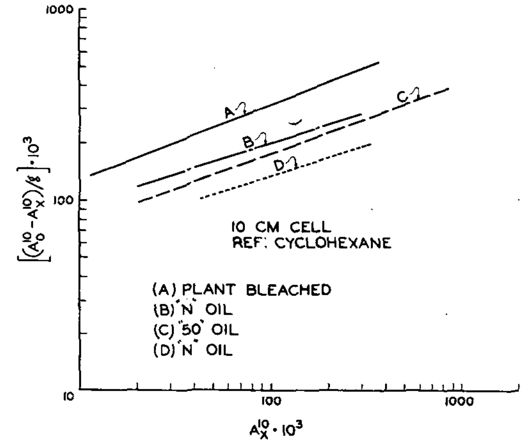

FIG. 4. Adsorption isotherms for the removal of green pigment from two different batches of "N" oil and from "50" oils by regular bleaching.

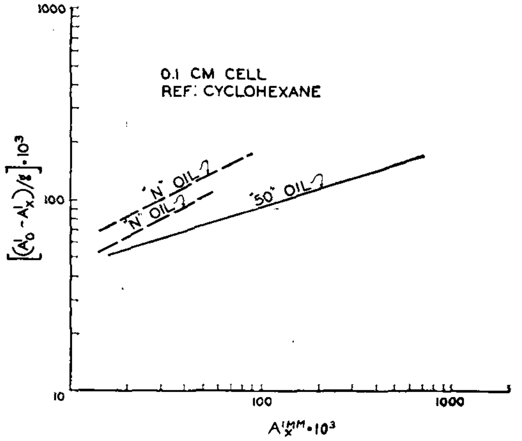

FIG. 5. Adsorption isotherms for the removal of yellow pigment from two different batches of "N" oil and from "50" oils by regular bleaching.

indicates the difficulty in maintaining optimum control in the alkali refining of soybean oils.

Plant Bleached Oils. The median absorbances for 14 "50" oils and 12 plant-bleached "50" oils (using Special Filtrol brand activated clay) were used to calculate one point, through which a line was drawn parallel to the isotherm for laboratory bleached "50" oil as shown in Figure 4. Using this estimated isotherm, a bleaching chart was prepared as shown in Figure 6. It follows from the Freundlich equation that the slopes of these lines should vary inversely as the equilibrium color (A_x), and this is seen to be the case. Knowing the absorbance (10-cm. cell) of the green pigment in a "50" oil entering a bleaching vessel (for example, $A_o = 2800$) and supposing that a bleached oil of 100 units ($=A_x$) is required, it follows from the chart that a 0.85% bleach, using activated clay (F), would be necessary.

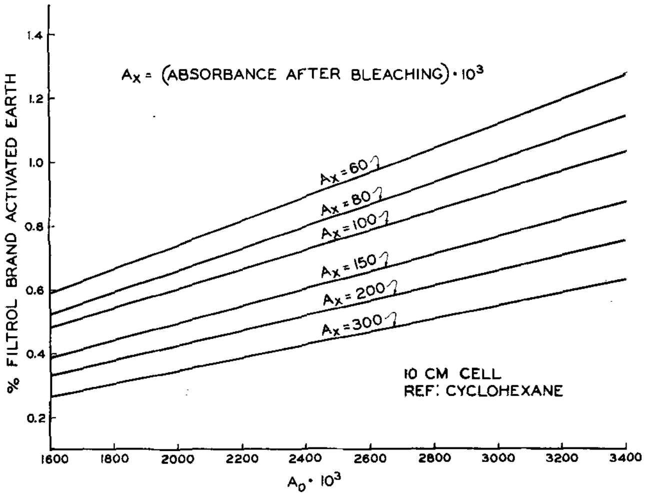

FIG. 6. Bleaching chart for the removal of green pigment from "50" oil. Plant bleaching using Special Filtrol brand activated clay.

Summary

Bleaching results are evaluated spectrophotometrically by measuring the change in the absorbances at 455 and 670 (or 665) millimicrons, respectively. Three bleaching clays (one was activated) and two activated carbons were used for decolorizing soybean oils made break-free by either alkali refining or acetic anhydride water degumming. Bleaching times varied from 10 to 40 min. with 30 min. being used in the evaluations. Although bleaching at a temperature of 265°F. removed more color than bleaching at 125° or 220°F., the latter temperature was used in this study. Most of the bleaching was done under vacuum although using a nitrogen pressure of 50 p.s.i.g. removed more color. Results are expressed by Freundlich isotherms, and a bleaching chart for the control of plant bleaching is given. It is shown that in the bleaching of soybean oil primary consideration should be given to the removal of green pigment.

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[Received July 10, 1957]

Solubilization—A Micellar Phenomenon

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AN UNUSUAL PHENOMENON associated with dilute surfactant solutions is their ability, in a micellar state, actually to solubilize water-insoluble substances. McBain (48) defined solubilization as the spontaneous passage of molecules of a substance insoluble in water into a dilute aqueous solution of a surfactant to form a thermodynamically stable solution.

