of dodecylamine hydrochloride, although both these substances are nearly insoluble in water (182).

Solubilization has been defined by McBain as the spontaneous passage of solute molecules of a substance insoluble in water into an aqueous solution of a soap or a detergent in which a thermodynamically stable solution is formed (144). The formation of such a system involves a decrease in free energy which indicates its thermodynamic stability. Solubilization involves the diffusion of the added solute molecules from bulk phase (insoluble solids, oil droplets, etc.) into the soap micelle. Beyond the point of saturation of the micelle with added solute, emulsification is seen to occur by the appearance of turbidity in those cases where the added solute is liquid in nature. Thus, the formation of a more or less stable system in which the dispersion of the added insoluble liquid is of such a nature that there is an appearance of turbidity due to the presence of the droplets of additive can be used as an indication of emulsification. It is then apparent that normally these two phenomena, solubilization and emulsification, can coexist, the latter beginning when the former reaches its limit. Hartley (84) objects to the use of a new term, "solubilization," to define the conditions described above, in that it appears to imply that an essentially new process is under investigation and that it is often held that the resulting solutions are not in equilibrium. The peculiarity is that the solvent is unusual in structure rather than that the solute is brought into an unusual state. Thus, a much smaller amount of a paraffin-chain salt than of acetone is necessary to bring a long-chain alcohol and water into complete miscibility. However, since the solvent power of the colloidal electrolyte, in contrast to that of acetone, is fairly constant over a wide concentration range, it is felt by this reviewer that the use of an apparently new term is justified. The current wide acceptance of the term also may validate its use.

Winsor (254) has extended the point of view put forward earlier by Lindau (137) and by von Hahn (246) that hydrotropy and solubilization are essentially similar processes. Qualitatively, this is based on the fact that the attractive forces between molecules and ions in solution may arise from mutual satisfaction of H (hydrophilic) solvent affinities (A_H), e.g., solvent affinities dependent on hydrogen bonding, and L (lipophilic) solvent affinities (A_L), e.g., van der Waals forces. Between any two species O (oil) and W (water) in a single liquid phase, the total intermolecular solvent attraction can be represented qualitatively as:

$$A_{OW} = A_{H_{OW}} + A_{L_{OW}}$$

The attraction will depend in detail on solvent affinities and concentrations of both O and W (242). The point of view extended by Winsor is not in opposition to the micelle theories of solubilization (144) but is considered supplementary to them. He attempts to correlate phase changes,[2] which are the observed results of

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[2] The problem of the use of the word "phase" in connection with soap solutions requires some clarification at the present time. Since it is agreed that soap solution and solubilized (dissolved) organic liquid form a thermodynamically stable solution, this must be a single phase, since a solution by definition is a single phase. If a system contains two phases, con-

changes in composition and temperature, in terms of displacements of an underlying micellar equilibrium. In this review the micellar aspects of solubilization will be favored, for most of the available experimental findings can be readily understood by means of this approach.

The evidence of molecular association, for example, as advanced by solvent effects on the spectra of polycyclic hydrocarbons (120) and the change in fluorescence of polycyclics in the presence of purine and pyrimidine bases (250), which can be considered to be hydrotropic phenomena, can be seen to involve a binding of one solute molecule with one or more added solvent molecules. Clar (22) has shown recently that ovalene in 1-methylnaphthalene has absorption bands at 4650, 4600; 4560, 4480, 4280, 4035, 3890; 3490 Å., and corresponding bands are observed in benzene at 4635, 4585; 4525, 4450, 4250; 3450 Å. The increase in solubility of benzoic acid in water containing added sodium benzoate over that in water alone probably also involves a type of molecular association which is similar to that involving polycyclic hydrocarbons. However, association in the former case almost certainly involves hydrogen bonding between the —COONa, —COOH, and water on the one hand (hydrophilic association) and the operation of van der Waals forces between the C_6H_5 groups on the other (lipophilic association), whereas only the latter forces can be considered to be operative in polycyclic association. In the solubilization of polar type compounds, these two types of association forces are operative, whereas when hydrocarbons are being dissolved in soap micelles, it is primarily the lipophilic forces which are involved. These interactions require relatively high concentrations of reactants, often of the order of 1 to 2 *N*. On the other hand, solubilization is found to occur at much lower concentrations, first being noted at that concentration where micelles begin to form. This is called the critical micelle concentration (C.M.C.) and is often as low as 10^{-3}–10^{-4} *M*. It has been shown to depend on such factors as chain length and structure of the surface-active agent, the presence of additives such as electrolytes, long-chain alcohols, amines, amides, etc., as well as temperature and the nature of the solvent. The effect of these factors on solubilization and the relationship of these results to the C.M.C. will be discussed below.

II. METHODS OF OBSERVATION

There are a number of methods for determining the extent of solubilization which depend on the structure of the solubilizate (the substance being solubil-

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tinuous and discontinuous, then by definition it can not be termed a solution. It must be recognized, however, that there are regions in these solutions in which there is practically nothing but paraffin-chain molecules (micelles) and other regions which contain water and simple ions. These latter systems approximate in their behavior to a two-phase system in certain respects, e.g., solvent power, but they are of course fundamentally different in others. It is convenient, though thermodynamically inaccurate, to classify certain of these systems as having a water-continuous phase or environment and others as having a hydrocarbon-continuous one. This concept must be considered to have only a geometrically descriptive meaning. The essential difference between the two-phase oil–water emulsion system and the "two-phase" soap solution is that the size of the region is of considerably different fundamental thermodynamic importance in the two cases. In a series of letters between Dr. G. S. Hartley, Dr. P. A. Winsor, and the author, it was deemed necessary that these concepts be clarified; the above discussion has made free use of this correspondence.

ized), the difference in refractive indices of soap solution and solubilizate, the vapor pressure of the solubilizate, and various other factors. Various methods which have been used and a few typical examples of each will be discussed.

A. OPACITY METHOD

If the refractive indices of the soap or detergent solution and the solubilizate (usually a liquid) are different, then the presence of solubilizate aggregates or droplets in the soap solution will be evidenced by a turbid appearance of the system. This onset of turbidity, due to the formation of aggregates, has been used to indicate the limit of solubilization. This phenomenon was utilized as early as 1892 by Engler and Dieckhoff (50) to determine the solubility of a series of hydrocarbons in various soap solutions and has since been used by many others.

To definite amounts of soap solutions in a series of vials, there are added known but different amounts of solubilizate. These vials are then shaken for from 1 to 60 days, for it has been shown that equilibrium is only reached in from 24 to 60 hr. when hydrocarbons such as *n*-heptane, benzene, or ethylbenzene are being solubilized (86) and as many as 60 days are required when very insoluble polyacenes such as benzanthracene and dibenzanthracene are the solubilizates (113). Typical of the data obtained by these opacity measurements are the curves in figures 1–3.

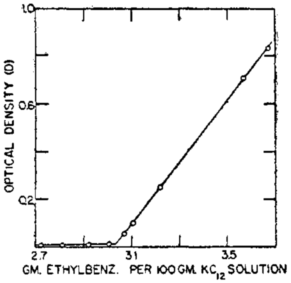


FIG. 1

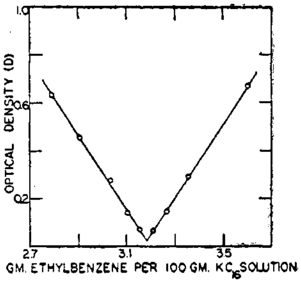


FIG. 2

FIG. 1. Limit of solubilization of ethylbenzene in 0.63 *M* potassium dodecanoate per 1000 g. soap solution as determined turbidometrically (25°C.).

FIG. 2. Solubilization of ethylbenzene in 0.21 *M* potassium hexadecanoate per 1000 g. soap solution (35°C.).

If soap solutions are initially clear, transparent systems, then the addition of solubilizate will show opacity characteristics similar to those observed in figure 1. The initial potassium laurate (KC_{12}) solution has an optical density (D) of about zero. Addition of various amounts of a hydrocarbon such as *n*-heptane or ethylbenzene or a polar compound such as 1-heptanol or *n*-heptylamine will show little or no change in D until the point of maximum solubilization. Any more solubilizate added will result in the formation of oil droplets (emulsification), as can be seen by a marked increase in D. The intersection of these two lines is taken as the point of maximum solubilization.

In those cases where the initial soap solution is initially opaque, as when potassium stearate (KC_{18}) solutions are used as solubilizers, the addition of solubilizate will cause an initial decrease in D until a relatively transparent solution is obtained. An example of this type is seen in figure 2 and, as above, the point of maximum solubilization is the intersection of the two lines. The initial decrease in turbidity upon addition of solubilizate is due to a decrease in size of the aggregated micelles.

Recently (112) opacity curves similar to that in figure 3 have been obtained in those cases of solubilization of hydrocarbons by long-chain polar compound–soap micelles. If, for example, the amount of 1-heptanol added initially exceeds its normal solubility in KC_{14} solutions and if, to these solutions, are added various amounts of *n*-heptane or ethylbenzene, changes in turbidity following the curves in figure 3 are obtained. The initial opacity is due to the presence of droplets of 1-heptanol emulsion in equilibrium with mixed KC_{14}–1-heptanol micelles. Addition of *n*-heptane, which enters the hydrocarbon-like center of the micelle, causes the micelle to swell, and, simultaneously, more alcohol molecules pass from the emulsion droplets through the water to the alcohol–soap micelle. This is indicated by the initial decrease in opacity. As more *n*-heptane is added, the micelle swells more until all emulsified alcohol has been solubilized. Addition of further *n*-heptane to this clear system yields the typical two straight lines as in figure 1, in which the intercept is the limit of solubility. This limit is then the second transition point. These results will be discussed below in the light of the various loci of solubilization which are present in the soap micelle.

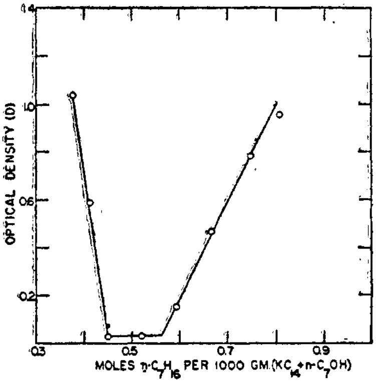


FIG. 3

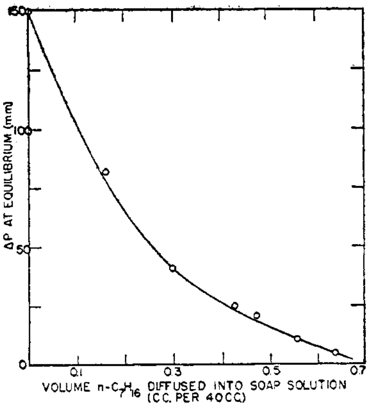


FIG. 4

FIG. 3. Solubilization of *n*-heptane in soap–alcohol micelles (0.375 *M* potassium tetradecanoate plus 0.315 *M* 1-heptanol) at 25°C.

FIG. 4. Difference in vapor pressure between *n*-hexane–water and soap solution during progressive addition of *n*-hexane to 5.62 g./100 ml. potassium oleate solution (159).

It can be seen that the opacity method is readily applicable to systems in which the solubilizate is a liquid, for in these examples the initial formation of liquid droplets of solubilizate can be used as an indication of the extent of solubilization. Davis, Krahl, and Clowes (31) measured the solubility of polycyclic hydrocarbons in water by a turbidometric method. They used concentrated solutions of the polycyclics in acetone or ether and added weighed amounts of these solutions to relatively large volumes of water. The acetone or ether was then boiled off under high vacuum and the turbidity of the system was measured by a sensitive Tyndallometer. It was assumed by these authors that the dissolved polycyclics were molecularly dispersed and that the limit of solubility involved the precipitation of microcrystals of these hydrocarbons. The solubilities of polycyclic hydrocarbons in water obtained by the turbidity method were essentially in agreement with those obtained by spectroscopic measurements, in which advantage was taken of the presence of absorbing chromophores in these compounds (113). There is no literature on the application of this technique to the solubilization of solids, but experiments using this method are now in progress in this laboratory to determine the solubilization of long-chain hydrocarbons such as *n*-octadecane, *n*-eicosane, and *n*-docosane. The preliminary results indicate that this method may be applicable for the determination of solubilities in soap solutions of those solid compounds which do not have absorbing chromophores or other properties which can be used as indications of saturation.

B. SPECTRAL METHOD

The presence of absorbing chromophores in solubilizates can be readily used to determine the degree of solubilization, especially in the cases where the compound being studied is a solid. Essentially, to soap solutions of known concentration, crystals of solubilizate are added and the system is shaken until equilibrium is reached. In those cases of solubilization of dyes such as Orange OT (*o*-tolylazo-β-naphthol) and Yellow AB (phenylazo-β-naphthylamine), McBain and collaborators (144, 155, 163) have found that equilibrium conditions were only reached after days and even weeks. Solubilization equilibrium of very slightly soluble polycyclics such as 1,2,5,6-dibenzanthracene was only reached after almost two months (113) at room temperature. Lambert and Busse recommend the use of 50°C. for the solubilization temperature instead of 25°C. and report that solubilization values sufficiently close to the equilibrium values could be obtained within 15 min. if the tests were made at 50°C. and if the amount of dye to be solubilized does not exceed certain limits (131). This latter method might be suitable for the comparison of results using various dyes and solubilizer systems but might not find general application. Kolthoff and Stricks (125) found that there was an increase in the solubilization of dimethylaminoazobenzene in various detergents when the temperature was increased from 30°C. to 50°C.

After equilibrium is reached, aliquots are removed from the solubilization system and diluted by suitable solvents. Care should be taken that no solid solubilizate is included with the aliquot. The spectral characteristics of the solubilizate which had been determined previously are used as a standard and by means of the proper use of the Beer–Lambert law, it is possible to calculate the concentration of the compound which has been solubilized. The spectra of colored compounds can, of course, be measured in the visible region, whereas use must be made of the ultraviolet region for compounds such as the polycyclic hydrocarbons. Solid residue, nonsolubilized solubilizate, may be allowed to settle for a number of days before removing aliquots or recourse to centrifugation may be made to hasten this process. Extreme care must be taken to insure that there is no suspending and protecting of these solid solubilizates in addition to solubilization. In the experiments of McBain and Woo (164), it was indicated that, in addition to solubilizing the dye (Yellow AB), there was also considerable suspending and protecting of colloidal particles of the dye, which resulted in too large values of solubilization.

C. VAPOR PRESSURE METHOD

Since there is a decrease in the vapor pressure of an insoluble volatile liquid when the medium is changed from water to a soap solution, McBain and O'Connor (158) were able to measure the solubilization of various volatile organic compounds. The colloidal solutions formed when volatile organic liquids are allowed to come in contact with soap solutions are thermodynamically stable because the vapor pressure is significantly less than that of the free hydrocarbon until the solution is approximately saturated.

Typical of the type of experimental results obtained by these measurements are the curves in figure 4 (158). Equilibrium vapor-pressure values are plotted and indicate the increase in vapor pressure of the indifferent hydrocarbon as the soap solution gradually becomes saturated with solubilized hydrocarbon. Saturation is reached when the vapor pressure of the hydrocarbon over the soap solution reaches its value over water. This method is not very sensitive to changes in environment, for the addition of various electrolytes does not show effects corresponding to those observed by other methods (159).

D. OTHER METHODS

X-ray measurements have indicated an increase in spacing of a particular band upon addition of hydrocarbon. (The interpretation and discussion of these patterns as related to micellar structure will be advanced later.) Thus, Kiessig and Philippoff (101) have indicated that the long x-ray spacings of a 9.12 weight per cent sodium oleate solution increase from 91 Å. to 127 Å. upon the addition of 0.791 g. of benzene per gram of oleate. There is a gradual increase in spacing upon increment addition of hydrocarbon until the saturation point is reached. Beyond this point, further addition of hydrocarbon will result in little or no increase in this x-ray spacing. Thus, Mattoon (73) has shown that in the solubilization of *n*-heptane in 25 per cent potassium laurate (KC_{12}) the value of ΔD_I (x-ray increment of intermicellar spacing in Ångström units) varies according to the relation:

$$\Delta D_I = 3.82C$$

where C is grams of *n*-heptane per 100 g. of soap plus water. Above a C-value of 3.6, the ΔD_I-values are constant. Thus, the measure of change in long x-ray spacing could be applied to the determination of solubilization and the limit of solubilization could be obtained at that concentration of C when ΔD_I began to be constant. Similarly, McBain and Hoffman (150) have shown from x-ray measurements of 50 per cent KC_{12} solutions that there is a linear increase in ΔD_I with added cumene up to a saturation limit where ΔD_I remains constant with further addition of oil. Up to the constant value the systems are clear; at oil concentrations above this, they appear cloudy.

There are indications from x-ray measurements that the molecular weights of soap micelles increase with added hydrocarbon. (The added hydrocarbon is not included in these calculations.) Preliminary light-scattering measurements at concentrations of added hydrocarbon just below saturation indicate about a doubling of the number of soap molecules per swollen micelle as compared with the hydrocarbon-free micelle (113). This latter method could be modified so as to determine the amount of hydrocarbon solubilized at a point just under saturation. Above this saturation value, the presence of oil droplets would interfere considerably.

In summary of the available methods, it can be seen that for liquid solubilizates whose refractive indices are not the same as that of the soap solution the turbidometric method would be simplest. For solids with absorbing chromophores in either the visible or the ultraviolet, the spectral method can be readily applied. For vapors, the vapor pressure method is applicable, and for indifferent solids such as solid alkanes or solid olefinic compounds (nonconjugated systems), a modification of the method of Davis *et al.* (31) could be used.

Since the absorption of a simple monoölefin has a maximum at about 1860 Å. (189) with a shift to about 1960 Å. with further alkylation (188), the measurement of solubilization of compounds of this class by spectral means would require the use of a fluorite vacuum spectrograph of the Cario–Schmitt–Ott type. However, it has been shown that many of these compounds have long-wave-length absorption tails which extend into the quartz region to about 2050–2100 Å. (119), and it has been possible to measure the solubilization of a number of biologically important sterols such as cholesterol and isocholesterol in this manner (118).

The presence of minima in surface tension and interfacial tension measurements has been attributed to the presence of impurities (173, 219, 221) which may be removed by foam extraction or by solvent extraction. This might be considered to be applicable as a method of determination of solubilization in the region of the critical micelle concentration for, although the minima occur at about the same surface tension values (221), the shapes of the surface tension–concentration curves with different amounts of additive are sufficiently different to warrant their use as indicators of solubilization.

III. TYPES AND MECHANISMS OF SOLUBILIZATION

The possibility of hydrotropy as one of the types of solubilization can be ruled out on the basis of the mechanisms involved. The phenomenon of hydrotropy involves the use of very large amounts, as much as 2 N or more, of the additive and probably acts through the processes of molecular association. This can be considered to be a solvent effect similar to that which has been observed in solvent effects with polycyclic hydrocarbons (22, 120 249, 250) (however, *vide supra*).

A number of other possibilities present themselves. First is the possibility of adsorption on the surface of the micelle; second, incorporation in the hydrocarbon center of the micelle, a form of solution; and third, incorporation by penetration into the palisade layer of the micelle with the solubilizate oriented in approximately the same manner as is the soap molecule in the micelle. These three possibilities will be discussed in detail below.

A. ADSORPTION BY THE MICELLE

The formation of films at liquid–liquid or at liquid–solid interfaces is such a common phenomenon that it is to be expected that solubilization would involve, to some degree, this action at the soap micelle–water interface. Whether this actually occurs is somewhat doubtful, as can be seen from the discussion below, but since definite evidence as to the absence of adsorption is not available, there is the possibility that this may play some role in solubilization.

When a charged dye such as pinacyanol chloride is added to a soap solution at concentrations below the C.M.C. there is often observed the formation of a precipitate (107), since the dye and the soap are oppositely charged. This insoluble complex salt is solubilized as the C.M.C. is passed by the addition of more soap to the system. As the C.M.C. is passed, there is a change in the association of the dye molecule which has been used as a method of determination of the C.M.C. (28). This would indicate that below the C.M.C. the dye molecules are in their P-form (dimer or higher) with one or more bound soap molecules, and that, upon solubilization, above the C.M.C. the dye goes to its M-form (monomer) when the soap molecules associate to form micelles. It must be accepted that the soap molecules which are acting as solubilizers and those of the soap–dye aggregates which are solubilized play an equal part in micelle formation and occupy essentially the same relative positions in the micelle. The charged, bound dye molecule, with a charge opposite to that of the soap molecules, thus can be considered to be adsorbed on the surface of the soap micelle, but it would appear more reasonable to expect that, because of their nonpolar nature, they would be more attracted toward the less polar region in the palisade layer of the micelle than toward the polar region of the water layer surrounding the micelle. It is probable that, since this dye is amphipathic, the charged end of the dye molecule penetrates into the water layer as does the soap molecule and the hydrocarbon end is oriented similarly to the corresponding hydrocarbon tail of the soap molecule. The penetration must be for only a very short distance, for the presence of the dye molecule does not decrease the C.M.C. by more than a few per cent. Also, the presence of short-chain soaps tends to increase the C.M.C. (105) and decrease the solubilizing power of longer chain soaps (114, 117). In contrast to these findings, the presence of short-chain alcohols (C_4–C_7) as additives decreases the C.M.C. (26, 199) and increases markedly the solubilizing power for hydrocarbons (114). The effect of these additives on solubilization will be discussed in detail below, but they appear to indicate that if sorption by micelles occurs, it is probably the type which involves the least amount of penetration into the palisade layer of the micelle and does not necessarily mean that the sorbed molecule is sticking out from the micelle surface into the surrounding water layer. Thus, rather than classify this as a separate type of solubilization, it would appear that this should be, at most, a subclass of the incorporation by penetration group. McBain and McHan (154) have recently shown that there is a marked increase in the solubility of dimethyl phthalate in soap solutions over that in water. They postulate an adsorption on the micelle surface based on the fact that there is a decrease in the long x-ray spacing (150). It is more probable that these small polar compounds are not adsorbed on the micelle but rather penetrate only a very short distance into the palisade layer of the micelle. This is in accordance with the penetration of alcohols into the soap palisade layers, as shown by recent x-ray evidence (74), and with the marked enhancement of solubilization of hydrocarbons when alcohols are used as additives (112, 114). These points will be discussed in more detail in the following sections.

B. INCORPORATION INTO THE HYDROCARBON CENTER OF THE MICELLE

There is very direct evidence that the addition of hydrocarbons to soap solution involves penetration of these additives into the hydrocarbon center of the micelle. The extensive x-ray work of Krishnamurti (127), Hess and others (88, 101, 228), Hughes, Sawyer, and Vinograd (97), and Mattoon (73, 143) indicates that, from the increase in long x-ray spacings upon the addition of hydrocarbons, the solubilizate enters the hydrocarbon center of the micelle. These long x-ray spacings are supposed to correspond to the layers of soap molecules placed end to end and to a double layer of these soap "bundles" plus a portion of the water layer between this double layer and adjacent "bundles." It has been shown that with increase in soap concentration there was a corresponding decrease in this long x-ray spacing (101). Calculations from x-ray measurements as to the degree of expansion of the soap micelles with increase in concentration of added hydrocarbons assume that there is no change in the thickness of the water layer during solubilization. On the basis of this extensive x-ray work, it has been proposed that solubilization takes place in these adjacent "bundles" or lamellar micelles (73, 144). Typical of the manner in which these findings are represented are the diagrams in figure 5, in which highly idealized schematic diagrams of both the lamellar micelle of McBain (144) and the spherical micelle of Hartley (79), with and without added hydrocarbon, are shown.

The expansion of the long x-ray spacing, D_I, which is associated with the distance between adjacent double layers of soap molecules and which varies with soap concentration, has been the foremost argument advanced for the existence of the lamellar micelle (144). However, it should be noted that these same x-ray data can also be interpreted in the light of the manner in which the two-layer micelles (spherical or oblate spheroid) pack. This concept has been advanced by Hartley (81) and will be discussed below in the section on structure and organization in soap solutions (Section IX). Recently, it has been shown that there is another very weak x-ray band, the spacing, D_M, which appears to be that of the double-layer micelle (143). This x-ray spacing is found to be independent of concentration, a fact which supports its identification as the two-layer micelle band. The D_M spacing has been shown to increase with added hydrocarbon, reaching a maximum at the limit of solubilization.

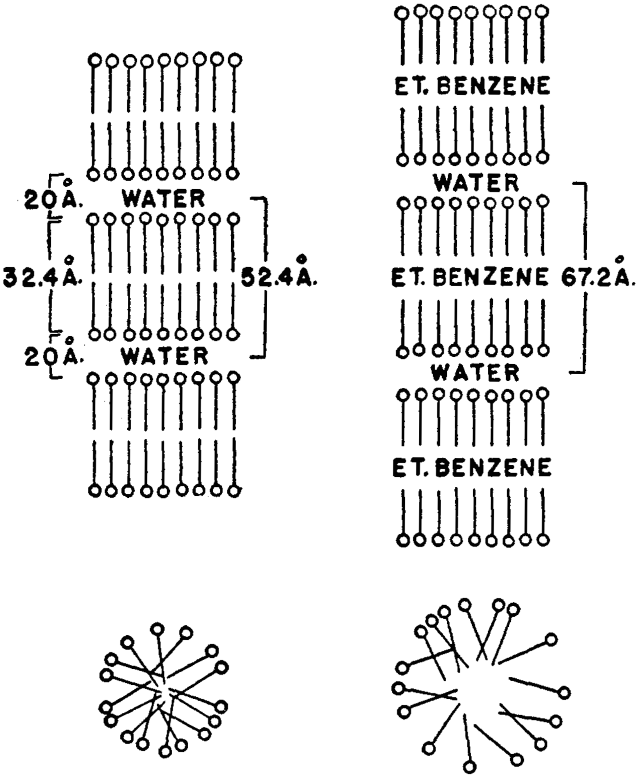


FIG. 5. Highly idealized schematic diagram of 0.63 N potassium laurate solutions showing effect of added ethylbenzene. Lamellar micelle of McBain and spherical micelle as pictured by Hartley are shown.

It was found that the solubility of azobenzene in aqueous solutions of cetylpyridinium chloride is approximately the same as in an equivalent amount of hexadecane (80), indicating that there is essentially a liquid paraffinic interior in the soap micelles. This will hold, of course, only for nonpolar solutes and will not be at all applicable to polar solubilizates which have a different locus of solubilization in the soap micelle.

Typical of the solubilization data is the solubilization of n-heptane in potassium tetradecanoate, shown in figure 6. In the solubilization of all simple hydrocarbon compounds, e.g., the liquid paraffins, benzene and alkylated benzenes, etc., it is noted that the rate of solubilization increases with increasing soap concentration. As the size of the hydrocarbon increases, as when the solubilizates are polycyclic hydrocarbons, the rate becomes constant (113). When simple polar compounds such as dimethyl phthalate (154), long-chain alcohols and amines up to about C_{10} (75, 112) are solubilized, the rate of solubilization decreases with increasing soap concentration. The data for 1-heptanol in KC_{14} are included in figure 6 for comparison. When the size of the polar compound increases, as when polar dyes, alcohols of C_{10} or more, etc. are the solubilizates, this rate again becomes fairly constant. It is evident that there are transition compounds which behave somewhat like the hydrocarbons in solubilization because the nonpolar portion of the molecule is large enough to counterbalance any influence exerted by the polar group.

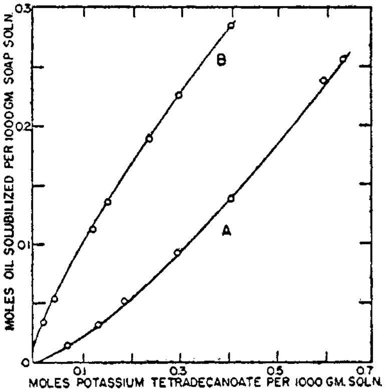


FIG. 6. Solubilization of *n*-heptane (A) and 1-heptanol (B) in potassium tetradecanoate solutions (25°C.).

It has been suggested (111, 254, 255a) that in any discussion of solubilization and solubilizing power (moles of oil solubilized per mole of micellar soap) it is necessary to distinguish between two quite different limiting cases of solubilization. In one type, as is exemplified by the solubilization of *n*-heptane, the limit is reached when the hydrophobic micellar regions can dissolve no more heptane and excess hydrocarbon separates as a phase containing negligible amounts of the other components of the system. In the other type, as in the solubilization of 1-heptanol, the limit is approached when the micellar regions of the solution become sufficiently lipophilic on account of the inclusion of the long-chain alcohols in the soap layer (penetration into the palisade layer of the micelle) to cause the separation of two phases. The fact that there are observable marked differences in viscosities of these alcohol-swollen and hydrocarbon-swollen micelles and that the micellar weights of the alcohol–soap micelles are at least ten times as large as those of the hydrocarbon–soap micelles (118, 121a) indicates that the limiting micellar structure causing phase separation in the first type is probably quite different from that causing separation in the second. Winsor (255a) further suggests that these micellar structures are limiting forms of

S_1 (hydrophilic layer on the surface of some form of "globular" micelle) and S_2 (hydrophilic layer predominantly towards the inner portion of a "globular" or lamellar micelle) types of micelles, respectively.

C. PENETRATION INTO THE PALISADE LAYER OF THE MICELLE

Solubilization of polar compounds such as alcohols, amines, longer chain soaps, fatty acids, insoluble soaps, various polar type dyes, possibly some mercaptans, etc. can be considered to involve penetration into the palisade layer of the soap micelle rather than incorporation into the micelle center. Solubilization of this type involves a more or less oriented solubilizate with reference to the position of the soap molecule in the micelle. Schulman and Hughes (211) have shown that mixed films of alcohol and soap are possible, as was indicated by an increase in film pressure when a solution of sodium hexadecyl sulfate was injected under a condensed monolayer of hexadecyl alcohol. This type of evidence, coupled with characteristic x-ray studies in which it has been indicated that there is no increase, but at times a decrease, in x-ray spacing, D_M, and also with typical solubilization data of polar compounds, supports the concept that solubilization takes place in the palisade layer of the soap micelle.

Probably the first indication of polar type solubilization in which there was no increase in long x-ray spacing was that involving the changes in D_I spacing for soap mixtures (72). Unrecognized by these authors was the fact that, since the long spacing of mixtures of KC_{12} and KC_{14} is a linear function of the mole ratio of the two soaps, solubilization of the less soluble soap by the other must involve penetration into the palisade layer. If there were any other type of solubilization involved, the long x-ray spacing would have to go through a maximum. More recent x-ray evidence on the changes in D_I with added dimethyl phthalate indicates a decrease with concentration of solubilizate (150). This same D_I spacing is seen to decrease with added alcohol, reaching a minimum for the C_3 alcohol, and to increase above that of the water value for C_6 and longer alcohols (74). However, when the micellar band, D_M, is considered, all spacings decrease below the alcohol-free value for alcohols up to C_{10} when the solubilizer is sodium dodecyl sulfate. It is quite likely that for the longer chain alcohols—C_{12}, for example—ΔD_M would be approximately zero. No data have been reported for this solubilizate, probably because of the experimental difficulties involved in the preparation of these systems. 1-Dodecanol, with a melting point of about 22–23°C., is found to solidify upon addition to soap solutions at room temperature and requires heating to disperse it completely (115). 1-Dodecanol, as well as other added long-chain polar compounds, and soap solution readily produce a viscous birefringent gel (115, 254) and this gel formation is especially marked in systems containing 1-alkanols in conjunction with 1-alkane salts (254, 255). Transition effects have been noted in comparing the solubilization of hydrocarbons and of long-chain alcohols in soap–electrolyte solutions (115). Thus, 1-decanol and 1-dodecanol appear to have solubilization properties intermediate between those of the shorter chain alcohols, up to C_8, and those of *n*-heptane in KC_{14}–potassium chloride solutions. When a shorter chain soap is used, as when KC_{12}–potassium chloride is the solubilizer, 1-octanol is seen to behave like a transition solubilizate between the shorter chain alcohols and hydrocarbons such as *n*-heptane (118).

Typical of this class of solubilizate, exhibiting properties which are interpreted as leading to solubilization in the palisade region of the two-layer soap micelle, is the example of 1-heptanol in KC_{14} included in figure 6. As mentioned above, in comparison with hydrocarbons, the rate of solubilization of this polar compound is seen to decrease with increase in soap concentration. A relatively unrecognized case of this type of solubilization (111) is the increase in solubility of insoluble calcium dodecylsulfonate in solutions of their corresponding sodium salts (233). Soap mixtures such as potassium laurate and potassium palmitate should be also included in this group (220), for the less soluble palmitate could be considered to be solubilized by the laurate (111). Similar types of solubilization data have been obtained in mixtures of lithium and potassium laurates (118).

The solubilization of various polar dyes, such as Orange OT (1-*o*-tolylazo-2-naphthol) in potassium laurate solutions (149) and Yellow AB (phenylazo-β-naphthylamine) in aqueous sodium desoxycholate and in laurylsulfonic acid solutions, has been thoroughly investigated by McBain and coworkers (157) and these data show properties characteristic of penetration of these molecules into the palisade layer of the soap micelles rather than solubilization in the hydrocarbon center of the micelle.

The solubilization of *n*-heptane in KC_{14} illustrated in figure 6 and many other similar data on a large number of polar and nonpolar solubilizates indicate that solubilization begins at the C.M.C. Below this concentration, it is assumed that no micelles are present and various experimental measurements such as conductivity, transference number, freezing-point depression, etc. show that the colloidal electrolytes at these concentrations are nonassociated. Below the C.M.C. the soap acts like an electrolyte, causing a decrease in the solubility of the hydrocarbon or the polar compound, such as another soap, below that in water owing to the well-known salting-out effect. This has been shown to occur in the case of ethylbenzene in KC_{12} (86) and in the decrease in solubility of calcium dodecylsulfonate in solutions of sodium dodecylsulfonate below the C.M.C. of the latter soap (233). It might be supposed that solubilization begins below the C.M.C., as observed in the appearance of color in insoluble dye–soap (below the C.M.C.) mixtures (125). However, the amounts dissolved are so small—often only a few per cent more than is soluble in water—that the individual dye molecule must be considered to be bound, at first, either by electrostatic or van der Waals forces, with an individual soap molecule. The fact that solubilization begins at the C.M.C. has been utilized in the determination of the C.M.C. (125, 126). These C.M.C values determined by dye solubilization have been found to be in good agreement with those obtained by refraction (106, 107, 109), by changes in the spectral character of various charged dyes (28, 105, 107), by conductivity (202, 256), by solubility (235), and by various other methods.

Another method of plotting these data does not show the onset of solubilization at the C.M.C. as clearly as the method in figure 6 but it does give other information. A plot of this type is shown in figure 7, where the manner in which the mole ratio (MR), moles of oil solubilized per mole of soap, varies with soap concentration is indicated. The curves in figure 7 for ethylbenzene (86) and Orange OT (149) indicate that the colloidal properties of potassium laurate begin just above the C.M.C., 0.025 *M*, and that this soap in the presence of hydrocarbons reaches full colloidal form at about 0.15 *M*. It is probable that, in the region between the C.M.C. and 0.15 *M* where the change in MR per unit soap concentration is greatest, both the size and the number of solubilizing soap aggregates, probably double-layer micelles, increase most rapidly. Above the concentration where the soap reaches its full colloidal form, there is probably only a small increase in micellar size. According to osmotic (146, 147) and conductance (153) measurements, this soap reaches full colloidal form in about 0.2 *M* aqueous solutions, a result which is in agreement with the concentration deduced from solubilization data.

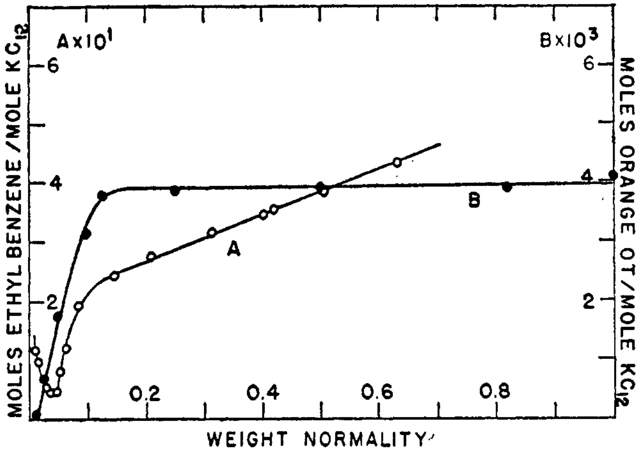


FIG. 7. Solubilization of ethylbenzene (A) and Orange OT (B) in potassium dodecanoate solutions (25°C.).

IV. Change in Continuous Medium

The major portion of the systems in which some substance other than water is the continuous medium involves the use of nonpolar hydrocarbons. The addition of soaps and detergents to various hydrocarbon systems will often result in a depression of the surface tension which might be associated with micelle formation. Thus the addition of about 0.1 per cent dodecylsulfonic acid to Nujol or mineral oil will result in decreases in surface tension of from 34 to 25 and 27.5 dynes/cm. (160). That phenomena similar to solubilization (= hydrotropy) occur in these systems is indicated by the fact that the addition of as little as 0.2 per cent of dodecylsulfonic acid to an organic medium will result in an uptake of dye, as is seen by the system becoming colored; 15–20 per cent ethanol and 4–8 per cent glacial acetic acid added to toluene is necessary before coloration is seen (156). The dyes used by these authors were eosin, fluorescein, crystal violet, and Calcomine Orange 2R (sodium *p*-sulfo-*o*-tolueneazo-β-naphthol) and use was made of both anionic and cationic detergents. No indication could be found from their data as to a preferential solubilization of a dye of one charge by detergent molecules of another charge.

Earlier Weichherz (244) had observed the uptake of water by solutions of soap in organic solvents. He found that ternary systems such as 79.94 per cent xylene, 12.91 per cent phenol, and 7.15 per cent sodium oleate remained homogeneous after the addition of 4.66 per cent water. It should be noted that this soap in xylene did not take up water. Pink (187) has shown that there is a linear relationship between water uptake and ethanolamine oleate concentration in benzene. Saturation was noted by the precipitation of the soap in a white curdy form. The addition of a large excess of water results in an inversion. In systems of aluminum palmitate in toluene, containing emulsified water, it was noted that, on cooling to −17.8°C., 26 per cent of the water was found to be "bound" (102). It would appear from these measurements that this fraction of water, in the light of our present knowledge of solubilization, was solubilized water which probably was "bound" by hydrogen bonding to the polar groups in the interior of the inverted micelle.

TABLE 1

Solubilization of water in organic solvents by detergents at 20°C. (69)

DETERGENT	SOLVENT	$\frac{\text{WEIGHT OF WATER}}{\text{WEIGHT OF SOAP}}$
Hexanolamine oleate	Cyclohexane	1.35
	Benzene	1.34
	Carbon tetrachloride	0.99
	Chloroform	0.00
Laurylsulfonic acid	Chloroform	0.19
	Benzene	0.14
Cetylpyridinium chloride	Nitrobenzene	0.00
	Chloroform	2.04

From osmotic pressure measurements on aluminum dilaurate–benzene systems, it was postulated that this soap is an association colloid in benzene (165). A more complete investigation of these systems led to a number-average molecular weight as determined by osmotic pressure measurements of this colloid of about 500,000 when the concentration of aluminum dilaurate was 0.3 per cent in benzene (222). Solubilization of water in organic solvents containing added detergents has been measured by the turbidometric method and was also found to be slow in reaching equilibrium (185).

The data in table 1 indicate the effect of changes in structure of the solubilizer as well as changes in the solvent on the solubilization of water at 20°C. (185). The nonsolubilization of water in the chloroform–hexanolamine oleate system is taken to be due to a competition and blocking of the carboxyl group by the solvent molecules. Cation-active soaps can supply the hydrogen bonding to the oxygen of the water molecules, and thus dodecylamine hydrochloride and cetylpyridinium chloride can solubilize water in the presence of chloroform. Bonding by nitrobenzene is sufficient to prevent water uptake by means of this mechanism.

Lawrence (133) has shown that soaps dispersed in oil are readily peptized by the addition of small amounts of polar compounds just as they are in aqueous systems and by the same sort of substances for the most part. It is seen that added water acts like other peptizers and that hydrolysis occurs (134). In conjunction with these systems, this author distinguishes between peptization and solubilization. The former term is used in its normal sense, meaning to increase the dispersion. Solubilization is considered to include three distinct cases: true internal solubilization of substances insoluble in water; solubilization of substances insoluble in water but containing polar groups, e.g., long-chain alcohols and amines, dyes; and those cases where the soap is peptized by the substance solubilized. This author speculates on the various complexities involved in soap and oil systems and emphasizes the importance of the presence of impurities in relation to various reported data.

Up to the present time there have been no very extensive measurements on the solubilization of polar compounds in soap–hydrocarbon systems. Based on previous findings that micelle formation in aqueous systems in the presence of certain dyes (28, 107) results in spectral changes in these dyes, it has been found that rhodamine B will fluoresce in soap–hydrocarbon systems above a certain soap concentration (6). Since the fluorescence increases with increasing concentration of soap (indicative of dye dissociation), it is evident that there is an increase in micellar size with concentration in these systems. By the use of this dye, calcium xylylstearate and calcium xenylstearate were shown to have C.M.C. values of 1×10^{-6} mole/liter and 8×10^{-6} moles/liter, respectively. The anhydrous calcium xenylstearate (3.48 g. of soap per 100 ml. of benzene) is found to be extremely viscous and the addition of as little as 0.05 per cent of water will convert this system to a mobile liquid (7). This is assumed to involve a breakdown of thread-like aggregates, termed micelles (probably incorrectly) by these authors.

Schulman and Riley (215) studied the change in x-ray patterns for systems containing oil, soap-solubilized water, and aliphatic or alicyclic alcohols as additives. A discussion of this work will be postponed to the section on the effect of additives. More recently, Mattoon and Matthews (141) have presented some qualitative results on systems of Aerosol OT (di(2-ethylhexyl) sulfosuccinate), *n*-dodecane, and water. For 15 per cent Aerosol OT in *n*-dodecane, the small-angle x-ray scattering intensity varied from weak to medium to strong as more water was solubilized up to the saturation point of 26 g. of water in 100 g. of soap solution.

Solubilization in ethylene glycol in which Aerosol OT, tetradecane-1 sodium sulfate, and undecane-1 ammonium chloride were the solubilizers has recently been reported by Winsor (255) and is found to be distinguished from those systems in which water is the continuous phase by the absence in glycol-solubilized systems of anisotropic gelation which is found to occur in comparable water-solubilized systems. It is proposed that the hydrogen-bonded pseudo-ice structure in water is necessary for the adhesion between the units of dispersed phase without which gel structure cannot be evident. In both glycol and water solubilizing systems, it is not the unsolvated soap which is the mutual solvent but the liquid complex produced in the presence of the two immiscible liquids. When this point is considered, the apparent contradiction mentioned by Palit and McBain (184), between the effect of soaps on benzene–propylene glycol systems and the commonly accepted point of view on mutual solvents, disappears.

When to a homogeneous solution of triethanolamine oleate in paraffin oil increasing amounts of water are added, an inversion is found to occur (129). The various factors which bring about these reversible inversions, such as soap, water, and oil concentrations, additives, temperature, and solvent, have been more thoroughly studied qualitatively by Winsor (255).

V. EFFECT OF STRUCTURE OF SOLUBILIZER

There are a number of factors regarding the structure of solubilizers such as chain length, substitutions in the chain, and position of hydrophilic group, which would be expected to have some effect on solubilization. There have only been a few systematic studies made using fairly well characterized soaps and detergents and these data will be discussed. An attempt will be made to integrate various isolated data and indicate the effect of structural changes on solubilization. Soap solutions have lower solvent power for phenylazo-β-naphthylamine than do solutions of salts of paraffin-chain cations and more complex salts (157). Merrill (162) finds a less marked disadvantage of the soaps for *o*-tolylazo-β-naphthol, and Soldate (162) indicates that potassium oleate is much less effective than Aerosol OT as a solvent for propene vapor.

The enhancement in solubilizing power of cationic detergents over soaps of corresponding chain length has also been noticed in the case where dimethylaminoazobenzene was the solubilizate (125). Thus, for measurements at 30°C., the solubilizing power (grams of DMAB per mole of soap) was 4.32 at 0.4 *M* dodecylamine hydrochloride; 1.50 for the soap containing the same number of carbon atoms, estimated 2.1 for KC_{13}, the soap of the same length as the dodecylamine hydrochloride, and 2.71 for KC_{14}. It is of interest to note that the long x-ray intermicellar spacing of the C_{12} cationic detergent is 69.9 Å. at 15 per cent, whereas the spacing for the same concentrations of KC_{14} and KC_{12} is 63.1 Å. and 54.2 Å. (72). These longer spacings would indicate a much larger micelle for the C_{12} amine hydrochloride than for the corresponding fatty acid soaps and thus a much larger volume available for solubilization. Solubilizing power for hydrocarbons will always increase with increase in micellar size, although in certain instances it will decrease for polar compounds (115). Much further work is indicated for these systems to show whether there is much more internal order in the anionics than in the cationics to account for this marked increase in solubilizing power.

A. EFFECT OF CHAIN LENGTH

The data in figure 8 and in table 2 show the effect of increase in chain length of potassium fatty acid soaps on the solubilization of ethylbenzene. It is to be noted that the increase in the rate of solubilization with soap concentration is consistent with the previous discussion concerning the loci of solubilization. It has been shown that there is only a very small decrease in C.M.C. with added hydrocarbon (116). It is possible then to plot the moles of ethylbenzene solubilized per 1000 g. of solution as a function of concentration of micellar soap. This is done in the case of the decanoate and the octanoate, the C.M.C. values of which are 0.095 M and 0.395 M, respectively. This serves to present a more accurate picture of the effect of chain length.

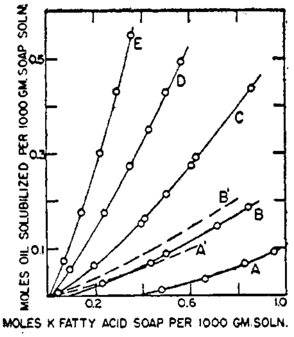
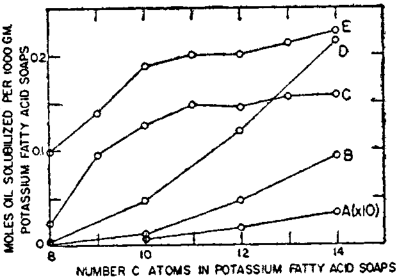


FIG. 8



|FIG. 9

FIG. 8. Solubilization of ethylbenzene in potassium fatty acid soaps (25°C.): (A) KC_8, (B) KC_{10}, (C) KC_{12}, (D) KC_{14}, (E) KC_{16}. Dotted lines indicate solubilization by micellar soap.

FIG. 9. Effect of chain length of potassium fatty acid soaps (0.3 N) on solubilization of (A) dimethylaminoazobenzene, (B) n-heptane, (C) 1-octanol, (D) ethylbenzene, (E) 1-heptanol (75, 86, 125).

Further data have been reported on the effect of alkyl chain length on the solubilization of Orange OT (1-o-tolylazo-2-naphthol) by McBain and Johnson (152) and by McBain and Green (149), of DMAB (dimethylaminoazobenzene) (125), and of various long-chain alcohols (75). The effect of the number of carbon atoms in the colloidal electrolyte ion is seen to result in an increase in solubilizing power towards various solubilizates, as indicated in figure 9. Marked differences are noted in the relative solubilities of the added oils. The effect of structural changes of the solubilizate will be discussed in a later section under this heading. It is seen, however, that the most marked changes with chain length are found for hydrocarbon solubilizates and that with polar additives there appears to be a transition occurring. There have been no systematic data reported on the use of the fatty acid soaps with an odd number of carbon atoms for the solubilization of hydrocarbons. It appears that, when long-chain alcohols are the solubilizates, there is an inversion in solubilizing power which might be compared with various physical properties, such as melting point, of the fatty acids themselves. This transition in solubilization of the long-chain alcohols, however, may be ac-

TABLE 2

Solubilization of ethylbenzene in soap solutions (25°C.)

(Values corrected for water solubility)

MOLES OF SOAP PER 1000 G. SOLUTION	MOLES OF MICELLAR SOAP PER 1000 G. SOLUTION	MOLES OF OIL SOLUBLE (S) PER 1000 G. SOLUTION	MOLES OF OIL PER MOLE OF SOAP	MOLES OF OIL PER MOLE OF MICELLAR SOAP	VOLUME OF OIL SOLUBLE PER 1000 G. SOLUTION	MOLECULES OF OIL PER SOAP MICELLE (150 MOLECULES)
Potassium octanoate						
0	0	0.0016			0.196	
0.30	0	0.0012	0.004		0.147	
0.48	0.085	0.012	0.025	0.141	1.47	21
0.662	0.267	0.033	0.048	0.124	4.04	19
0.827	0.432	0.066	0.080	0.152	8.08	22
Potassium decanoate						
0.10	0.005	0.0014	0.014		0.171	
0.232	0.137	0.027	0.116	0.197	3.30	30
0.435	0.340	0.067	0.154	0.197	8.20	30
0.500	0.405	0.087	0.174	0.214	10.6	33
0.717	0.622	0.145	0.202	0.233	17.8	35
Potassium dodecanoate						
0.042	0.017	0.007	0.166	0.411	0.855	62
0.195	0.170	0.062	0.318	0.364	7.60	54
0.396	0.371	0.151	0.382	0.407	18.4	61
0.500	0.475	0.212	0.424	0.446	26.0	67
0.603	0.578	0.273	0.452	0.472	33.5	71
0.628	0.603	0.291	0.463	0.482	35.7	72
0.860	0.835	0.435	0.506	0.522	53.4	78
Potassium tetradecanoate						
0.096	0.090	0.054	0.563	0.600	6.60	90
0.242	0.236	0.176	0.728	0.745	21.6	107
0.347	0.341	0.272	0.784	0.798	33.4	120
0.432	0.426	0.348	0.807	0.817	42.7	123
0.500	0.494	0.427	0.855	0.866	52.3	130
0.566	0.560	0.492	0.872	0.888	60.3	133
Potassium hexadecanoate						
0.070	0.068	0.074	1.06	1.09	9.07	159
0.154	0.152	0.176	1.14	1.15	21.6	173
0.228	0.226	0.302	1.32	1.33	36.9	190
0.292	0.290	0.430	1.47	1.48	52.7	220

counted for on the relative hydrophilic and hydrophobic character of these polar compounds and on the extent to which they penetrate into the palisade layer of the soap micelle (115). Winsor has suggested that this transition is between those relatively hydrophilic compounds whose solubilization is limited by the formation of a Type II system (S_2 micelles plus excess aqueous liquid) and those more lipophilic compounds whose solubilization is limited by the formation of a Type I system (S_1 micelles plus excess organic liquid) (255a).

A plot of the solubilization data of Kolthoff and Stricks (125) on DMAB shows that there is an almost linear increase in solubility with chain length or number of carbon atoms in the normal fatty acid soaps between C_{12} and C_{18}. The oleate values fall considerably below these curves, whereas the alkylamine hydrochloride (C_{12}) shows a stronger solubilizing effect when both are compared with soaps of corresponding chain lengths. There is an effect of branching noted in the use of Aerosol AY (diamyl sulfosuccinate), where the solubilizing power is much below that of the corresponding C_{14} soap (considering the length of the entire alkyl chain) and above that of the corresponding C_{10} soap (considering the length being equivalent to distance from terminal carbon atom to charged group).

The comparison above has included solubilization data for variation in chain length for the same family of compounds, the fatty acid soaps. It has been indicated that sodium and potassium soaps have the same C.M.C. values (110) as do the cetylpyridinium chloride and bromide (80) and sodium and potassium decyl and dodecyl sulfates (28, 110). Hartley (80) indicated that the ratio of solubilized azobenzene to cetylpyridinium is approximately constant over a wide range of concentrations. The constancy is not exact, and the ratio varies somewhat with the nature of the anion, indicating that the solvent power of the micelle is slightly modified by its ionic environment. Thus $Br^- > Cl^- > SO_4^{--} > OCOCH_3^-$ in their solvent powers for azobenzene. The solvent powers of the micelles increase in the same order as do their sizes as deduced from mobility measurements (209). McBain and Green (149) report a considerable enhancement of solubility of Orange OT when sodium laurate is used in place of potassium laurate as the solubilizer. Thus at 25°C., 540 and 300 mg. of Orange OT are solubilized per liter of 0.3 M NaC_{12} and 0.3 M KC_{12}, respectively. These values are much larger than would be expected and are not at all of the minor order found for the cetylpyridinium salts. In addition, they find that sodium oleate solubilizes more Orange OT than does the potassium salt and that dodecylamine hydrochloride dissolves more than KC_{12} (66). Kolthoff and Stricks (125) find no differences in the solubility of Orange OT at 30°C. in NaC_{12} and KC_{12}, a result which is more in accord with the findings that the C.M.C. values of sodium and potassium fatty acid soaps are essentially equal (110, 125). In the solubilization of dimethylaminoazobenzene, sodium and potassium salts of C_{10}, C_{12}, and C_{14} fatty acids are found to be equal for each pair of equal chain length (125).

It has previously been reported that the C.M.C. values of various straight-chain soaps and detergents depend almost exclusively on the chain length (not to be confused with the number of carbon atoms in the chain) and are relatively independent of the nature of the charged head (110, 201). However, a change from the chloride to the nitrate salt of dodecylamine has been shown to result in a decrease in solubility and in a change in C.M.C. from 0.014 *M* to about 0.01 *M* (200). Thus, a series of colloidal electrolytes such as potassium tridecanoate ($CH_3(CH_2)_{11}COOK$), dodecylammonium chloride ($CH_3(CH_2)_{11}NH_3Cl$), sodium dodecylsulfonate ($CH_3(CH_2)_{11}SO_3Na$), and sodium undecyl sulfate ($CH_3(CH_2)_{10}OSO_3Na$), all of about equal chain length (length between terminal carbon and ion charge), have approximately the same C.M.C., as can be seen in table 3. No systematic attempt has as yet been made to determine the effect of chain length rather than number of carbon atoms on solubilization. Various isolated data collected in table 3 indicate that solubilization values of polar compounds do not agree for solubilizers of the same chain length as do the C.M.C. Thus 0.3 *N* dodecylamine hydrochloride solubilizes 950 mg. dimethylaminoazobenzene (DMAB) per liter (125), whereas sodium tridecanoate would be expected to solubilize about 600 mg. (average value between 400 mg. for NaC_{12} and 800 mg. for NaC_{14}). The effect of polarity in the DMAB molecule may exert some influence on its solubility in the soap micelle. Hartley (80) has indicated that the solubility of azobenzene in soap micelles is considerably less than ideal when compared to its solubility in paraffins and more nearly approaches its behavior in some polar solvents. This would indicate a solubilization of azobenzene, in part at least, in the palisade layer of the soap micelle. This apparently is also true when the solubilities of various long-chain alcohols in KC_{14} and sodium dodecyl sulfate (75) (C.M.C. = 0.0066 *M* and 0.0058 *M*, respectively) and in KC_{12} and sodium decyl sulfate (118) (C.M.C. = 0.025 *M* and 0.023 *M*, respectively) are compared. In the first group the solubilities are different when the C_7 and C_8 alcohols are the solubilizates and are similar for longer alcohols. In the second group the values for the C_7 alcohol are different, whereas those for C_8, C_9, and C_{10} are about equal. This is of interest in the light of some recent work on the effect of various additives on the solubilization of long-chain alcohols (115). It was found that, when KC_{14} was the solubilizer, there was a transition in solubilization properties between C_8 and C_{10} alcohols. Similarly, when KC_{12} was the solubilizer, this transition was noted between C_7 and C_8 alcohols. The importance of these findings with relation to the effect of additives will be discussed below, but it is of some import to note that similar transitions occur in the solubilization of alcohols when the chain length of the solubilizer is considered. These transitions involve the solubilization of polar compounds in which the hydrocarbon portion of the solubilizate begins to overcome the contribution of the polar group to the solubility of the molecule. This depends not only on the extent of the nonpolar portion of the solubilizate, but also on the nature of the polar group and on the length of the solubilizer molecule. The solubilities of the much less polar compound, *n*-heptyl mercaptan, in KC_{12} and the decyl sulfate and in KC_{14} and the dodecyl sulfate are about equivalent, as would be expected if the idea of the transition phenomenon is correct. The solubilities of the typical hydrocarbon *n*-heptane are about equal in each group

TABLE 3

Effect of chain length on micellization and on solubilization

(0.3 *N* solubilizer)

TYPE OF DETERGENT	LONG-CHAIN GROUP	L	C.M.C.	SOLUBILIZATION						
				n-Heptane	DMAB	$C_7H_{15}SH$	ALCOHOLS			
							C_7	C_8	C_9	C_{10}
		Å.	*moles/liter*	*moles/liter*	*mg./liter*	*moles/liter*	*moles/liter*			
Fatty acid	*n*-$C_{13}O^-$	17.86	0.012	(0.07)*	(600)*					
Sulfonates	*n*-$C_{12}SO^-$	18.43	0.010	0.077						
Sulfates	*n*-$C_{11}OSO^-$	18.19	(0.012)*	(0.075)*						
Amine hydrochloride	*n*-$C_{12}NH^+$	17.53	0.014	0.26	950					
Fatty acid	*n*-$C_{14}O^-$	19.13	0.0066	0.093	800	0.090	0.226	0.158	0.140	0.136
Sulfates	*n*-$C_{12}OSO^-$	19.46	0.0057	0.101		0.0925	0.260	0.171	0.144	0.138
Fatty acid	*n*-$C_{12}O^-$	16.59	0.026	0.043	400	0.0393	0.201	0.146	0.126	0.111
Sulfates	*n*-$C_{10}OSO^-$	16.92	0.023	0.050		0.040	0.220	0.150	0.129	0.115

* Values estimated from higher and lower detergents of the same type.

of anionic solubilizers of approximately the same length and C.M.C. That the addition of hydrocarbons has been found to cause only very small decreases in C.M.C. (116, 199), whereas the addition of alcohols and other polar additives results in considerable decreases in C.M.C. (26, 199), is a phenomenon which parallels the use of hydrocarbons and polar compounds as solubilizates.

It has been observed that the amount of 1-hexanol required to give an S_1 type system decreased for identical systems (although the detergent solutions were prepared on a per cent basis rather than on a mole basis) when sodium undecane-3 carboxylate, sodium undecane-3 sulfate, and undecane-3 ammonium chloride, respectively, were the solubilizers (254). This is in accord with the data in table 3 and with the aforementioned much larger intermicellar x-ray spacing observed in the cationics than in the anionics.

It has been inferred by Hartley (80) that the minor differences in the solubility of azobenzene in various cetylpyridinium salts varied somewhat as do the micelle sizes. If solubilization were to depend on micellar weight, then by the addition of a certain amount of added electrolyte, it would, for example, be possible to form micelles of a C_{12} soap which would have a molecular weight equal to that of a C_{14} or a C_{16} soap. This is in accord with light-scattering results of changes in micellar weight with added electrolyte (33). However, while this increase in micellar size with added electrolyte would increase the solubility of the hydrocarbons, it would result in a marked decrease in the amount of polar compound solubilized (115). There are insufficient data on micellar weights at the present time to indicate whether micelles of the same molecular weight though of different chain length paraffin-chain ions would have equal solubilizing power for a hydrocarbon.

B. EFFECT OF SUBSTITUTION IN THE CHAIN

The replacement of a C—C by a C═C bond in the alkyl chain results in an increase in the C.M.C. value. Thus, the C.M.C. of potassium oleate has been found to be 0.0006 (30°C.) by solubilization measurements (125), 0.0007–0.0012 (25°C.) by the spectral dye method (28), and 0.0011 (25°C.) by refraction (109) as compared with values of about 0.0004–0.0008 (60°C.) (109, 227) for potassium stearate as determined by refraction and pH measurements. Solubilization data show corresponding decreases when the amounts of DMAB solubilized by potassium stearate and potassium oleate are compared (125). Since there is still considerable difficulty in the preparation of linoleic and linolenic acids of purity even up to 95 per cent, no valid solubilization data are available with the use of these solubilizers. Recently, a whole series of aryl and alkylated stearic acids have been prepared (230, 231), but no information as to the effect of substitution of this type on solubilization is available. Recently, the substitution of a hydroxyl group in the alkyl chain to form 9,10-dihydroxystearate has resulted in an increase in the C.M.C. (67), but no solubilization data are available with the use of this compound. Previously, Dreger, Miles, Ross, and Shedlovsky (41, 171, 218) in a series of papers described the preparation and surface and interfacial tension properties of a series of very interesting detergents in which the charged head, the sulfate group, was systematically moved along the alkyl chain. Solubilization data on compounds of this type would be very interesting and, when obtained, will assist greatly in our complete understanding of the factors involved in micellization and in solubilization. Hartley (82a) has measured the interfacial activity of branched-paraffin-chain salts (sulfonated dialkyl esters of dihydric phenols) and found marked decreases in interfacial tension against various nonpolar liquids. However, evidences of typical micelle formation, such as the solubilization of azobenzene and changes in the equilibrium of suitably buffered indicators, were not observed. Winsor (254) has studied the effect of position and of type of charged group on solubilization and has found that, while the lipophilic solvent affinity of the *n*-alkyl group is essentially the same, the hydrophilic solvent affinity of the $—SO_4Na$ group diminishes markedly as its point of attachment to the *n*-alkane chain recedes from the terminal. Since there is a high degree of molecular order in solubilized systems, steric factors would be expected to be strongly influential in producing the above results.

TABLE 4

Effect of position of $—SO_3Na$ group of n-tetradecane sodium sulfates on critical micelle concentration and on solubilization

POSITION OF $—SO_3Na$	C.M.C. (1)	C.M.C. (2) STRAIGHT-CHAIN SULFATE	$\frac{\text{C.M.C. (2)}}{\text{C.M.C. (1)}}$	(*S*) CYCLOHEXANOL PER 10 ML. CYCLOHEXANE + 10 ML. 20 PER CENT NaC_{14} SULFATE	$\frac{(S)\ n\text{-TETRADECANE SULFATE}}{(S)\ \text{BRANCHED SULFATE}}$
	(moles/liter) $\times 10^{-3}$			*ml.*	
1	1.65	1.65	1.0	2.0 -2.3	1.0
2	3.26	3.30	1.01	2.0	1.0
3	4.52	6.5	1.44	1.3 -1.5	1.5
4	5.76	13	2.29	0.84–1.0	2.3
5	7.95	26	3.27	0.55–0.60	3.7
6	12.3	52	4.23	0.25–0.30	7.6
7	15.8	100	6.22	0.025–0.075	40

Critical micelle concentrations in the tetradecane sulfate series increase as the point of attachment of the $—SO_4Na$ group on the *n*-alkane chain recedes from the terminal position (254). These concentrations were determined by the spectral dye method of Corrin and Klevens (28), which is a modification of the technique used by Sheppard and Geddes (223), and the increases noted were in accord with those changes seen in the surface tension curves on similar compounds (41, 171, 218). These data are given in table 4, as well as some comparable data on straight-chain alkyl sulfates of the same chain length (110). If only the straight-chain portion of the molecules is considered, it can be seen that substitution of only a methyl group on the α-carbon atom does not contradict the relationship which indicates that the C.M.C. depends on chain length and is virtually independent of substitution on atoms of the chain up to about 5 Å. from the charged head (110). This is in accordance with the data of

Ralston *et al.* (201), which show only minor changes in C.M.C. when groups containing up to three atoms are substituted for the amine hydrogens in the alkylamine hydrochlorides. It is evident from a comparison of the data in table 4 that the size and position of the alkyl side chain influence the total van der Waals attraction energy (necessary to overcome the repulsive energy of the like charged heads before micelle formation can start). The decrease in C.M.C. in comparing straight-chain and branched-chain pairs is not as large as has been observed upon the addition of long-chain alcohols, a result which would indicate a greater penetration of the alcohol into the palisade layer of the micelle than the branched chain which is, of course, held in position.

Although somewhat simpler solubility data, such as with heptane and 1-heptanol as solubilizate and additive, are not available, the effect of the position of the —SO_3Na group in the detergent chain on solubilization can readily be advanced. The data in table 4 (255) indicate that there is a decrease in the amount of cyclohexanol required to dissolve cyclohexane in solutions of sodium tetradecane sulfates as the —SO_3Na group is moved from position 1 to position 7. The important generalization which can be derived from these results is that the solubilization of organic compounds increases from the 1- to the 7-sulfate. With the use of *n*-alkyl soaps and detergents it has been found that as the C.M.C. decreases the solubilizing power of a system increases. However, it is seen that there is an increase in the C.M.C. with movement of the —SO_3Na group from the 1- to the 7-position. When these values are compared with C.M.C. values of straight-chain sulfates (of chain length equivalent to maximum length up to —SO_3Na in the branched-chain compounds), there is some enhancement over that of the corresponding nonsubstituted alkyl sulfate, owing to the presence of the branched chain which increases as the size of this branched chain increases. It has also been shown that there is a decrease in the solubilization of water as the —SO_3Na in the tetradecane series is changed from the 1- to the 7-position (255).

A considerable amount of data has accumulated in the literature in which many of the commercial preparations of detergents have been used as solubilizers. As will be shown in a later section on additives, the addition of any compound which will reduce the C.M.C., such as electrolytes, amines, alcohols, etc., will also markedly effect the solubilizing power of a detergent. Thus, for example, in the preparation of an alkyl sulfate, the presence of any residual nonsulfated alcohol will result in a much more active solubilizer than if all the alcohol had been sulfated. The presence of electrolytes will result in a marked increase in the solubility of hydrocarbons and a marked decrease in the solubility of polar compounds (115). Some data using commercial preparations have recently been reported (125), and much more will be found in the work of McBain and his coworkers (144, 151, 157).

The solubilizing power on a weight basis of nonionic detergents such as carbowax and the polyethylene oxides has been found to be very weak (151). However, the condensation of a fatty acid radical or a substituted benzene ring on the end of the polyethylene oxide chain increases its solubilizing power. The complex detergents such as hexanolamine salts of fatty acids have been shown by x-ray studies (206) and by osmotic behavior, conductivity, and viscosity to behave like colloidal electrolytes (65) but no systematic studies on pure preparations of this type of detergent have been reported. Many tables of solubilization of dyes such as Yellow AB and Orange OT are available (144), but since these solubilizers contain various additives or impurities only their relative solubilizing power is important. Solubilization data comparing hexanolamine oleate and two nonionic detergents, nonaethylene glycol monolaurate and a condensation product of (2-methylheptyl)phenol and ethylene oxide, called detergent "X," indicate that on a molar basis these detergents solubilize more than KC_{12} (163). Their C.M.C. values are also much below that of KC_{12}.

VI. Effect of Structure of Solubilizate

There are numerous factors with regard to the structure of the solubilizate which are seen to affect markedly the amount of solubilization of these compounds. The polarity, charge, molar volume, chain length, branching, substitution, planarity, etc. are found to be important in determining the degree to which these compounds will dissolve in the soap and detergent micelles. The physical state of the excess solute—solid, liquid, or gas—is an important factor in solubilization (255). In the solubilization of a solid compound the latent heat of fusion opposes the change of state from crystalline solid to solubilized or dissolved compound, and the ease of solubilization of a solid compound is therefore expected to be considerably less than that of the same compound existing as a supercooled liquid or of a closely related liquid compound. This would in part account for the much longer time required to dissolve solid polycyclics than liquid hydrocarbons (113) and would explain why the differences in the solubilities of liquid methylnaphthalene and naphthalene are much smaller than those between benzene and the alkylated benzenes (118). Winsor also indicates that the fugacity as well as the constitution of liquids forming the excess phase is of great importance in limiting their solubilization (255a).

A. EFFECT OF CHAIN LENGTH, CYCLIZATION, UNSATURATION, AND BRANCHING

For a particular preparation of soap or detergent, there are numerous examples of solubilization of families of compounds. As will be shown in the section on the effect of additives, the addition of an electrolyte, alcohol, amine, hydrocarbon, another soap, etc. will have some effect on the solubilization of various solubilizates. However, for any one preparation of solubilizer, it can be assumed that any differences in solubility will depend on the structure of the solubilizate, i.e., unless molecular interaction or specific binding occurs between one or more of the components in the system. Thus some indication of the effect of structure on solubilization can be gleaned from the very early work of Engler and Dieckhoff (50), as seen in table 5. Similar effects are noted in a study by Smith (225), in which the solubilization of various organic compounds in a commercial preparation of sodium oleate was investigated. Some of Smith's data are collected in table 6, where again some indications as to the influence of various factors such

TABLE 5

Solubility (ml.) of hydrocarbons in 100 ml. soap solution (room temperature) (50)

SOAP	BENZENE	TOLUENE	XYLENE	TURPENTINE
	ml.	*ml.*	*ml.*	*ml.*
Sodium oleate (10%)	10	9.6	7.4	7
Sodium palmitate (10%)*	1.8	1.3	1.4	0.4
Sodium rosin soap (15%)	8.8	8.2	8.0	11.2
Potassium rosin soap (15%)	8.4	8.0	6.8	9.0
Sodium stearate (10%)*	1.6	1.5	1.0	0.8
Sodium stearate (10%)* + 10 ml. phenol	9.2	13.9	37.0	101.0

* At elevated temperatures.

TABLE 6

Solubility of various organic compounds in 100 g. 0.4 N sodium oleate (225)

COMPOUND	SOLUBILITY	COMPOUND	SOLUBILITY
	grams		*grams*
Phenol	108	Methyl acetate	71
Cyclohexanol	59	Ethyl acetate	18.7
Aniline	11.5	Carbon tetrachloride	20.6
		Chloroform	6.65

TABLE 7

Effect of chain length, unsaturation, and cyclization on solubilization in 0.63 N potassium dodecanoate at 25°C.

COMPOUND	MOLAR VOLUME	SOLUBILITY IN MOLES PER LITER OF SOLUTION	VOLUME OF OIL IN MICELLES PER LITER OF SOLUTION	MOLECULES OF OIL PER MICELLE (150 MOLECULES)
n-Pentane	113.4	0.247	27.9	59
n-Hexane	131.5	0.178	23.2	42
Hexatriene		0.425		99
Benzene	88.5	0.533	47.2	126
Cyclohexane	104.5	0.430	45.9	102
n-Heptane	147.8	0.125	18.4	30
Toluene	107.0	0.403	43.7	96
n-Octane	163.1	0.105	17.2	24
Ethylbenzene	123.0	0.280	34.0	66
Styrene	120.0	0.332	39.6	78
n-Nonane	178.2	0.082	14.6	20
n-Propylbenzene	140.5	0.209	29.2	50
n-Decane	192.1	0.058	11.7	14
n-Butylbenzene	157.0	0.147	22.3	35
Naphthalene	112.2	0.042	4.7	10
Phenanthrene	174.1	0.0085	1.03	2.0
Fluorene		0.0056		1.3
Anthracene	142.3	0.00108	0.123	0.26

as polarity, unsaturation, and length of chain on solubilization are seen. Numerous other reports have dealt with similar structural aspects (75, 80, 113, 157, 161, 229). Recently, a number of attempts have been made to show more completely the effect of various structural factors on solubilization (113, 161, 229). It can be seen from the data in tables 7 and 8 that:

TABLE 8

Solubilization of various hydrocarbons in 0.1 N detergent solutions at 25°C. (161)

COMPOUND	MOLECULAR WEIGHT	MOLAR VOLUME	SOLUBILITY IN WATER	AMOUNT SOLUBILIZED		
				KC_{12}	NaC_{18}	$C_{12}HCl$
			grams/liter		*moles/liter*	
n-Hexane	86	131.3	0.14	0.18	0.46	0.75
n-Heptane	100	147.1	0.05	0.12	0.34	0.54
n-Octane	114	163.3	0.02	0.08	0.18	0.29
n-Nonane	128	178.2		0.06	0.11	0.22
n-Decane	142	191.4		0.03	0.052	0.13
n-Dodecane	170	226		0.005	0.009	0.063
n-Tetradecane	198	261				0.008
n-Cetane	226	293.5				
2,2-Dimethylbutane	86	133.7		0.13	0.45	0.73
2,3-Dimethylbutane	86	131.1		0.14	0.46	0.75
2,3-Dimethylpentane	100	144.1		0.11	0.35	0.62
3,3-Dimethylpentane	100	145.1		0.10	0.31	0.55
2,2,4-Trimethylpentane	114	165.7		0.05	0.16	0.27
2,2,3-Trimethylpentane	114	160.4		0.09	0.18	0.30
Diisobutylene	112			0.10	0.38	0.43
Methylcyclopentane	94			0.032	0.26	0.40
Cyclohexane	84	108.5		0.23	0.56	0.87
1,2,4-Trimethylcyclohexane	126	160.0		0.012	0.012	0.019
Benzene	78	88.5	0.70	0.29	0.76	0.65
Toluene	92	106.7	0.49	0.13	0.51	0.49
Ethylbenzene	106	122.5	0.14	0.20	0.40	0.38
p-Xylene	106	123.5	0.13	0.20	0.36	0.34
p-Cymene	134	156.5		0.08	0.26	0.19
Amylbenzene	148	172.7		0.04	0.17	0.12

1. Increase in the chain length of a normal paraffin or of an alkyl group on a benzene nucleus will result in a marked decrease in solubility.
2. Cyclization will result in enhanced solubility.
3. Unsaturated compounds will be more soluble than their saturated counterparts.
4. Branched saturated compounds have approximately the same solubility as their normal isomers.

These regularities start to break down in part when one considers the solubilization of polycyclic hydrocarbons. The presence of a second ring, as in the substituted biphenyl or, more particularly, in the simplest polycyclic, naphthalene, causes a change in the opposite direction so that these compounds are even less soluble than the normal paraffins of about the same molecular weight. Thus naphthalene is much less soluble than either *n*-decane or *n*-butylbenzene. It has also been found that tetralin and decalin are more soluble than naphthalene, with the decalin slightly more soluble than the other two compounds (118). Although cyclohexane is less soluble than benzene, owing probably to the more polar, partial double bonds of the latter compound (also possibly owing to the smaller size of the benzene molecule), it is more soluble than the linear *n*-hexane.

TABLE 9

Solubility of various polycyclic hydrocarbons in 0.5 M KC_{12} *at 25°C.*

(Corrected for water solubility)

COMPOUND	MOLECULAR WEIGHT	GRAMS OF OIL PER LITER OF SOLUTION	(*S*) MOLES OF OIL PER LITER OF SOLUTION ($\times 10^3$)	LOG *S*	MOLECULES OF OIL PER MICELLE
Benzene	78.05	30.6	391	−0.41	118
Ethylbenzene	106.08	22.0	208	−0.68	63
n-Butylbenzene	134.11	14.9	112	−0.95	33
Naphthalene	128.16	4.26	33.3	−1.48	10
Acenaphthene	154.20	1.00	6.48	−2.19	2.0
Fluorene	166.21	0.728	4.38	−2.36	1.3
Phenanthrene	178.22	1.21	6.65	−2.18	2.0
Anthracene	178.22	0.155	0.85	−3.07	0.26
Fluoranthrene	202.24	0.578	2.86	−2.54	0.86
Pyrene	202.24	0.453	2.24	−2.65	0.68
Chrysene	228.28	0.143	0.627	−3.20	0.19
1,2-Benzanthracene	228.28	0.145	0.635	−3.20	0.19
Triphenylene	228.28	0.0765	0.336	−3.47	0.10
Naphthacene	228.28	(0.023)*	(0.10)	(−4.0)	(0.030)
Methylcholanthrene	248.34	0.087	0.323	−3.49	0.10
1,2,5,6-Dibenzanthracene	278.33	0.024	0.0862	−4.06	0.026

* Approximate value.

As the size of the solubilizate is increased by annelation (ring closure), the solubilities of these polycyclics decrease markedly, as the data in table 9 indicate (113). The relationships which hold for the solubilization of the more simple hydrocarbons cannot be extended to these complex polyacenes. A possible explanation for this may be found in the fact that much larger micelles are necessary to solubilize these polycyclics. Thus, whereas more than one molecule of the simpler compounds can be solubilized per micelle of 150 soap molecules, as seen in table 7, only a fraction of one polycyclic molecule would be soluble in micelles of this size. (A value of 150 soap molecules per hydrocarbon-swollen micelle is an average value of a number of different calculations for a soap of this chain length: (*1*) a value of 140 as calculated from x-ray evidence of swollen micelles (143), in which it is indicated that swollen micelles have about twice the number of soap molecules as the hydrocarbon-free micelles; (*2*) one of 130 calculated from equations describing the size of swollen micelles (110), using as a basis the molecular weight values of nonswollen micelles as determined by light scattering (32); and (*3*) one of 140–160 as obtained from preliminary light-scattering measurements on hydrocarbon-swollen micelles (118).) Since the solubilization of hydrocarbons has been shown to involve the presence of a suitable hydrocarbon-like atmosphere, it is not necessary to postulate another mechanism of solubilization for the polycyclics and similar very insoluble molecules. Rather it should be sufficient to recognize the fact that each molecule of dibenzanthracene, for example, requires a certain critical volume of hydrocarbon atmosphere for its solubility. This atmosphere can only be supplied by a large aggregate of soap molecules. The smaller aromatics and simpler hydrocarbons need a much smaller volume of hydrocarbon per solubilized molecule and thus many more can fit into a single swollen micelle. The data in table 10 indicate the probable minimum size of micelle necessary for the solubilization of polycyclic hydrocarbons (113). Whether micelles of this magnitude are possible has not been experimentally verified, but it has been indicated that micelles of some 1000–2000 molecules exist at low soap–high electrolyte concentrations (34) and it has been indicated that at higher soap concentrations the size of the micelle is larger than at lower concentrations. As the soap concentration increases, there is effectively less free volume between neighboring micelles and the ionic atmosphere around one micelle may be affected by those of its nearest neighbors. Experimentally, as seen in figure 6, this is indicated by an increase in the rate of solubilization of hydrocarbons with soap concentration as well as by a decrease in this rate when polar compounds are the solubilizates (115).

TABLE 10

Probable minimum size of micelle necessary for solubilization of polycyclic hydrocarbons
(N = number of soap molecules per micelle)

COMPOUND	MOLECULES OF OIL PER 150-MOLECULE MICELLE	N	D
			Å.
Benzene	118	150	60
Naphthalene	10	150	60
Acenaphthene	2.0	150	60
Phenanthrene	2.0	150	60
Anthracene	0.26	600	120
Fluoranthrene	0.86	175	65
Pyrene	0.68	220	73
Chrysene	0.19	790	138
1,2-Benzanthracene	0.19	790	138
Triphenylene	0.10	1500	190
Naphthacene	0.030	5000	360
Methylcholanthrene	0.10	1500	190
1,2,5,6-Dibenzanthracene	0.026	6000	390

1. *Effect of molar volume*

X-ray measurements of potassium laurate solutions indicate that the chemical nature of the solubilizate markedly affects the change in long spacing (72, 74, 97, 150). When the change in spacing expressed in Ångström units per mole of additive per mole of soap is plotted against molar volume of liquid two straight lines are obtained, one for normal paraffins, the other for alkylbenzenes, as seen in figure 10, which extrapolate to about 50 ml. per mole or 4.4 Å.^{3} per molecule (97). The micelle aggregates are here considered to consist of at least five double layers of soap molecules oriented side by side and tail to tail. On the basis that the oil is layered between the ends of the hydrocarbon tails of the soap molecules in the micelle, the extrapolated lines should begin at the origin. Thus a portion of the solubilized additive is adsorbed elsewhere, perhaps between the side of the hydrocarbon chain in the soap palisade layer or, as will be seen in a later discussion, perhaps the model used by these investigators is in error.

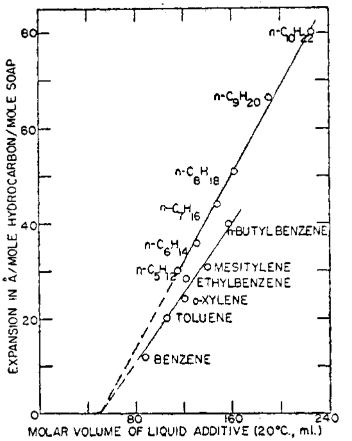


FIG. 10

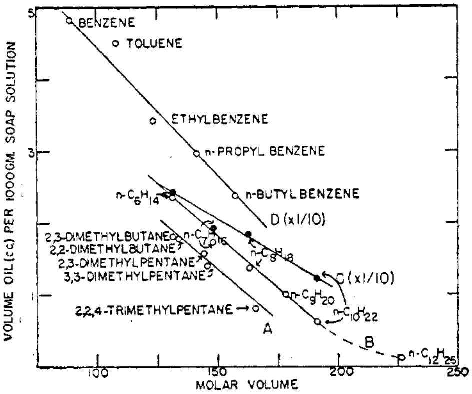


FIG. 11

FIG. 10. Change in micelle repeat distance of 22.1 weight per cent potassium dodecanoate solutions with molar volume of additive (97).

FIG. 11. Effect of molar volume of various paraffinic hydrocarbons and alkylated benzenes upon solubilization in (A) 0.1 *M*, (B) 0.1 *M*, (C) 0.63 *M*, and (D) 0.63 *M* potassium dodecanoate solutions (86, 161, 229).

Following these findings that the long x-ray spacing varies with molar volume of additive, attempts have been made to show how molar volume as well as other factors influence solubilization (113, 161, 229). McBain and Richards report that solubilization appears to fall off linearly with molar volume and then to decrease more slowly for larger molecules (C > 10) and that the more highly branched compounds are more soluble than straight-chain paraffins of the same molecular weight (161). However, this is not borne out by their data, for the values of grams of oil per 100 ml. of soap solution are 0.64, 0.63, 0.64 for *n*-hexane and the 2,2- and 2,3-dimethylbutanes; 0.54, 0.63, 0.55 for *n*-heptane and the 2,3- and 3,3-dimethylpentanes; and 0.33, 0.30, 0.34 for *n*-octane and the 2,2,4-

and 2,2,3-trimethylpentanes, respectively. A plot of their data showing grams of oil solubilized per 1000 g. of 0.1 *N* KC_{12} solution as a function of molar volume shows this reported linearity, but this plot must be made using volume instead of weight of solubilizate. When this is done, curves similar to those in figure 11 are obtained. It can be seen that two lines must be drawn through these data, one for the normal paraffins and the other for their highly branched isomers. When solubilization data at higher KC_{12} concentrations, 0.63 *N*, are included (113, 229), it is seen that this linearity carries over to the alkylbenzene series and that there is a difference in the slopes of the alkylbenzene and normal paraffin series which is consistent with the x-ray data. There are also differences observed in the slopes of the data for normal paraffins at the two concentrations (0.1 *N* and 0.63 *N*) of KC_{12}. This can be explained on the basis that the maximum rate of increase of solubilization is not reached in KC_{12} until about 0.15 *N*.

Figure 11 shows that as the solubility of a hydrocarbon decreases, as in the case of *n*-decane, the linearity of volume of oil *vs.* molar volume no longer holds and the solubility approaches asymptotically a zero value. On this basis, the plots of log solubility as a function of molar volume of the polycyclic hydrocarbon solubilities are seen to have some validity (113). Two linear plots were necessary for the polycylic data,—one for the linear polyacenes, the other for the nonlinear polycyclics. This is in accord with the treatment of the paraffin data in figure 11, where two curves are found to be necessary to fit the linear and the nonlinear data.

2. Apparent densities of solubilized oils

In the light of the discussion in the last few paragraphs, the reported changes in density of KC_{12} solutions to which *n*-heptane and triptane (2,2,3-trimethylbutane) (73) and ethylbenzene are added (229) is of interest. These solubilizates show a linear change in apparent density with increase in concentration of added oil. The first and last oils have apparent densities much higher than their bulk densities when the concentration of added hydrocarbon is small and approach their bulk densities with saturation. This might be expected if the center of the spherical or oblate spheroid micelle is considered to be filled by hydrocarbon-like solubilizates before the micelle takes on its most normal configuration in which there is a minimum of strain, e.g., a spherical swollen one if the oblate spheroid is the nonswollen micelle. Triptane, on the other hand, has an apparent density in low solubilizate concentrations about equal to its bulk density and a much higher apparent density near saturation. It is apparent that more information will be necessary before speculation on this finding is advanced, particularly to determine whether the division of properties of normal paraffins and branched-chain hydrocarbons as seen in figure 11 will carry over to these measurements.

B. POLARITY OF THE SOLUBILIZATE

The differences in x-ray spectra, rates of solubilization with increase in soap concentration, the discussion of types and mechanism of solubilization, as well as some of the data shown in tables 5 and 6, indicate that the presence of a polar group on the solubilizate will have a marked effect on its solubility. The very early work of Engler and Dieckhoff (50), as well as the later work of Smith (225), indicates in a qualitative manner that the polarity of the molecule influences the solubilizing power of a particular system. The marked differences in the solubilization of hydrocarbons and their polar counterparts will be illustrated most strikingly in a later section on additives, in which the simultaneous solubilization of polar and nonpolar compounds (114) and the effect of various electrolyte additives on the solubilization of both types of solubilizates (115) will be discussed. The formation of mixed soap micelles, as is indicated by a decrease in the C.M.C. when a soap of a lower C.M.C. is added to a more soluble soap (105), must be considered to be due to a solubilization of the less soluble soap by the more soluble one. As mentioned previously, soap mixtures of KC_{12} and KC_{14}, of NaC_{12} and NaC_{16} (220), of Na and CaC_{12} sulfate, and of Na and CaC_{12} sulfonate (233) should be considered to involve a polar type of solubilization in which the less soluble soap is solubilized by the more soluble one (111). The rates of solution of one soap in another have been studied by Shedlovsky, Miles, and Scott (220).

TABLE 11

Solubilization of various polar compounds in 0.1 N detergent solutions at 25°C. (156)

COMPOUND	MOLECULAR WEIGHT	MOLAR VOLUME	SOLUBILITY IN WATER	AMOUNT SOLUBILIZED		
				KC_{12}	$NaC_{18}^{=}$	$C_{12}HCl$
			grams/liter	*moles/liter*		
Methyl *tert*-butyl ether	88	118	51.26	1.66	2.20	2.05
Methyl *tert*-butyl ketone	100	125.0	18.20	1.20	1.82	1.78
Amyl acetate	116	134.1	1.73	0.89	1.71	1.45
Isopropyl *tert*-butyl ether	117	157.3	0.50	0.14	0.73	0.53
Octylamine	129	166.0	0.20	0.07	0.07	0.13
n-Octyl alcohol	130	157.8	0.59	0.29	0.59	0.18
2-Ethyl-1-hexanol	130		0.13	0.064	0.47	0.36
Dodecanol	158	191.7		0.03	0.13	0.052
Oleic acid	290	339.6		0.018	0.05	0.024
Tributyrin	302	295.7		0.11	0.37	0.22

The results of solubilization of a series of polar compounds by three different solubilizers are shown in table 11 (161). It is interesting to note that whereas the solubilizing power for hydrocarbons was C_{12} amine hydrochloride > sodium oleate > KC_{12}, the order now is sodium oleate > $C_{12}HCl$ > KC_{12}, which would indicate a rough correlation between chain length and volume available for solubilization in the region of the palisade layers of the two-layer soap micelle. These authors compare the solubilization of polar and nonpolar compounds and indicate that molar volume is apparently not generally applicable to all types of compounds. Of course, it must be recognized that molar volume–solubility relationships can only hold for solubilization in the hydrocarbon center of the micelle. As will be shown later, the degree of polarity or hydrogen-bonding capacity determines the position of the polar compound in the palisade layer of the micelle and thus controls the volume available for the solubilization of these solubilizates (114).

Ward considers that the lower alcohols are held predominantly in the micelle surface (247), and Angelescu and Manolescu consider that phenols are similarly located or even oriented outside the micelles (4). For alcohols up to C_3 which are quite miscible with water, it cannot be determined whether there is a distribution of alcohol molecules which favors penetration into the palisade layer. However, with longer chain alcohol additives, a decrease in C.M.C. is observed, the decrease being larger with increase in chain length of the additive (26). It has also been observed that, for equal chain length of additive, the C.M.C. will decrease more with decrease in the hydrogen-bonding capacity or polarity of the additive (118). Thus *n*-butylamine, for example, will decrease the C.M.C. value of a number of detergents more than an equal concentration of added C_4 alcohol. Transition effects, the importance of which has only recently been noted (115), are also seen in the small changes observed in C.M.C. with amphipathic additives which approach in size that of the colloidal electrolyte (199).

TABLE 12

Solubility of normal primary alcohols, amines, and mercaptans in solutions of 0.3 mole per 1000 g. solution

(Solubility in moles per 1000 g. soap solution)

SOAP	KC_8	KC_9	KC_{10}	KC_{11}	KC_{12}	KC_{13}	KC_{14}	NaC_{12} SULFATE
Alcohols:								
$C_7H_{15}OH$	0.099	0.139	0.188	0.201	0.201	0.212	0.226	0.260
$C_8H_{17}OH$	0.023	0.095	0.127	0.148	0.146	0.156	0.158	0.171
$C_9H_{19}OH$	0.004	0.076	0.0965	0.1165	0.126	0.132	0.140	0.144
$C_{10}H_{21}OH$	0.003	0.063	0.0923	0.104	0.111	0.122	0.136	0.138
$C_{11}H_{23}OH$	0.003	0.072	0.0865	0.107	0.1075	0.116	0.114	0.125
$C_{12}H_{25}OH$*	0.002	0.056	0.0840	0.0870	0.082	0.077	0.034	0.123
Amine:								
$C_{10}H_{21}NH_2$	0.004	0.102	0.11	0.113	0.113	0.113	0.119	0.110
Mercaptan:								
$C_7H_{15}SH$	0.0007	0.0014	0.0102	0.0171	0.0393	0.0591	0.090	0.0925

* Values taken from figures (75).

The solubility of polar compounds in salt-free soap solution is much greater than that of the corresponding hydrocarbons (75, 115). The effect of an increase in concentration of the solubilizer is seen in figure 6, which is typical of these systems. Recently a systematic study was made by Oppenheimer (75), in which he varied both the length of the potassium fatty acid soap and the alcohol chain. These results are collected in table 12. A number of interesting conclusions can be drawn from these data:

1. A general increase in solubility of alcohols with chain length of the soap is seen, with the greatest increase between C_8 and C_9 soaps, except for 1-heptanol. The decrease in the C.M.C. of the C_8 soap from its alcohol-

free value of 0.39 *M* (109) may not be very much when the additives are equal to or longer than the soap molecule (199), and thus very little micellar soap would be available for solubilization in these experiments where 0.3 *M* is the concentration of solubilizer. The C.M.C. values of the C_9 and C_{10} soaps are 0.20 *M* and 0.095 *M*, respectively, and thus smaller changes in solubilization would be expected in going from C_9 to C_{10} soaps. A comparison of the type made in figure 8 and in table 2, where corrections are made for nonmicellar soap, is not possible when alcohols are the solubilizates because the C.M.C. values are not known for long-chain alcohol additives.

2. A decrease in solubility with number of carbon atoms in the alcohol chain, with the greatest decrease between C_7 and C_8 alcohols, is noted.

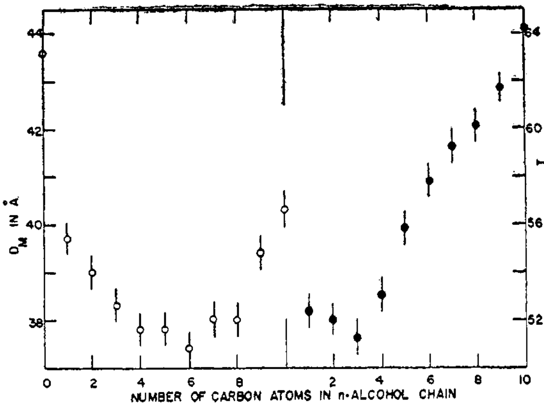


FIG. 12. The effect of normal alcohols on the diameter of micelles (D_M) and on the long (intermicellar) spacing (D_I) of 1.02 *M* sodium dodecyl sulfate solutions (74).

3. It appears that as more penetration into the palisade layer occurs, owing either to an increase in the chain length of the alcohol or to a decrease in the polarity by going from —OH to —NH_2, some transition occurs as is evidenced by a leveling off of solubility values in the C_{10} amine and C_{11} alcohol with increase in chain length of the soap. A complete reversal is observed in the C_{12} alcohol, in that there is initially an increase in solubility with increase in length of soap molecule followed by a decrease with further increase in the number of carbon atoms in the fatty acid soap.

More data as to the effect of variations in concentration on the solubilization of these alcohols are necessary before these interesting results can be fully interpreted from a mechanistic point of view. In this connection, figure 12, which shows the changes in the long x-ray spacings, D_I, and in the micellar spacing, D_M, of sodium dodecyl sulfate with added alcohols (74), is of some interest in indicating the loci of solubilization of these solubilizates. In the case of solubilization of dimethyl phthalate, the lack of an increase in D_I was interpreted as indicating the adsorption of these additives on the micelle surface (150). It would appear that polar, and particularly amphipathic, molecules are likely to be oriented in the surface region of the micelle aggregate. Since the diameter of the latter is only of molecular dimensions, it is expected that orientation will have a very great effect on solubility and that this orientation will be an important factor in the changes observed in the x-ray spectra of alcohol–soap systems. The increase in long x-ray spacing with added long-chain alcohols would appear to indicate solubilization in the micelle center. However, the changes in micellar spacing indicate some decrease with added alcohols, a result which is to be expected if palisade penetration is the mechanism involved in solubilization of this type. The importance of these results in the interpretation of micellar structure will be discussed in a later section.

VII. TEMPERATURE EFFECTS

It appears that most factors which decrease the C.M.C. and increase the size of the micelle will result in an increase in the solubility of hydrocarbons and usually in that of polar compounds. Thus, increase in chain length of solubilizer, the use of many additives (salts, other soaps, alcohols, amines, etc.), as will be seen in the following section, and decrease in temperature result in decrease in C.M.C., increase in micellar size, and usually increase in solubilizing power. Thus it has been shown (109) that for each member of an homologous series at a constant temperature, if the C.M.C. is known for any member:

$$\log \text{C.M.C.} = A + BN$$

where N = number of carbon atoms in the chain, B = an empirical constant (may be taken to be log 2 with sufficient accuracy), and A = a constant for the particular temperature and homologous series, which may be determined from a known value of the C.M.C. for one member of the series. The constant B has recently been shown by Debye (32) to be a factor in the energy function associated with attractive forces resulting in micelle formation. The increase in solubilization with increase in length of soap chain has been shown above and light-scattering measurements have indicated a corresponding increase in micellar size (32). By means of the spectral dye method (28) applied to soap–salt systems (27) and by refraction measurements (106, 109), it has been shown that the log of the C.M.C. of anionic soaps is linearly dependent on the log of the cation concentration of added salt and is independent of the nature of the salt anions. These results are in essential agreement with the surface tension and interfacial tension measurements of Powney and Addison (191), who studied the change in C.M.C. of dodecyl sulfate solutions containing various concentrations of added sodium chloride and calcium chloride.

Various results have been reported regarding the effect of temperature on the C.M.C. From conductivity measurements of sodium alkyl sulfonate solutions by Wright *et al.* (256), of alkylamine hydrochlorides by Ralston and Hoerr (202), from refraction measurements on some soaps and alkyl sulfonates (109), as well as a number of other measurements, it has been shown that the C.M.C. increases slightly with increasing temperature. Bury and Parry (19), from density measurements on KC_{12} solutions, indicate that the C.M.C. decreases with increase in temperature, and Ekwall finds that the C.M.C. of some fatty acid soaps is independent of temperature (46). Brady and Huff (16) report an initial decrease in C.M.C. followed by an increase above 45–50°C. The application of the spectral dye method to temperature effects indicates that the C.M.C. decreases with increasing temperature, but these results have been shown to be a property of this particular method (107). From the solubilization of dyes with detergents, Kolthoff and Stricks (125) find that the addition of salt has little effect on the C.M.C. values at elevated temperatures. This result does not agree with that obtained by Wright *et al.* (256), who conclude from conductance measurements of sodium dodecylsulfonate solutions in the presence of added sodium chloride that the effect of the sodium ion on the lowering of the C.M.C. decreases considerably with rise in temperature.

TABLE 13

Temperature and salt effect on solubilizing power

(Grams of dimethylaminoazobenzene per mole of soap) (126)

TEMPERATURE	DETERGENT											
	Caprate		Laurate		Myristate		Oleate		C_{12} amine hydrochloride			
									At 0.4 *M*		At 0.06 *M*	
	No salt	1.0 *N* KCl	No salt	1.0 *N* KCl 0.3 *N* KC_{12}	No salt	0.5 *N* KCl 0.3 *N* KC_{14}	No salt	0.05 *N* KCl	No salt	0.05 *N* NaCl	No salt	0.05 *N* NaCl
°C.												
50	1.19	0.95	2.43	2.16	4.15	4.87	5.72		5.63	5.9	3.30	3.9
30	0.64		1.50	1.55	2.71		3.24	3.30	4.32		2.23	3.35
Ratio: 50/30	1.86		1.62	1.39	1.53		1.76		1.3		1.5	1.16

The change in solubilizing power with temperature is seen in table 13 for the case of solubilization of dimethylaminoazobenzene (DMAB). It is apparent that the ratio of the solubilizing power of a soap with temperature is different for different soaps. It has also been observed that, at least in the solubilization of dyes, the solubilizing power depends also on the structure of the molecule which is solubilized (66, 125, 149). Lambert and Busse (130, 131) have indicated that the use of 50°C. temperatures for solubilization would decrease the time necessary to reach equilibrium from a number of days to as little as 15–30 min. and the resulting values of solubilizing power would not be affected by the use of this higher temperature. This would appear to be a contradiction of the previous results. It is seen that in the solubilization of DMAB (table 13) and for other dyes (126) (Orange OT and azobenzene) the ratio of the solubilizing power is usually lower in the presence of electrolytes and the solubilizing power is increased with increase in temperature.

The reported increase in solubility with temperature in these systems is in accord with the effects of temperature which are noted in normal solubility phenomena in which paraffin-chain salts are not the solvent. In these latter systems, the increase in temperature results in an increase in molecular dispersion of the solute, owing to increased thermal motion and a corresponding increase in the wetting of the solute by the solvent molecules. It is probable that the enhancement in solubility of DMAB in the presence of paraffin-chain salts is due in part to this normal temperature effect rather than to a specific increase in the solubilizing power of the soaps. The finding by Debye (33) that the molecular weight of a micelle of trimethyldodecylammonium bromide decreases just as the C.M.C. increases with increase in temperature lends support to this contention. This decrease in micellar weight would be expected to result in a decrease in solubilizing power rather than in an increase. It will be shown later that the effect of added electrolytes on the solubilization of DMAB (126) is similar to that observed when long-chain alcohols are the solubilizates (115), indicating that the solubilization of DMAB is probably of the polar type in that this substance is solubilized in the palisade layers of the soap micelle.

The anomalous effect of temperature on solubilization in various systems has been discussed from the point of view of its effect on the miscibility of the organic liquid (single compound or mixture) and aqueous liquid (water or salt solution) as separated from the effect on the amphipath (255). When the amphipath is an alkali metal salt, a rise in temperature usually diminishes the solubilization of organic liquids in micelles in which polar groups are oriented outward and results in an increase in the amount of water or other polar liquid solubilized in those cases where one has a system of inverted micelles (polar groups oriented toward micelle center). However, many exceptions to these regularities have been observed, particularly in the first type of systems.

VIII. Effect of Various Additives

There is a very considerable literature, both in journal reports and in patents, concerning the effectiveness of a whole series of builders or additives which enhance the detergent action of all types of surface-active agents. The role of detergency involving removal of dirt and solubilization of this dirt by higher concentrations of soaps has been discussed by McBain (144) and the relationship between detergent action and solubilization has been also reviewed by Preston (192), who summarized the many radical property changes which occur at the C.M.C. Summaries of the aspects of detergency and the function of various additives have been published by Aickin (2), Sisley (224), and Chwala and Martina (21). Goette has indicated that the cleansing action of a solution of NaC_{12} sulfate can be increased by adding a certain amount of any neutral salt but that if this optimal amount is exceeded, the cleaning action is retarded (64). The phenomenon of solubilization and the role of soaps and detergents in the presence of various additives in the light of textile processing have been recently reviewed (29). The action of added electrolytes on the C.M.C. of soaps has been shown to depend on the number of equivalents of added cations and is independent of the nature of the anion (27, 109). However, it has been found that the optimum cleaning action of a liquid, at concentrations below the C.M.C., will be reached at a lower equivalent concentration of sodium pyrophosphate than by adding sodium sulfate and this latter requires a lower concentration than sodium chloride (2, 78, 186). Similarly, in contrast to the effect of various additives on the C.M.C., potassium ferrocyanide has been found to be less effective than potassium sulfate, potassium sulfate less than potassium chloride, and potassium chloride less than sodium chloride, all in equivalent amounts, in increasing the solubility of various hydrocarbons (115, 229). Just the opposite has been found to occur in the solubilization of polar compounds, a result which indicates very definitely the presence of at least two loci of solubilization in the soap micelle (115). These findings would appear to indicate a more direct relationship between detergent and solubilization properties in the presence of various additives, whereas detergent action, C.M.C., and solubilization can be related in the absence of these additives. This latter relationship has been reviewed by Preston (192), but it is seen not to be valid in the presence of added electrolytes.

Various mixtures have been prepared for specific purposes. Thus a soap composition suitable for use in hard water and sea water is described in typical vague terms as being composed of a water-soluble soap and a mixture of alkyl derivatives of an aromatic (not more than two benzene nuclei) sulfonate (51). An improvement in detergent action is claimed for the use of small amounts of a C_{10}–C_{14} fatty acid nitrile of *N*-acylmorpholine, or of hydroxy acid amides as additives to water-soluble salts of alkylsulfonic acids (240). A recent summary discusses the effect of mixtures and impurities or additives on the properties of various commercial preparations of detergents (52). Tests such as lowering of surface tension, foaming, detergency, and wetting time by the canvas disc method have been used to show the effect of valency of additives, using various alkyl sulfates (41). Harris (76, 77) has recently reviewed the effect of electrolyte builders or additives for surface-active agents. The addition of electrolytes reduces surface and interfacial tensions, reduces critical conductivity, improves wetting speeds, and enhances detergent action. The valence of the additive has marked effects on these properties, since much smaller amounts of polyvalent ions are required to produce a given change in property. Excessive amounts beyond the optimum generally result in significant decreases in surface activity.

The above indicates in brief that the emphasis on builders or additives has been for the main part from the point of view of application. The importance of the part played by solubilization in detergency has been discussed by McBain (144) and as a transition factor in emulsification by Schulman *et al.* (210, 215). The marked increase in the past few years in reports concerned with additive effects can, of course, be correlated with the preparation of a host of new detergents, some of very interesting structural properties. Since by far most of these are commercial preparations, their descriptions and properties have not reached the academic literature. When they have been studied, "technical preparations have most often been used and too little help seems to have been given by the preparative chemist to his physical colleague—a state of affairs which could be remedied by more preparative activity on the part of the latter" (84).

Many additives have been shown to influence both C.M.C. and solubilization. The addition of a more soluble soap in large concentrations will increase the

C.M.C. and decrease the solubilizing power, whereas when a soap of a longer alkyl chain or a less soluble one is added the opposite effects are noted if, of course, the same cation is present (105, 109, 117, 229). The addition of long-chain alcohols and amines will greatly enhance the solubilization of hydrocarbons, and the presence of solubilized hydrocarbon will enhance the solubility of polar compounds (114). Weichherz (248) has shown that the addition of phenol to soap in benzene solution is necessary for the solubilization of water, and Pink (187) indicates that the addition of 1.1 g. phenol to 3.4 g. ethanolamine oleate in 39 g. benzene increases the solubility of water from 0.45 ml. to 5.2 ml. The addition of 1.5 g. cresol results in a similar increase. The addition of electrolytes produces complex effects which depend on various factors such as the nature of the solubilizer, its concentration, the polarity of the solubilizate, the type of electrolyte, etc. (66, 80, 115, 126, 149, 161, 229, 254). Various complex additives such as the sodium carboxymethylcelluloses have been shown to enhance detergent properties considerably (9, 96, 243) but, as yet, no solubilization data are available concerning this type of additive. The addition of carboxymethylcellulose to KC_{12} solutions results in a decrease in C.M.C. similar to that observed when equivalent amounts of other electrolytes are added (169).

A. Solubilization by soap mixtures

It is now recognized that the solubilizing power of a soap or detergent will decrease and the C.M.C. increase as the purity of the preparation is increased. This is, of course, valid only if the impurity is a soap of longer chain length (lower solubility). Thus the defatting power and turbidity point of a fatty acid sulfate were reduced by the addition of increasing amounts of C_5–C_{11} sulfates (53). Commercial soap mixtures, even those free of electrolyte and unneutralized fatty acids, are excellent solubilizing agents, for the lower soaps solubilize the normally insoluble longer chain soaps and because of this their solubilizing power is enhanced. However, to understand better the various factors involved in solubilization with soap mixtures, it has been necessary to prepare mixtures of known composition.

Various phenomena related to solubilization, such as changes in the long x-ray spacings (72) and in C.M.C. (105, 109), are included in figure 13, which shows also the effect of various soap mixtures on the solubilization of ethylbenzene (229) and *n*-heptane (117). It is seen from the linear changes with mole fraction that there is a direct correlation in the change in long x-ray spacing and the amounts of ethylbenzene and *n*-heptane solubilized, indicating a constant volume available for saturation with hydrocarbon. The nonlinearity of solubilization in various mole fractions of KC_{14} and KC_8 is due in part to the fact that the total concentration is 0.1 *M*, well below the C.M.C. of 0.395 *M* for the KC_8 (109). However, there is some enhancement in the solubility of ethylbenzene in KC_{14}, since the shorter chain soap acts like a salt which depresses the C.M.C. and correspondingly increases its solubilizing power.

Another approach to the effect of soap mixtures is indicated by the data in figure 14 (117), in which the effect of varying concentrations of soap of different chain lengths added to 0.35 *M* KC_{14} is seen. There is the usual enhancement in concentration when the same soap, KC_{14}, is the additive. The added KC_{16}, normally insoluble at room temperature, is found to be readily solubilized by KC_{14} and greatly enhances the solubilization of *n*-heptane. The addition of KC_{12} at very low concentrations of additive acts somewhat like an electrolyte but at higher concentrations the diluent effects of the shorter chain soap with its lower solubilizing power are seen. Similar initial salt-like effects followed by a decrease in solubilizing power are noted when KC_8 is the additive.

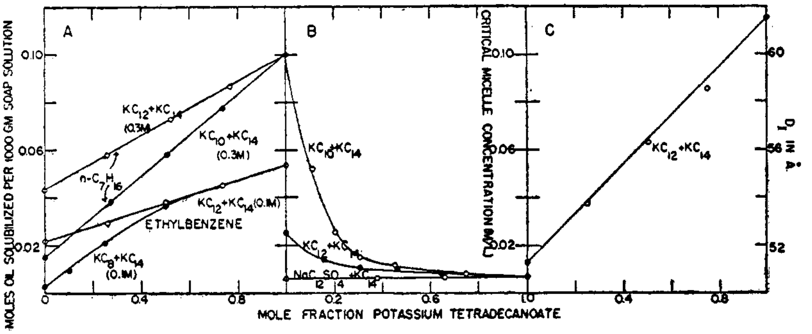


FIG. 13. Changes in (A) solubilization of *n*-heptane and ethylbenzene, (B) critical micelle concentration, and (C) the intermicellar x-ray spacing in various soap mixtures (75, 105, 109, 117, 229).

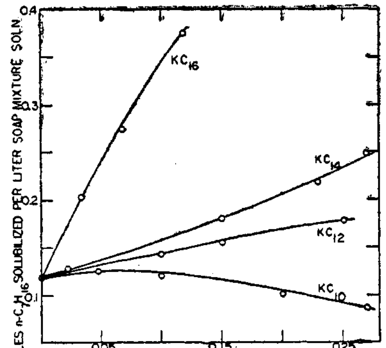


FIG. 14. Solubilization of *n*-heptane in soap mixtures all of which contain 0.35 *M* potassium tetradecanoate.

McBain and Green (149) have obtained, for the ratio of grams of Orange OT solubilized per mole of soap for 50:50 mixtures of KC_{12} and KC_{14}, constant values which are found to lie between those for the single soaps. Thus at 25°C. these ratios are 1.04 for KC_{12}, 1.92 for KC_{14}, and 1.42 for equimolar mixtures of KC_{12} and KC_{14}. At 50°C. these values were 1.62, 2.95, and 2.18, respectively.

B. Effect of other polar additives

The first investigation of mixed films was the work of Leathes (135, 136), who found that when the proportions were one molecule of lecithin to two or four molecules of myristic or another fatty acid which gives an expanded film, the effect of the lecithin was to condense the film. The addition of hydrocarbons such as tetradecane to fatty acid films over 0.01 M hydrochloric acid has been shown to have very little effect on force–area curves (177), whereas a stable mixed layer due to molecular interactions in the film is obtained when a soluble substance—and one therefore incapable of giving by itself a stable film—is injected into the substrate on which the normal layer is formed (214). Schulman and Stenhagen (216) have shown the formation in films of complexes of compounds such as cetyl alcohol and sodium cetyl sulfate which in the presence of water cannot be expected to form compounds in the chemical sense of the word. Cockbain and Schulman (23) indicate that there are different modes of interaction according to the nature of the chains and the polar groups. Further, it has been indicated that a liquid-expanded film is made more condensed by addition of a substance which gives a condensed film (139) and the condensing action is found to increase with the length of the hydrocarbon chain (71). Also, an alcohol condenses an acid more than the corresponding acid, and an amine additive is found to show the largest effect. These monolayer effects can be seen to be directly correlatable with changes in solubilization when various polar compounds are used as additives or builders. When alcohols of varying chain length are added to opaque viscous masses of sodium oleate (concentrations $>$ 25 per cent) containing equal amounts of water and benzene, these systems become transparent (212), indicating that this involves an enhancement of solubilization according to the interpretation which will be discussed below (114). According to conductivity measurements, up to amyl alcohol the transparent systems have water as the continuous phase; *n*-hexyl and longer alcohols are oil-continuous systems. In contrast, marked increases in resistance of some 3 to 4 decades are observed in similar systems, in which undecane-3 sodium sulfate (255a) and Aerosol AY and Aerosol MA (118) are the solubilizers, when increasing amounts of various long-chain alcohols are used as additives. Branching in the alcohol chain, probably a function of steric effects in adlineation between the two molecules (91), results in the use of about 2.5 times more 2-ethyl-1-hexanol than 1-hexanol to arrive at transparent fluid systems. It has been proposed by Schulman and coworkers that x-ray and light-scattering measurements (210, 213, 215) on these systems should throw some light on the gap between swollen micelles (solubilization) and emulsion droplets (emulsification). However, it must be emphasized that solubilization must be considered to be a thermodynamically stable solution, i.e., a single phase, whereas emulsification involves the formation of two distinct phases. The following discussion must thus be considered solely from the point of view of emulsification. The diameters of the droplets are seen to increase in a regular manner with decrease in potassium oleate concentrations in both the oil- and the water-continuous systems. The data on light-scattering experiments in figure 15 agree with those calculated on the concept of uniform water spheres in oil or uniform oil spheres in water according to the formula:

$$\frac{3 \times \text{volume of dispersed phase}}{\text{area of interfacial monolayer}} = \text{radius of oil or water droplet}$$

It was found that the corrected Bragg x-ray figures for large diameters are greater than those calculated from surface chemical data. All three measurements are in close agreement for diameters less than 300 Å. These authors consider these systems to be structures of short cylinders or short lamellae of soap–alcohol molecules with oil and water between the layers. In similar qualitative measurements, Winsor (254) assumes that the inversions occur from oil to water continuum containing spherical micelles through a series of lamellar micelles. Dervichian and Pillet (38) have shown that complex formation occurs between lecithin and fatty acids. A mixture of 1 mole of lecithin with 2–10 moles of oleic acid spreads over an area about 18 per cent less than the calculated areas for the quantities of components used. Dreger *et al.* (41) have shown that the detergency of sodium alkyl sulfates diminishes as the sulfate group recedes from the end of the hydrocarbon chain. These results were confirmed by Winsor (253), who showed that sodium stearate readily displaced sodium *n*-tetradecyl sulfate from the surface layer of aqueous solutions and that the more readily displaced surface-active materials (those with poorer detergent properties) were those with the sulfate group farthest from the terminal carbon.

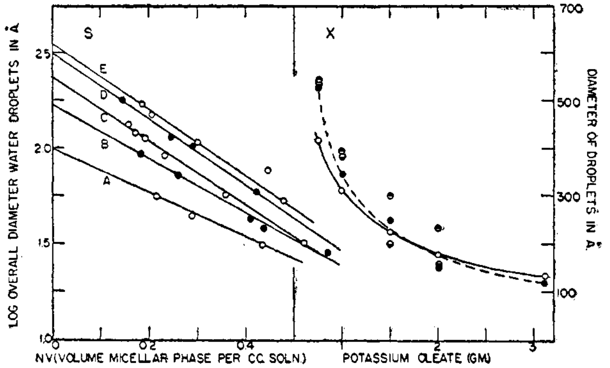


FIG. 15. Light-scattering (S) and x-ray (X) diameters of system potassium oleate–5 ml. water–benzene–cyclohexanol. S: (A) 0.75 ml. oleic acid, (B) 1.00 ml. oleic acid, (C) 1.50 ml. oleic acid, (D) 2.00 ml. oleic acid, (E) 3.16 ml. oleic acid. X: dimensions of corrected x-ray spacings in oil-water systems with varying soap-alcohol concentrations; 5 ml. oil and 5 ml. water. Water droplets: ●, observed; ○, calculated. Oil droplets: ◒, observed; ◓, calculated (210, 215).

If the evidence as to two loci of solubilization based on film penetration, x-ray, and changes in rate of solubilization data are correct, then it should be possible to show that hydrocarbons and polar compounds are incorporated in micelles independently of each other. The addition of hydrocarbons which swell the center hydrocarbon region of the micelle should make it possible for the micelle containing solubilized hydrocarbon to incorporate more polar compound in its palisade layer. The data in figure 3 show this effect (114), and an explanation based on these assumptions is included at that point. When long-chain alcohols are added to soap solutions, the soap–alcohol micelles that are formed are found to solubilize as much as eight to ten times the amount of hydrocarbon normally soluble in soap solutions of the same total normality (114). The data in table 14 show the increase in solubilization of n-heptane in KC_{14}–1-heptanol micelles and these are compared with the solubilities of n-heptane in KC_{14} solutions. The effect of increasing alcohol chain length on the enhancement of solubilization is shown in figure 16 and the changes in solubilizing power with change in polarity of the additive are indicated in figure 17. A higher degree of order in the alcohol–soap micelles can be advanced from the results on penetration and changes in film pressure (139) for the mixed micelles than for soap micelles, which, however, cannot account for these enhanced solubilizations. The penetration of the alcohol into the soap palisade layer, coupled with a somewhat lower degree of order, would result in the production of a much larger volume capable of solubilizing hydrocarbons. A greater penetration with decrease in polarity $COO^- > OH > NH_2 > SH$ would account for the data in figure 17. In the light of the forces involved in micelle formation, there is an increase in total energy of attraction upon the addition of alcohol molecules to the soap micelle without a corresponding increase in the forces of repulsion, those due to the charged colloidal electrolyte heads. The increase in alcohol chain length and changes in polarity of the amphipathic additive would result in a larger contribution per carbon atom to the energy of attraction, a lower degree of order, and thus to an enhancement of solubilizing power. On the basis of the above hypothesis, the increase in solubilization of Orange OT by KC_{12} to which was initially added small amounts of benzene, toluene, or hexane and the corresponding decrease in amount solubilized when 5 per cent alcohol is added (66) can readily be explained. Recently, it has been found that the solubility of hydrocarbons such as n-heptane in various fatty acid soaps is increased when equivalent amounts of 1-, 2-, 3-, and 4-octanols are the additives (118), the increase being larger with movement of the hydroxyl group from the 1- to the 4-position.

TABLE 14

Solubilization of n-heptane in solutions of 0.35 M potassium tetradecanoate plus polar additive

MOLES OF ADDITIVE PER 1000 G. KC_{14} SOLUTION	MOLES OF n-C_7H_{16} SOLUBLE PER 1000 G. KC_{14} + KC_{14} SOLUTION	MOLES OF n-C_7H_{16} SOLUBLE PER 1000 G. KC_{14} + n-C_7OH SOLUTION	$\frac{\text{SOLUBILITY IN } KC_{14} + \text{ALCOHOL}}{\text{SOLUBILITY IN } KC_{14} + KC_{14}}$
0	0.116	0.116	1.0
0.0411	0.126	0.174	1.38
0.0812	0.142	0.222	1.56
0.120	0.160	0.268	1.67
0.195	0.200	0.356	1.78
0.230	0.217	0.395	1.82
0.270	0.245	0.442	1.81
0.318		0.500	

Palit has found that a mixture of solvents would greatly enhance the solubilization of water by cetyldimethylethylammonium bromide when neither pure solvent would be effective (183). Thus in this system, the addition of chloroform to either benzene or carbon tetrachloride would result in an initial increase in solubilization of water followed by a decrease when the concentration of chloroform was further increased, as is seen in figure 18. If these solubilization data are due to the formation and breakdown of the McBain-Hess lamellar micelle, it is difficult to see how these micelles can accommodate about five times their own weight of water in the interlayer spaces without producing a great perceptible heterogeneity. It appears that these results are more readily explainable on the basis of phenomena noted by Winsor (254), in which there is a transition from one micellar form to another, on the results noted by Schulman *et al.* (210, 213, 215) on the marked increase in solubility upon the addition of cyclohexanol, and on

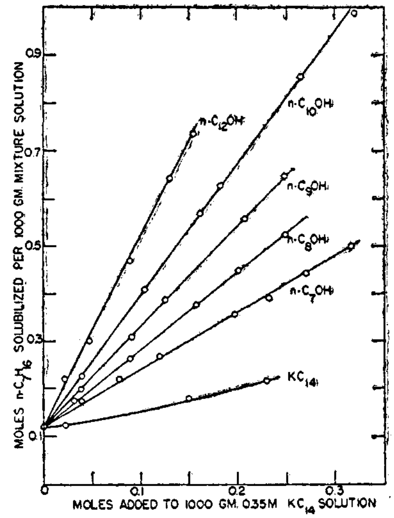


FIG. 16

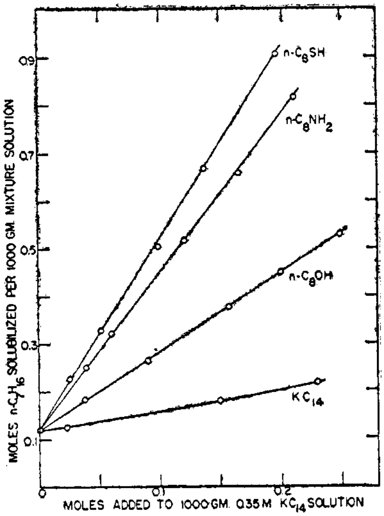


FIG. 17

FIG. 16. Enhancement of solubilization of *n*-heptane in 0.35 *M* potassium tetradecanoate solutions containing various long-chain alcohols as additives (25°C.).

FIG. 17. Effect of change in polar group of additive upon solubilization of *n*-heptane in 0.35 *M* potassium tetradecanoate solutions (25°C.).

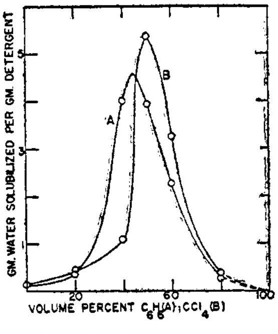


FIG. 18. Solubilization of water in solutions of 1 g. cetyldimethylethylammonium bromide in 5 ml. chloroform-additive solvents at 30°C. (183).

the data reported on eight- to ten-fold increases in the solubilization of *n*-heptane by added long-chain alcohols and amines (112, 114). Further viscometric, optical, and x-ray investigations on all these systems will assist in a final clarification of these phenomena.

Detergent and solubility properties of commercial preparations were enhanced by the addition of fatty acid amides of an alkylolamine (156) and of lauryl alcohol to naphthalenesulfonates (159). The addition of 0.1–20 per cent by weight of an organic builder such as the lower monohydric alcohols or the glycol esters of higher fatty acids to alkyl sulfates or sulfonates produces a detergent composition with improved stable foams (254). Various other organic builders and mixtures, as well as mixtures of surface-active agents with each other, have been mentioned by Schwartz and Perry (217), particularly with regard to the patent literature.

TABLE 15

Figures indicate mole ratio of builder to hardness required for effective soap protection at 57°C. (174)

	$Na_6P_4O_{13}$ QUADRAFOS	$Na_5P_3O_{10}$ POLYFOS	$Na_6P_6O_{18}$ CALGON	$Na_4P_2O_7$ TSPP	Na_3PO_4 TSP	$Na_2O\cdot 3.2SiO_2$	Na_2CO_3
Oleate	1	1	1	1	5	4	>5
Laurate	1	1	1	2	5	>5	>5
Ricinoleate	1	2	2	3	>5	5	>5
Myristate	2	2	1	3	>5	>5	>5
Elaidate	2	2	2	4	>5	5	>5
Palmitate	2	3	3	>5	>5	5	>5

C. Electrolytes as additives

The effect of added electrolytes on the solubility of calcium and magnesium soaps in the sodium soaps, using a foam stability test (172), shows that a minimum mole ratio of builder to calcium or magnesium salts is required to prevent the formation of alkaline earth soaps (174). The mole ratios, as seen in table 15, vary for each soap studied and with the particular calcium or magnesium salt and builder combinations. However for a particular soap, it is seen that a smaller amount of builder with increased charge is necessary for effective soap protection. The effect of added electrolyte on the solubilization of hydrocarbons is found to proceed in the same way, but the opposite effect is noted when polar compounds are solubilized in the presence of electrolytes (115). However, a transition occurs as the length of the polar compound is increased so that the effects noted in table 15 may be explained on this basis. The addition of sodium chloride and lithium chloride is found to decrease the rate of solution of KC_{16}, whereas potassium chloride increases this rate (220).

The brief discussion in the introduction to the section on additives mentioned the presence of a considerable technical and patent literature involving the use of electrolytes as additives for various commercial preparations. Since it is not possible to cover this application completely, no attempt will be made here to do so, since no information may be obtained from these systems as to structural effects coupled with electrolyte addition on solubilization. Rather, those data which involve the effect of electrolytes on well-characterized soaps and detergents will be discussed particularly from the point of view of information regarding loci of solubilization which might be obtained from them. However, it is worth noting that, in a recent review, Harris (76) has indicated that the addition of ionic electrolytes to anionic surface-active agents can bring about the following changes: reduce surface and interfacial tension, reduce critical conductivity, improve wetting speed, increase lather, and increase detergency. The addition of anionic electrolytes (silicates, phosphates, etc.) to cationic surface-active agents in general results in inactivation of the detergent. The addition of cationic electrolytes (calcium and aluminum chloride) in general exhibits only a slight effect. Addition of ionic electrolytes to a nonionic surface-active agent results in essentially no effect upon wetting. The valence of the added anionic or cationic builder has a marked effect upon the physicochemical properties of anionic surface-active agents. Markedly smaller amounts of polyvalent anionic or cationic builders are required to produce a given change in property. Excessive amounts beyond the optimum generally result in significant reduction in surface activity. Builders for anionic surface-active agents which hydrolyze to yield alkaline or acid solutions are better builders than those which provide essentially neutral solutions. Builder addition to anionic agents can result in a two- to ten-fold decrease in the amount of surface-active agent necessary to produce a given result.

Hartley (80) studied the effect of added sodium chloride on the solubilization of azobenzene in cetylpyridinium chloride. The most complete data in this study cover the low concentration range of detergent, as seen in figure 19. A plot of these data in this manner, in contrast to the manner in which the author treated his data, allows one to determine the C.M.C. of these systems from the intersection of the two lines which show the solubility changes. The insert in figure 19 indicates the change in C.M.C. with added sodium chloride as obtained from these intercepts. Many similar studies have been made (4, 66, 80, 115, 126, 149, 152, 155, 161, 162, 163, 169, 229). Thus McBain and Johnson found similar effects when potassium chloride was added to KC_{12} and KC_{14} (152) and McBain and Green (149) extended these studies to wider concentrations of KC_{12} in 1.0 N concentrations of different salts. For the solubilization of Orange OT in KC_{12}, $KOH > KCNS > KCl = K_2SO_4 >$ no salt when added in equimolar concentrations (149). However, it was found for the solubilization of ethylbenzene (229) in KC_{14} that $NaCl > KCl > K_2SO_4 > K_4Fe(CN)_6 \cdot 3H_2O$ when added in equivalent amounts, a result which does not agree with the work of the previous authors. Also, in the solubilization of n-heptane the increase in solubilization is seen in figure 20 to follow the same order: $KCl > K_2SO_4 > K_4Fe(CN)_6 \cdot 3H_2O$. It should be repeated here that these salts in equivalent amounts have been found to result in an equal depression of the C.M.C. (27, 109). No data are available which would indicate whether changes in solubilization in the region of the C.M.C., as is seen in figure 19 (80), would occur when equivalent amounts of various electrolytes are used as additives.

Recently, differences in the effect of added salts on the solubilization of various compounds have been noted (115, 126, 204). The addition of sodium chloride or potassium chloride to 0.1 N cetylpyridinium chloride (C.M.C. = 0.0009 N in salt-free systems) will result in an initial increase in the solubilization of benzene followed by a decrease at about 0.5 N salt concentration and an increase for n-octane up to about 1.0 N salt (204). However, when 1-octanol is solubilized a decrease is noted upon the addition of electrolyte. Similar results are reported to occur in dilute (0.0125 N) solutions. When compared to the C.M.C. values of cetylpyridinium chloride in the presence of added salt (about 0.0001–0.0003 N, as seen in the insert in figure 19) this concentration is seen to be about 100 times the C.M.C., and thus micelles with maximum colloid properties may have been formed at this concentration. These authors suggest that with this polar compound, the solubilization occurs on or between the polar ends of the micelles that are exposed to the water. Further, they believe that the added salt is in competition with the solubilized material at the polar ends of the detergent molecules and interferes with its solubilization. They use the evidence of Tartar and Cadle (233), which indicates that salts are sorbed by the micelles.

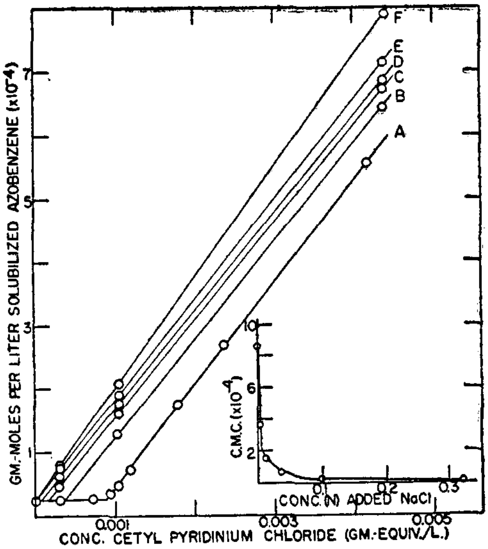


FIG. 19

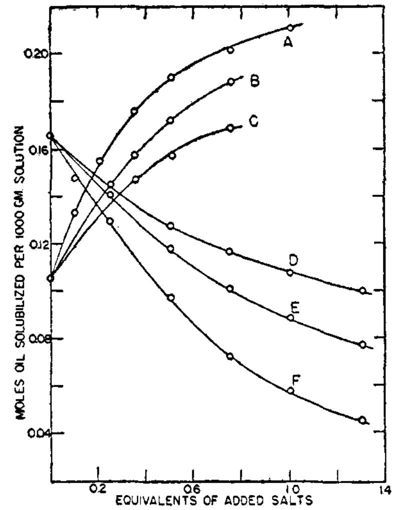


FIG. 20

FIG. 19. Effect of added sodium chloride on solubilization of azobenzene in cetylpyridinium chloride at 25°C.: (A) 0, (B) 0.0032 N, (C) 0.01 N, (D) 0.032 N, (E) 0.1 N, (F) 0.32 N sodium chloride. Insert shows the effect of added sodium chloride on critical micelle concentration as obtained from the solubilization of azobenzene (80).

FIG. 20. Effect of addition of various electrolytes on solubilization of n-heptane in 0.32 M KC_{14}: (A) potassium chloride, (B) potassium sulfate, (C) potassium ferrocyanide. Effect of addition of various electrolytes on solubilization of 1-octanol in 0.32 M KC_{14}: (D) potassium ferrocyanide, (E) potassium sulfate, (F) potassium chloride.

A careful investigation of the solubilization data of various dyes in fatty acid soaps and in dodecylamine hydrochloride in the presence of added salts (126) shows cross-overs in plots of amount of dye solubilized in the presence and absence of salts. Thus, at about 0.045 *M* KC_{14} there is a transition in the amount of dimethylaminoazobenzene (DMAB) solubilized in the presence of added potassium chloride. Below this concentration, DMAB is more soluble in the salt–soap system than in the pure soap; above this concentration the relative solubilities are reversed. This transition occurs at about 0.125 *N* NaC_{12} in the presence of 0.1 *N* sodium chloride, at about 0.112 *N* KC_{12} in 1 *N* potassium chloride, and at about 0.4 *N* KC_{10} in the presence of various salts. When other dyes such as *trans*-azobenzene and Orange OT are solubilized in similar systems, no such transitions are found to occur.

These changes in solubilization between polar and nonpolar compounds in the presence of various electrolytes and the data from some experiments which were so planned as to give additional information as to the loci of solubilization (115) can best be explained on the hypothesis that at least two of these loci exist in the micelle. If, as has been mentioned previously, one accepts the hypothesis that the energies involved in micelle formation are the forces of repulsion of like-charged heads and the attractive forces, van der Waals in nature, of the long hydrocarbon tails, then any additive which results in an increase or a decrease of either or both of these forces will result in a change in size and/or shape of the micelle and a corresponding change in the volume available for solubilization. It has been shown, in a previous section on polar additives, that an increase in the solubilization of a polar compound will occur when a hydrocarbon is added and that the addition of a polar compound will greatly enhance the solubility of hydrocarbons (114). Thus other additives, such as electrolytes, which result in changes in these repulsive and attractive forces, should show corresponding changes in solubilization. These additives will result in an effective decrease in the energy of repulsion of like-charged soap heads and will thus increase the equilibrium size of the micelle. The added electrolyte will screen

TABLE 16

Solubilization of n-heptane and 1-octanol in 0.05 N potassium tetradecanoate with added potassium chloride

MOLES OF KCl PER 1000 G. OF SOLUTION	SOLUBILITY (*S*) IN MOLES OF n-C_7H_{16} PER 1000 G. OF SOLUTION	$\frac{S\ n\text{-}C_7H_{16}\ (\text{ADDED KCl})}{S\ n\text{-}C_7H_{16}\ (\text{NO KCl})}$	*S* MOLES OF n-C_8OH PER 1000 G. OF SOLUTION	$\frac{S\ n\text{-}C_8OH\ (\text{ADDED KCl})}{S\ n\text{-}C_8OH\ (\text{NO KCl})}$
0	0.0087	1.0	0.024	1.0
0.10			0.028	1.16
0.20	0.016	1.84		
0.25			0.032	1.33
0.35	0.019	2.18		
0.50	0.023	2.65	0.036	1.50
0.75			0.029	1.20
1.00	0.030	3.45	0.020	0.83

the action of the charges on the micelle and will result in a decrease in the electrical work of repulsion. Debye has shown that there is a linear increase in the molecular weight of the dodecylamine hydrochloride micelle with equivalents of added chloride-ion concentration (32, 33). Thus for the solubilization of hydrocarbons, those which enter the micelle center and result in increases in long x-ray spacings, it is to be expected that there will be an enhancement in solubility upon the addition of electrolytes. Further, since there is this decrease in the energy of repulsion upon the addition of electrolytes, it would follow that there would be a decrease in the effective volume in the soap palisade layer available for solubilization. Thus one would expect a marked decrease in the amount of solubilized long-chain alcohols in the presence of added salts.

The data in figure 20 (115) show the effect of added electrolyte on the solubilization in 0.32 *M* KC_{14} of both hydrocarbon, *n*-heptane, and polar compound, 1-octanol. The addition of potassium chloride results in an increase in the solubility of *n*-heptane and a corresponding decrease in that of 1-octanol. The added electrolytes which have least effect on the enhancement of solubilization of *n*-heptane are seen to cause the smallest decrease in the solubility of 1-octanol.

Richards and McBain (204) report that at both high (0.1 *N*) and low (0.012 *N*) concentrations of cetylpyridinium chloride, the addition of electrolytes results in a decrease in the solubilization of 1-octanol. In contrast to these results it has been found that at 0.007 *M* KC_{14}, the addition of potassium chloride results in an increase in the solubility of both *n*-heptane and 1-octanol and at 0.32 *M* KC_{14} plus added salt the solubility of the hydrocarbon increases while that of the polar compound decreases (115). At 0.05 *M* KC_{14} a transition region for the solubility of 1-octanol is noted. There is an increase up to about 0.5 *N* potassium chloride, followed by a decrease at higher added salt concentrations. The data covering the transition region are seen in table 16. It is expected that this transition region will shift with change in nature of the electrolyte additive. This transition is probably related to the KC_{14} micelles attaining maximum colloidal properties at this concentration in the presence of 0.5 *M* potassium chloride.

It is to be expected that, if these transitions occur, similar effects should be noted if the added electrolyte is kept constant while the soap concentration is varied. Thus when *n*-heptane and 1-octanol are solubilized in KC_{14} and in KC_{14} plus 0.25 *M* potassium chloride, results such as those seen in figure 21 are obtained (115). The cross-overs are similar to those which have been obtained in the solubilization of DMAB (126) in soap–salt and in salt-free solutions but are more striking because of the somewhat higher initial solubility of the 1-octanol. It is probable that the cross-overs noted in the dye solubilization can be accounted for by this mechanism.

Certain anomalies are to be expected in the effect of salts on solubilization of alcohols if the length of the alcohol is increased so that the overall effect of the polar group is diluted as the hydrocarbon portion of the alcohol is increased. This factor is indicated by the data in figure 22, where the solubilities of C_7, C_8, C_{10}, and C_{12} alcohols in the presence of increased potassium chloride concentrations show another transition effect. The continued increase in hydrophobic properties as the chain length of the alcohols is increased is quite evident from their solubilization data. It is seen that a marked change occurs between the C_8 and the C_{10} alcohol where KC_{14} is the solubilizer. This might indicate that little or none of the C_8 hydrocarbon tail extends into the hydrocarbon center of the micelle and that a portion of the C_{10} and more of the C_{12} alcohol penetrates into the micelle center and possibly into the adjacent palisade layer. Preliminary results from this laboratory with KC_{12} indicate that the transition occurs with the C_8 alcohol, but additional evidence, now being obtained, will be necessary before more definite ideas as to the extent of penetration of these long-chain alcohols into the soap micelle can be advanced. The x-ray data showing the changes in both long spacing and in the micellar spacing with increase in alcohol chain length, as seen in figure 12, would indicate some penetration into the micelle center if only the data on the changes in long x-ray spacings were known and if the lamellar theory of micellar form were still predominant. However, it is to be noted that there is a transition occurring between the C_8 and the C_{10} alcohols in these systems in that the D_M spacing which is fairly constant between C_4 and C_8 is seen to increase beyond the C_8 alcohol. If the addition of alcohols to soap solutions produces a change from an expanded to a condensed film,

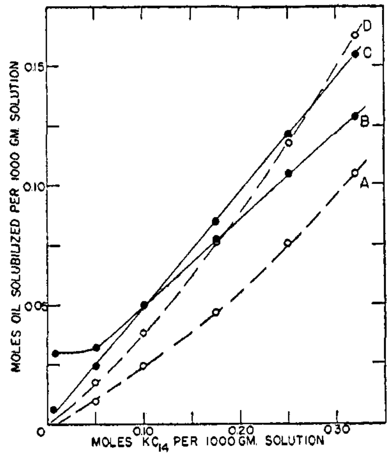


FIG. 21.

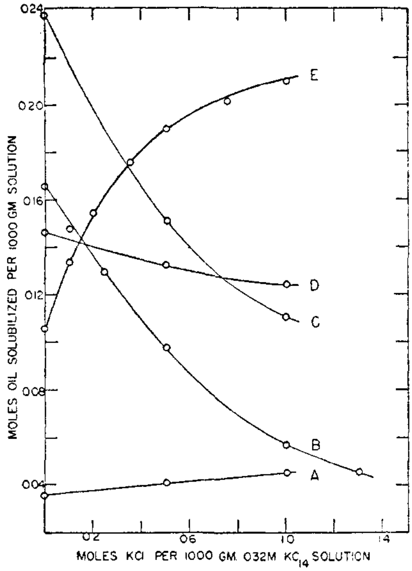


FIG. 22.

FIG. 21. Effect of added potassium chloride upon the solubilization of *n*-heptane and 1-octanol in potassium tetradecanoate solutions at 25°C.: (A) *n*-heptane in KC_{14}, (B) 1-octanol in 0.25 M KCl + KC_{14}, (C) 1-octanol in KC_{14}, (D) *n*-heptane in 0.25 M KCl + KC_{14}.

FIG. 22. Effect of chain length of alcohol on solubilization in 0.32 M KC_{14} solution plus added potassium chloride: (A) 1-dodecanol, (B) 1-octanol, (C) 1-heptanol, (D) 1-decanol, (E) *n*-heptane.

as has been observed in film balance studies (139), then the increases in D_M above C_8 can be explained on the basis of swelling within the micelle. Since the two solubilizers, KC_{14} and NaC_{12} sulfate, are of equal chain length and equal C.M.C. values (110), it is to be expected that the transitions which have been noted in solubilization and in x-ray studies should occur with the same alcohol.

The possible free-energy changes involved in the effect of added salts on the solubilization of solids have been discussed qualitatively (255) in the light of the results found by McBain *et al.* (152, 155, 157). If a definite quantity of crystalline hydrocarbon is dissolved in a soap solution, the free energy decrease will be due to a free energy of solution of liquid (or molecularly dispersed) hydrocarbon (as when the oil is initially a liquid) minus the free energy of lattice formation. The total free energy will be less than in the case of the solution of a supercooled liquid oil. For the S_1 systems, the addition of an inorganic salt should at first increase and then decrease the solubility of a solid. For the S_2 systems (polar groups on amphipaths oriented towards each other in the micelle center) it is expected that there will only be a decrease in the solubility of the solid solubilizate upon the addition of an inorganic salt. These effects only partially account for the phenomena observed by McBain *et al.* (152, 155, 157) and by Kolthoff and Stricks (126) working with somewhat similar systems.

IX. Structure and Organization in Soap Solutions

Solubilization data and x-ray diffraction patterns have been coupled to indicate the presence of different types of associated molecules in soap and detergent solutions. Thus various phenomena such as changes in conductivity, refraction, effect on dye association, freezing point, viscosity, etc. indicate some association at low concentrations, i.e., at the C.M.C. McBain has long postulated the existence of a lamellar, weakly conducting micelle and a small, highly charged, and very highly conducting micelle (144). In contrast to this view Hartley (79) and Lawrence (132) adopted the idea of the spherical micelle originally postulated for soaps by Reychler (203). The strongest argument in favor of the lamellar micelle was the discovery in 1937 by Hess and Gundermann (88) of the production by transparent soap solutions of an x-ray diffraction pattern of a much more definite nature than that produced by normal liquids. This concept has been accepted until very recently by most investigators, particularly by those using x-ray techniques such as Hess, Kiessig, and their collaborators (88, 89, 101), Krishnamurti (127), Dervichian and Lachampt (37), McBain and his coworkers (144), Harkins *et al.* (72), Hughes, Sawyer, and Vinograd (97), and Stauff (228). The strongest proponent for the spherical micelle during this period was Hartley (79, 84). Winsor (254) postulates the existence of a lamellar micelle if the ratio (R) of the solvent attraction between detergent and oil in the solubilized phase to the solvent attraction between detergent and water (or inorganic salt solution) is equal to 1. The detergent in this ratio is taken to be the amphipathic substance solvated by chemical and van der Waals forces by both oil and water. In this system, there would be no tendency for distortion in the lamellae and the plane would have maximum extension, resulting in gelation. The formation of very viscous, gel-like birefringent systems has been observed in many of the mixtures described above (36, 115, 254, 255). If *R* were to increase or decrease markedly, it is proposed that there might be a tendency for the planes of the lamellae to curl and to result in spheroidal lipophilic or spheroidal hydrophilic micelles, respectively. Winsor believes in a probable coexistence of these three forms in equilibrium in solution, the configuration present to the greatest extent varying according to the temperature and the composition of the system. In the isotropic systems the configurational changes, the intermicellar equilibrium, are probably much more mobile, and any particular configuration or micelle would have only a transient individual existence (255a). He appears to go to the opposite extreme to that of the x-ray workers, in that he minimizes the importance of organized structure, although he does picture his intermediate anisotropic gel phase (intermediate between systems containing excesses of water or of oil) as being a lamellar intermediate.

McBain believes in the existence of small colloidal particles (smaller than the spherical micelle), as well as spherical and lamellar micelles, since he says that it is impossible for anyone to explain all the properties exhibited by soap solutions or even their x-ray behavior with only one kind of micelle (144a). He states that, "if there is any way in which ions or ion pairs can come together or associate with any reduction in free energy, as by reducing interfacial energy or by more uninterrupted hydrogen bonding of the water, then that complex must exist, however slight, in soap solutions. Each size, shape, and arrangement will form in proportion to the reduction of free energy that it offers under each condition of concentration, temperature, and the presence of other salts and materials."

This concept of polydispersity in soap solutions does not agree too well with the monodispersity of soap and detergent solutions, as determined by the diffusion and ultracentrifugal studies of Hakala (68) and Vetter (244), nor with the concepts as advanced by Debye (32, 33) from calculations resulting from light-scattering measurements on alkylamine hydrochlorides. Hartley (84a), in a discussion of the multiplicity of micelle form as advanced by Winsor, points out that the transition from molecular dispersion to micellar dispersion in a soap solution does approximate in mathematical form to a phase change. It is noted that simple unaggregated soap molecules convert to micelles at a fairly sharply defined critical concentration (C.M.C.), and it is to be expected that the change from one type of micelle to another would have a similarly critical transition point. This concept finds added support in the sharpness of the range in which the resistance changes very markedly, owing to micelle inversion brought about by small changes in temperature or in the concentration of electrolytes or long-chain alcohols (118, 255a).

Stauff (228) found in curd fibers of NaC_{14} sulfate two rings due to short spacings at 20°C. and one in a clear solution of this system at 70°C. These values were 4.55, 4.00, and 4.60 Å., respectively. These values fused together in solution to 4.60 Å. and were found to be constant with concentration, whereas the bands due to long spacings were found to decrease with increase in concentration.

A major point emphasized by the proponents of the lamellar micelle was the fact that one had to have a certain degree of order or orientation to obtain x-ray patterns of the type found for soap solutions and that spherical micelles could not produce an x-ray pattern. Thus when Mattoon, Stearns, and Harkins (142) first found x-ray evidence for the presence of a two-layer micelle from a more thorough investigation of the x-ray diffraction photographs, the concept of the idealized lamellar micelle was carried over to promote the idea of a cylindrical micelle (70). These cylindrical micelles were conceived of as being small, nonspherical, and of a thickness equal to double the length of the soap molecule, as being capable of becoming thicker in the presence of added hydrocarbon but not with added alcohols, and as increasing in diameter with added electrolyte; it was also believed that the number of soap molecules would increase with added oils. However, at a second critical concentration, above 7 per cent in the case of KC_{14}, there would be restricted motion of these soap cylinders and the long x-ray intermicellar band would appear. Because this model would present a hydrocarbon interface on a large portion of its surface, it has very recently been changed again by Harkins to one of a quasi-oblate spheroid (74), which is taken as a cross between a cylindrical micelle and an oblate spheroid. An oblate spheroid micelle was presented some time previously (108) on the basis of the interpretation of x-ray and solubilization data then available. From changes in C.M.C. with chain length, it was possible to obtain calculated molecular weights of micelles, using the oblate spheroid as a model (110), which were found to be in good agreement with those determined by light scattering by Debye (32). Corrin has briefly discussed the x-ray diffraction evidence and the idea of a spherical micelle and finds the two not incompatible (25). He dismisses the cylindrical micelle, which has been characterized by Bragg law "spacings," and finds that "the observed x-ray diffraction patterns can arise from a system of spherical micelles and that the Bragg law 'spacings' may be meaningless." In an effort to reconcile the points of view of McBain and of Hartley, Stauff has postulated the existence of at least two types of micelles in soap solutions. Dervichian (35) shows that all the properties of these solutions can be accounted for on the basis of a single type of micelle. The results of x-ray analysis are interpreted by assuming that water molecules are sandwiched between layers composed of elementary micelles of soap. These micelles can also form microcrystalline fibers, in which form they constitute the coagulated gel (coagel) and account for the phenomena observed below the Krafft point. The manner in which layers, ribbons, and fibers can be produced by aggregation of the micelles is discussed (35).

A further point which appears to negate the necessity for the existence of the lamellar micelle is the problem of accounting for the volume changes when hydrocarbons are solubilized. If the added hydrocarbon occupies a non-water layer, between the terminal methyl groups (73, 89), the increase in spacing is much more than would be expected from its inclusion in this location. It has been proposed that there is some secondary effect, by an unknown mechanism, on the water layer (73), or that some of the hydrocarbon penetrates into the soap layers (97).

There would appear to be no mechanism which would limit the size of the lamellar micelle. The formation of spherical or oblate spheroid micelles (minor axis = two times the length of the soap molecule) can be shown to have limits in size in various environments. The formation of these micelles is controlled by a balance between the work necessary to bring the charged heads together and that gained when the hydrocarbon tails leave the water and come in contact with each other and is in accordance with the thermodynamic principle that the gain in free energy associated with micelle formation can be calculated from the critical concentration. A definite micelle size has been found by Debye (32) by light scattering, by Hartley and Runnicles (85) by diffusion measurements, by Miller and Andersson (175) by ultracentrifuge and diffusion measurements, and by Hakala (68) and Vetter (244) by density, viscosity, and diffusion experiments. The addition of electrolytes will result in a decrease in repulsive energy of the charged heads of the soap molecules, in a decrease in the effective area occupied per head, the curvature of the micelle will decrease, and the equilibrium micelle will increase in size but again will have a limit as does the salt-free micelle. This is in agreement with the experimental increase in micellar size with added electrolyte (32). The changes associated with the addition of other materials—long-chain alcohols, hydrocarbons, and other soaps—can also be explained on this basis. This reasoning has been applied (*vide supra*) to explain the effect of added electrolyte on the increase in solubilization of hydrocarbons and the decrease in the amount of polar compounds solubilized (115).

In a discussion of the laminar micelle theory, particularly in reference to a paper by Dervichian (36), Bernal (12) indicated that the increase in spacing between alternate ionic planes could account for only a fraction of the total water present if the increase is taken to be due to the entry of water between adjacent planes. To take as an example the data of Stauff (228), it is seen that for a C_{14} sodium sulfate system, the long spacing has increased from its water-free value of 38 Å. to 48 Å. upon the addition of 40 per cent water. The lamellar hypothesis would account for only 40 per cent of the added water; the other 60 per cent of the added water would have to be in contact with the exposed hydrocarbon chains in the lamellar bundles.

If any two-layer micelle structure is accepted, oblate spheroid, quasi-oblate spheroid, sphere, or prolate spheroid, and if an average value of the number of molecules per micelle is taken to be 50–75, then, since there can be no appreciable amount of hydrocarbon surface exposed to the surrounding water medium, it can be seen that the effective area occupied by the charged soap head must be between 60 and 70 Å.^{2} (110). This is in agreement with the value of about 8.5 Å. calculated by Hartley (84) as the minimum mean distance apart, center to center, of the charged ionic heads. This is, of course, much larger than the value of 3 Å. for the radius or 28 Å.^{2} for the area which have been used for the values as calculated from the x-ray data on the basis of the idea of a lamellar micelle (72, 228). The outer diffraction band, 4.6 Å., reported first by Stauff (228) and by others (72, 97), must be due to the somewhat regular orientation of that portion of the hydrocarbon tails of the soap molecules some distance removed (at least 5 Å.) from the charged ionic heads.

Hartley (83) has suggested that a distortion of the spherical micelles present at low soap concentrations might occur as the soap concentration increases, which would bring the shape of his micelle more in line with the one proposed by the author (110). It has been shown (*vide supra*) that there is a decrease in solubilization of 1-heptanol and an increase of *n*-heptane as electrolyte is added to these systems (115). This would correspond to an increase in micellar size due to the addition of an electrolyte (32), resulting in more volume available for hydrocarbon in the micelle center and less for the polar compound in the palisade layer. Further, it is seen in figure 6 that the rate of solubilization increases for hydrocarbons and decreases for polar compounds as the concentration of soap is increased. The presence of ionic charges around one micelle might be expected to have an influence on those of its neighboring micelles and, as the concentration of soap is increased, this effect would be enhanced. Thus the addition of more soap to a soap solution would result in an increase not only in micellar number but also in micellar size and would account for the different rates of solubilization for polar and nonpolar solubilizates.

In a recent contribution (84) it has been suggested that in concentrated solutions the strong repulsive charges between neighboring micelles will tend to orient these micelles in a regular fashion such that each is at a maximum distance from its nearest neighbors. This order might involve a second critical concentration at which the appearance of the intermicellar x-ray bands first are noticed. This type of close-packed assembly leads to the simple relationship

$$l = r(8\pi/3\phi\sqrt{2})^{1/3}$$

where l = distance between centers of neighboring spheres,
r = radius of the spheres, and
ϕ = fraction of the volume occupied by the spheres.

Calculations based on this structure can account for the changes in l with both added water and added hydrocarbon.

A similar approach was used in calculating the changes occurring in micelle diameter with added hydrocarbon (110). If it is assumed that a soap molecule in the micelle occupies an effective volume corresponding to a truncated cone (effective diameter of charged end about 9.5 Å., corresponding to the closest approach of charged ionic heads of soap molecules on the micelle surface; the hydrocarbon tail has an effective diameter, center to center, of about 5.0 Å.), each cone or soap molecule is found to occupy an effective volume of 630 Å.^{3} It is possible to determine that an oblate spheroid, with minor axis equal to two times the length of the soap molecule (about 29 Å. for potassium tetradecanoate) and major axis about 61 Å., which can be calculated from the dimensions of the truncated cone, would have a volume of about 45,000 Å.^{3} This would correspond to a micelle of 78 soap molecules, a value which is in agreement with other values for soaps of this length (32). The hydrocarbon-swollen model would approximate a sphere with radius equivalent to that of the major axis of the spheroid, and the volume available for solubilization would be the internal "free" volume of this expanded micelle. On this basis, there would be approximately 12,000

Å.^{3} per micelle available for a hydrocarbon such as *n*-heptane. At 0.5 *N* KC_{14} there would be 2.7×10^{21} swollen micelles, which are seen to solubilize about 17.0 g. *n*-heptane per 100 g. solution (see figure 6). This corresponds to about 11,000 Å.^{3} of *n*-heptane per swollen micelle as compared with a value of 12,000 Å.^{3} based on the geometry of an oblate spheroid micelle. The agreement for *n*-heptane and similar hydrocarbons is good, but this reasoning does not carry over too well when similar calculations are made for ethylbenzene (volume of ethylbenzene solubilized = 19,000 Å.^{3} per micelle), which appears to swell the micelle to about the same extent as does *n*-heptane. The change in micellar spacing, D_M, with added hydrocarbon, of 0.30 *M* sodium dodecyl sulfate is 11.2 Å. and 11.4 Å. for ethylbenzene and *n*-heptane, respectively (75). The much larger solubilizing power of the alkylamine hydrochlorides as compared with fatty acid soaps or alkyl sulfates of equal chain length can best be explained by accepting the fact that there is much less order in these former micelles and that the effective area per detergent molecule head is smaller in the amine hydrochlorides than in the other soaps. Film balance studies in which the compression of alcohol or amine films is studied as a function of added soaps and amine hydrochlorides will add much to a clearer understanding of these differences.

This model accounts for part of the solubilization data on hydrocarbons which are available but cannot explain the solubilities of the relatively insoluble polycyclic hydrocarbons. As can be seen in table 10, these compounds require micelles containing up to 6000 molecules. Further, the formation of viscous systems even at relatively low concentrations, as upon the addition of salts and/or polar additives (36, 38, 81, 115, 212, 255), would require some explanation. It is possible that these oblate spheroids may have a large major axis as compared to the minor axis in the presence of added salts, for then the effective area of the charged head will decrease and will approach the area occupied by the hydrocarbon tail as a limit.

The problem of the presence in isotropic soap solutions of more than one type of micelle, of more than one size and/or shape, is still not answerable. It would appear that a carry-over from the crystalline state, in which a certain degree of order is found (lamellar like), to liquid solutions is not at all necessary. The presence of a small, two-layered, spherical or oblate spheroid (ionic micelle of McBain) seems to be universally accepted. Winsor (254), in discussing certain hydrotropic phenomena, talks about the energy differences between three types of micelles being small and believes that they can coexist in equilibrium with each other in various systems. In discussing the solubilization of various dyes, Kolthoff and Stricks (126) believe that two different types of micelles with different solubilizing power occur and that with increasing soap concentration more of the micelles with the greater solubilizing power are formed. This may be explained, however, as was done above, as a type of salt effect in which the ions of one micelle influence those of its closest neighbors. McBain and coworkers (151, 154) state that soap solutions contain different proportions of various micelles in different concentrations. They consider that not only are small two-layered micelles and lamellar micelles present but that other forms may be expected to be in equilibrium with these. They use x-ray evidence to indicate the presence of the first two forms and various changes that they have observed in studies on solubilization to explain the other nonspecified forms. However, since it has been indicated above that the presence of various additives has a marked influence on the solubilizing power of a soap or detergent, the solubilization evidence advanced to show the existence of other micellar forms can not be readily accepted. Thus Kolthoff and Stricks (126) have shown anomalous breaks in their plots of milligrams of dye solubilized as a function of detergent concentration when potassium nitrate is the additive as well as in other cases. It is known that there is a definite mode of interaction between polycyclics and even between polycyclics and linear molecules containing substituted groups which give to the molecule at a particular point a certain electronic character which is necessary for bonding (22, 120, 249, 250). Further examples of this type of interaction are the starch–iodine and starch–fatty acid complexes which have been explained by Rundle (207, 208) on the basis of a helical arrangement of starch molecules. The polyvinyl alcohol–iodine complexes are blue only under certain definite conditions, but a variation of the structure of the alcohol in part to polyvinyl borate extends considerably the range of conditions in which this latter compound will show blue colors with iodine (251). Thus the complex solubilization patterns exhibited by a number of commercial preparations of detergents (144, 151) some of which contain one or more cyclic or polar groups and probably some electrolyte or other additive could also be explained on the basis of molecular interaction or on the presence of various additives.

Dervichian and Lachampt (37) have reviewed the various possible structures which might be present in soap solutions over the whole concentration range, particularly with reference to the changes which occur at various transition regions, i.e., from molecular dispersion to micellar solution, through the second transition which is indicated by the intermicellar x-ray spacing, and through the Kraft point to water-free systems. They indicate that, upon gelation, the vapor pressure, conductivity, osmotic coefficient, and optical transparency, in contrast to other systems, are preserved in soap solutions. They suggest that gelation involves association or crystallization of the two-layer systems in two directions, however with one favored over the other. This is in contrast to the growth of the lamellar type of micelle in all directions which was postulated by Thiessen and Spychalski (238).

Optical anisotropy as measured by streaming birefringence has not been applied to the determination of macroörientation, such as the presence of lamellae, in soap solutions. It is possible, of course, that the application of high shearing forces necessary for these measurements would tend to break these hypothetical structures apart, since the forces binding adjacent double layers would have to be extremely weak especially when these layers are separated by a water layer of about 40 Å., as in 10 per cent sodium oleate solutions. However, it is known that, in the presence of nonsolubilized polar additives over narrow concentration ranges, these systems appear double refracting. Upon the addition of high concentrations of salt, just before coagulation, as would be expected, soap solutions show streaming birefringence (148). By means of polarizing microscopy, Thiele (236, 237) has indicated the presence of five forms of associated molecules in aged, but otherwise nonspecified, sodium oleate. These forms are, in order of complexity: (*1*) hydrophilic soap fibril composed of double layers of soap molecules, (*2*) a radial sphere made up of clusters of short fibrils, (*3*) a tactoid-like structure of associated fibrils, (*4*) a long soap fibril found in hydrophilic sols, and (*5*) a form of leaflet or plate which appears in hydrophobic sols.

Ralston (197) believes that the concept of the ionic or spherical micelle structure is open to the criticism that an excessive degree of hydration would be encountered, because of the fact that the chains are separated much further as they approach the surface of the sphere. He adds, however, that the internal structure of the micelle would be antagonistic to a high degree of hydration, since it is composed of hydrocarbon chains. This criticism has also been raised by Meyer and van der Wyk (170) and has been answered adequately by Hartley (82). It is worth noting here that Ralston (197) and McBain (144) believe that there are small ionic micelles present below the C.M.C. and that the changes observed at this concentration must be attributable to a solubility effect and not to a spontaneous formation of ionic micelles. Hartley (79) and Tartar (234, 256), on the basis of extensive conductivity studies of the alkanesulfonates, do not accept this premise for, in their opinion, there is no or very little association of the type which results in micelle formation below the C.M.C.

X. Applications of Solubilization

The application of solubilization to problems of detergency has been reviewed (2, 21, 30, 63, 144, 224, 239) and nothing can be gained by repetition. The phenomenon of solubilization and the role of soap and detergents in textile processing have been reviewed by Creely (29) and the application of this to various factors in the textile field such as wool scouring, efficiency of grease recovery, and dry-cleaning soaps has been described. However, various biological aspects of emulsification and of solubilization are now becoming more fully understood and a number of applications of these phenomena should be mentioned. It is not planned to be all-inclusive here with regards to this subject, but a number of problems in which solubilization plays a role will be discussed. Those aspects of emulsion polymerization which involve solubilization also will be reviewed briefly. These few applications will serve to indicate the importance of the role of solubilization as applied to biochemical as well as to chemical and industrial problems.

A. BIOLOGICAL ASPECTS OF SOLUBILIZATION

The importance of solubilization as applied to biochemical problems cannot be omitted in any discussion of this phenomenon. The action of surface-active agents in biology and medicine has recently been reviewed by Valko (241), and the nature of the bactericidal action of surface-active agents has been reviewed by Hotchkiss (95). Interaction of proteins and detergents was the subject of a recent article by Putnam (193), and Glassman has discussed the bactericidal aspects of various surface-active agents (62). The utilization in parasitology of surface-active agents, detergents, and emulsifiers has been the subject of a survey by Dufrenoy and Langeron (44). However, by far the major portions of these reviews cover the interactions of surface-active agents, as electrolytes rather than as micelles, with corresponding media. Certain aspects of the role of solubilization in biological systems have been discussed (93, 226) and only more recent aspects of this subject will be mentioned here.

Even in very small concentrations, the high surface activity of bile salts is indicated by their emulsifying and solubilizing power, which is their most obvious function in digestion. The speed of diffusion of various substances through natural and artificial membranes by bile salts is thus of great importance in resorptive processes. The diffusion of Victoria Blue and Congo Red through Chamberlain filters and collodion ultrafilters (24) and of hemoglobin through collodion (17) is accelerated by bile salts, and bilirubin and eosinate, which are retained by collodion membranes, can pass through when solubilized by bile salts (1, 20).

Merrill (168) found that various solubilizers were effective in bringing insoluble substances into solution even though a membrane permeable only to ions separated them. Vinograd (245) showed that solubilized dye does not pass into water, although the detergent does, and that if the water is replaced by a detergent solution the dye will also come through the membrane. The rate of diffusion of detergent through a membrane is not affected by the presence of solubilized dye. However, when a dye in 1 per cent Aerosol OT is allowed to diffuse into 1 per cent Aerosol OT, its rate is about one-sixth that of the detergent into water. These results indicate that detergents can carry insoluble substances through membranes even though these membranes act as molecular sieves. Mukherjee and Banerjee indicate that the transport and sorption of quinine involves its solubilization by bile salts (176). In the feeding of dehydrocholic acid with other fats to normal persons, icterus patients, or those with cholecystitis or tuberculosis, a decrease is noted in the total fat elimination over that without this added bile acid. This is caused by an increase in the absorption of calcium ions in the intestine in the presence of the bile acid, owing to the formation of bile salt–fat solutions (39). Jones *et al.* (99) demonstrated clinically that fat absorption can be aided by the addition of solubilizing agents, and Kellner (100) showed that when a solubilizing agent is administered to rabbits with cholesterol, blood cholesterol levels become two to three times as high as those obtained without the emulsifier. The above two reports merely confirm past observations that lipids and other water-insoluble material are more readily absorbed when solubilizers and emulsifiers are present. Quagliariello and Foscolo (196) have shown that the rate of diffusion through a cellophane membrane of oleic acid dispersed in sodium glycocholate is not increased by the addition of lecithin, cholesterol, or bile to the mixture. Frazer (56) believes that the lipolytic hypothesis of fat absorption, in its present form, fails to explain an increasing number of observations in this field, and many of the assumptions on which it is based are in need of reconsideration. The partition theory has been advanced as an alternate working hypothesis upon which further investigation of the many outstanding problems of fat absorption might be based.

A difference between physical adsorption on a surface and solubilization or complex formation was recently indicated by Beck and Meier (10), who found that the invert soap, phenoxyethyldimethyldodecylammonium bromide, reacts with the lipoids of erythrocytes while it reacts by adsorption only with yeast cells. This was shown by the parallel action of reaction equilibrium curves of the invert soap and lecithin and the soap and erythrocytes, while there were found two similar adsorption curves for the invert soap on the yeast cells and on Norit.

The germicidal action of various soaps and detergents is the subject of a number of recent reviews (43, 103, 104), particularly since Domagk (40) in 1935 pointed out the high potency of the cationic detergents. Both soaps and various synthetic detergents have been used in mixtures with nonsurface-active germicides such as phenols, chlorine derivatives, heavy-metal ions, etc. Gershenfeld and coworkers (59, 60, 61) have discussed the effect of various solubilizers on the activity of these germicides. It has recently been established that soap increases rather than hinders the germicidal action of phenols, and a large number of anionic and cationic detergents have been used as solubilizers for various phenols (217). The fatty acid sulfates (90) and sulfonated oils (60) have been used with phenolic germicides, and various cationics, which are germicidal themselves, have been used as solubilizers with various phenols (94). According to Ordal and Deromedi (181) two synthetic detergents, dodecylsulfonate and the dioctyl ester of sodium sulfosuccinate, enhance the germicidal action of some phenolic compounds. Berry and Bean (13) report in a preliminary note that the bactericidal activity of a phenol soluble in potassium tetradecanoate commences at the C.M.C. and is a function of the concentration of phenol in the micelle. The maximum bactericidal activity, as measured by the death time of *B. coli,* is attained when the micelles are fully saturated with phenol. The influence of the solvent properties of the paraffin-chain salt micelle on the bactericidal effect of dissolved phenols has been the subject of a recent extensive review (3). With salts of saturated acids of eight to fourteen carbon atoms, it has been shown that the bactericidal power against *Ebethella typhosa* rises with increasing concentrations of *p*-chloro-*m*-cresol (205).

The precipitation of a series of carbonates and phosphates, sulfides, calcium stearate, and a number of important biological constituents has been prevented by the addition of nucleic acids (180) and of sodium adenosine triphosphate (179) to these systems. Similar properties have been ascribed to the alkali salts of triphosphate and other polyphosphates (55). All these substances which act like solubilizing or hydrotropic agents are of the utmost biochemical importance, and they are subject to degradation and transformation by widely distributed and specific enzymes. The appearance, disappearance, and reappearance of these compounds in the light of their remarkable solubilizing properties can probably best be explained in the light of the mobilization, transportation, and sedimentation of insoluble substances in tissues and in the soil.

Stotz (232) has followed leads recommended by studies of natural digestive processes and, by the simultaneous addition of sodium cholate and various types of enzymes, has found it possible to separate various components of the heart muscle oxidase system. Bieri and Schultze (14) have taken advantage of the solubilizing power of the commercial detergent, Tween, to disperse molecularly known amounts of the insoluble β-carotene for intramuscular injections into vitamin A-deficient rats. Halpern and Biely (69) report that solubilized vitamin A has a greater biological value than its vegetable oil solution. This observation was confirmed by Popper and Volk (190).

Further extension of the solubilizing or dispersing action of detergents has been applied by Ekwall and Setälä (47) to various polycyclic carcinogenic polycyclics. Concentrations of solubilizates were measured qualitatively by the fluorescence of colloid solutions of these polycyclics. These polycyclics are readily adsorbed when animals are painted with these solutions, and indications of skin tumors are evident. Further experiments along several directions are now in progress, and it will be of interest to see whether carcinogens dispersed in this manner and those dissolved in other solvents behave similarly in subcutaneous and intravenous injections. Competition for available carcinogen (*p*-dimethylaminoazobenzene) has been noted when, in addition to this dye, lauric acid or fatty acids of hydrogenated coconut oil are added to the diet (121). No liver tumors were found in rats fed this diet, while 20 per cent of the rats on a fat-free diet and 80, 33–53, and 87 per cent, respectively, of the rats fed on diets containing corn oil, olive oil, and oleic acids showed the development of hepatomas.

The addition of paraffin-chain salts to proteins, enzymes, viruses, bacteria, etc. cannot be considered solubilization as discussed above but, in a larger definition of this term, may fall into this classification. Many water-soluble proteins react with the soap molecules, usually by attraction of oppositely charged ions. This is supported, in part, by the finding that any reaction of nonionic detergents with proteins does not involve this type of electrostatic binding (241), for the interaction in this case, probably of a van der Waals type, is far less effective than in colloidal electrolyte–protein systems. It is not expected that individual micelles would react as a unit with a single protein molecule, for this would mean that about 65–75 soap molecules (number composing a micelle of a C_{12} soap) would combine with any protein molecule.

Putnam and Neurath (194) have indicated that reaction between protein and detergent will occur at pH values on both sides of the isoelectric point. The reaction of serum albumin with sodium dodecyl sulfate will occur at a pH below the isoelectric point (where protein and detergent are oppositely charged) with the appearance of a precipitate over the mole ratio range of protein to soap of about 0.01 to 0.02. This would indicate an increase in the hydrophobic nature of this complex due to the presence of the hydrocarbon tails of the detergent at the protein interface and would account for the turbidity through flocculation. It appears doubtful, as Ralston has proposed, that association between protein and detergent possibly involves the binding of small ionic micelles (198), for the number of dodecyl sulfate ions bound per serum albumin molecule is initially only 52 and the second complex has about 100 ions per protein molecule (195). Similarly, egg albumin will react with 15 and 28 molecules of detergent per protein molecule at the isoelectric point (18). If the initial soap molecules bind with the oppositely charged groups, and if the initial binding sites can be assumed to be symmetrically distributed on the surface of the protein molecule (taken as a prolate spheroid), then the minimum area per bound detergent molecule would be about 325 $Å.^2$ of protein surface. This would appear to invalidate the concept of interaction with associated detergent molecules, for no association can be considered present at such distances of separation. Addition of further detergent results in a loss of opacity through the formation of another complex (194). This, an example of solubilization in these systems, is probably due to the binding of the hydrocarbon tail of the added detergent with the hydrophobic portion of the soap molecule of the original complex, replacing each detergent hydrophobic tail of the original complex with a hydrophilic group.

Addition of detergent will result in a number of changes when added to protein systems such as denaturation (5), stabilization as by inhibition of coagulation (5), complex formation and precipitation, inactivation of enzymatic properties, etc., all of which have been discussed in a recent review (193). Foster was able to make physicochemical studies of the water-insoluble protein, zein, in aqueous detergent solutions (54). These complexes of zein and detergent, in which the detergent must be considered to be bound by van der Waals forces through its hydrophobic tails with corresponding hydrophobic groups on the protein surface, are similar in properties to the soluble complex mentioned above. The original protein, zein, the material being solubilized, must correspond to the insoluble protein–detergent complex as well as to such other compounds as the insoluble dyes.

The influence of solubilizing power in addition to known alkalinity effects on skin irritation can be inferred from the data of Emery and Edwards (48), in which a maximum effect is noted with NaC_{12}. Sodium soaps of shorter fatty acids do not form micelles at the concentrations used and the longer chain soaps form white suspensions (C_{14}) or white gels (C_{16}, C_{18}). The addition of salts enhances the irritation effect (49). Soap mixtures, in general, showed the expected irritation effects (167). A nonirritating soap is produced by removing from soap-making oils, such as coconut and palm, the low-molecular-weight fatty acids which produce the irritation (42).

B. EMULSION POLYMERIZATION

A tremendous impetus has been given to the problem of solubilization with the advent of the use of surface-active agents in emulsion polymerizations. Large amounts of fatty acid and resin soaps are now used in this application. The present consensus of opinion is that the monomer is solubilized in the soap micelles and that at least a part of the polymerization actually takes place in the solubilized state, i.e., that the initial loci of polymerization are the soap micelles (58, 87, 92, 257, 258). The rate of polymerization is directly dependent on the concentration of soap, and the number of polymer particles formed, for any one soap, is a linear function of the number of micelles present in the initial system (87). Marvel *et al.* (140) have noted that the presence of impurities in the soap affects the polymerization. In the standard GR-S recipe, the use of standard soap results in an 80 per cent conversion at 50°C. in 4 hr., while the use of potassium oleate and sodium alkanesulfonates results in a 67 per cent conversion and a 6 per cent yield, respectively, under the same experimental conditions. Dunbrook (45) has recently reviewed various factors involved in emulsion polymerization and reports that in the GR-S recipe, fatty acid soaps less than eight carbons in length are not suitable for polymerization and that the rate of polymerization increases with concentration and with the chain length of the soap. Soaps above eighteen carbons in length are too insoluble in water to be effective. The addition of lecithin up to 0.4 per cent and ethanolamine up to 1 per cent of soap does not retard polymerization. Wilson and Pfau (252) report that linoleic and linolenic acid soaps retard the polymerization rate of GR-S, whereas purified oleate, elaidate, stearate, and palmitate give about the same yields. Alkali-isomerized linolenic acid shows no retarding action.

Kolthoff and Harris (122) have shown that changes in molecular weight distribution are possible through control of mercaptan availability by increment addition of mercaptan or by changes in mercaptan solubility by structural modification. The types of solubilization discussed above can be applied to explain the formation and properties of certain polymers prepared with identical formulae except that the modifier, often a long-chain mercaptan, in one case is added initially to the soap–water–persulfate mixture before the addition of monomers, and in the second polymerization is added dissolved in the monomers. Depending on the relative reactivity of the monomers used, quite different molecular weight distributions should be possible.

These results can only be explained on the basis of mercaptan availability, for in one case the mercaptan is a part of a mixed micelle, with the —SH group oriented toward the water–detergent interface, and in the other it is partially solubilized with the monomer, occupying the center portion of the micelle around the hydrocarbon tails of the soap molecules. If the soap micelle is the initial locus of emulsion polymerization, as has been indicated, then the availability of mercaptan, in the first case as part of a mixed soap–mercaptan micelle, and in the second, readily available in the solubilized monomer, will markedly affect the molecular weight distribution of the initially polymerized product.

The pH, which is known to affect the solubilizing power of various emulsifiers, is important in emulsion polymerization. Cationics are most effective in acid media, whereas a slightly alkaline system is found to be most suitable for anionic emulsifiers. Nonionic agents of the polyoxyethylene ether type are claimed to be more effective if the pH is kept below 7 (98).

X-ray diffraction studies by Hughes *et al.* (97) on KC_{12} solutions were used to interpret some of the mechanisms occurring during polymerization of styrene in soap solutions. In this process, the addition of styrene results in an increase in the long spacing, D_I; upon polymerization, this spacing decreases almost to its original value. Further addition of styrene results in another increase in D_I, which decreases again upon polymerization. These results, coupled with the finding that the number of polymer particles formed is a linear function of the number of micelles present (87), lend support to the hypothesis that the soap micelles are the most important initial loci of polymerization.

XI. SUMMARY

Solubilization, defined as the spontaneous passage of solute molecules of a substance insoluble in water into a dilute aqueous solution of a soap or detergent in which a thermodynamically stable solution is formed, is distinguished from hydrotropy, blending, and emulsification. However, it must be emphasized that solubilization and hydrotropy and related phenomena are essentially similar solubility processes and that this concept of similarities can much better explain the existing data than the use of minor differences which may be found in these various phenomena. There are various methods for determining the limit of solubilization which are based on structural and optical properties of the compounds being solubilized (solubilizate). Limits may be determined by the formation of emulsion droplets (turbidity) when the solubilizates are liquids and by a spectroscopic method when the solubilizate contains an absorbing chromophore. Other properties, such as change in vapor pressure, change in micellar spacing as determined from x-ray spectra, etc., may also be used.

Three types of solubilization are illustrated and the mechanism involved in each class is discussed in the light of the present concepts of micellar size and shape. These are (*1*) adsorption by the micelle usually on or near the soap–water interface; (*2*) incorporation into the hydrocarbon center of the micelle; and (*3*) penetration into the palisade layer of the micelle. There is only fragmentary evidence to support type 1, which may involve solubilizates which are structurally low-molecular-weight polar–nonpolar compounds such as the phenols. Type 2 involves hydrocarbon solubilization, in which the solute molecules are not oriented with respect to the soap–water interface and possibly not oriented in the hydrocarbon-like micelle center. There is evidence that both micellar, D_M, and intermicellar, D_I, x-ray bands increase with added hydrocarbon up to the solubility limit. The third type involves the solubilization of polar–nonpolar compounds in which the solubilizate molecules are oriented fairly perpendicularly to the water interface with the hydrocarbon portion of the molecule penetrating between the hydrocarbon chains of the soap molecules and lying fairly parallel to them. There is no increase, and in certain cases there is a decrease, in D_M, and the high adhesion energy between long-chain alcohol and water as compared with hydrocarbon and water further supports the concept of orientation in these systems.

Solubilization depends on the nature of the solvent, the chain length and

charge of the solubilizer, the structure of the solubilizate, the temperature, and the presence of various additives. Increase in temperature normally results in an increase in the solubilization of hydrocarbons and an increase in the solubilization of water but there are, however, many exceptions. Lengthening the chain of a solubilizer of one particular homologous series increases solubilization. The cationic detergents, such as dodecylamine hydrochloride, are more powerful solubilizers for hydrocarbons than the corresponding anionics of equal chain length. Polar compounds are solubilized more in electrolyte-free systems than are nonpolar hydrocarbons of similar structure. Increase in the molar volume of the solubilizate results in a decrease in solubilization. The addition of electrolytes will enhance the solubilization of hydrocarbons and will decrease the amount of polar compounds incorporated in the micelles. The addition of long-chain polar compounds will markedly increase the solubilization of hydrocarbons above that of a corresponding amount of added colloidal electrolyte. Hydrocarbon addition will swell micelles and will allow for more penetration of polar compounds into the palisade layers of the micelle. It is to be noted that opposite effects are observed in the solubilization of apolar (hydrocarbons) and highly polar (water or inorganic salt solutions) compounds when various changes (additives, temperature, etc. but not concentration) are made in the solubilizing systems.

The various factors involved in solubilization can best be explained on the basis of an oblate spheroid or spherical micelle. Structure and organization in soap and detergent systems are discussed from the solubilization data presented in this review. The importance of solubilization in biological and chemical processes is reviewed.

XII. References

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