Micelles, as regular aggregations of molecules, appear in aqueous and nonaqueous media. The present

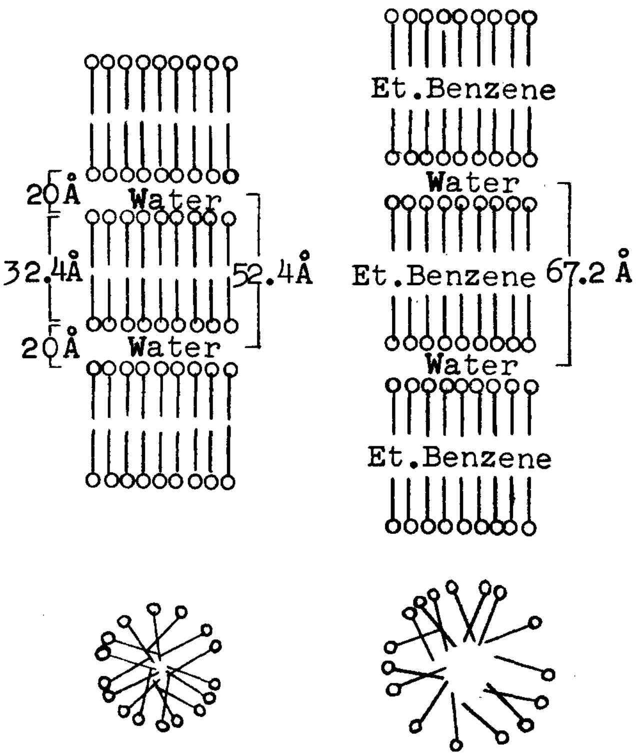

FIG. 1. McBain lamellar micelle. Hartley spherical micelle.

discussion is concerned only with solubilization in systems in which water is the continuous medium. These systems encompass the solubilization of gaseous, liquid, of solid substances, with or without hydrophilic groups, partially soluble or insoluble in water. The solubilized systems are notable for their stability as they can be passed unaltered through a semipermeable membrane. This stability is accounted for by a decrease in free energy for the system.

Systems of water, surfactant, and solubilizate may take several forms. Even though exception (24) has been taken to the term "solubilization" on the basis that it implies a new process and suggests that the resulting systems are not in equilibrium, the term is now well established. "Hydrotropy" (62) is the term used to describe the increase in solubility of a substance in water because of the presence of large amounts of additives, as contrasted with relatively small amounts of surfactant in the solubilization process. "Blending" (65, 66) is a broad term; the process involves the mutual solubility of two normally immiscible solvents by the addition of a colloidal electrolyte. These systems are best described by using diagrams. "Emulsification" occurs beyond the point of saturation of the micelle by added solute; droplets of the additive become apparent.

Lawrence (44) suggested that American workers, by using tubidity as an end-point indication of solubilization, had not carried the solute addition sufficiently far because the opacity actually is a liquid crystal phase and not initial emulsion formation. Winsor (76), in an extensive investigation, indicated the possibility of multiphase formation, only one of which appeared to be true solubilization. He and Klevens (30) suggested that two quite different limiting cases of solubilization occur: a) with n-heptane where, when the limit has been reached, excess hydrocarbon separates; and b) with 1-heptanol in which, when the limit of solubilization is reached, two phases separate.

The purposes of this paper are to review the mechanism of solubilization, to show the mutual effect of structure of both surfactant and solubilizate, and to relate this phenomenon to practical detergency. The effect upon these systems of detergent builder materials will be discussed.

Micellar Structure in Solubilization

Solubilization in Micelle Center. The familiar schematic diagrams of the McBain (48) lamellar and Hartley (23) spherical micelle are shown (Figure 1), as supplemented by Klevens (31), to suggest the effect of solubilized hydrocarbon. Calculation from X-ray measurements (17, 48) suggests that solubilization occurs in the lamellar micelles, but Hartley (23) points out that these same X-ray data can be interpreted in the manner in which two-layer micelles pack (spherical or oblate spheroid).

Micelle Adsorption. Corrin, Klevens, and Harkins (5), in discussing adsorbed dye, indicated that the insoluble dye complex first formed goes back into solution as the cmc is passed. The charged, bound dye molecule of charge opposite to the surfactant was expected to be adsorbed on the surfactant micelle, attracted more to the hydrophobic region of the micelle palisade layer and less toward the polar region of water surrounding the micelle. The penetration could be for only a very short distance because the presence of the dye molecules decreased the cmc not more than a few per cent. The same conclusion was reached with short-chain alcohol additives.

Harkins and Oppenheimer (20) objected to solubilization as fitting the circumstance when the X-ray data show either no change in thickness or an actual decrease when polar-nonpolar molecules penetrate the micelle. They suggested the term "film penetration" to fit this occurrence and point out that substances which enter the micelle by penetration lower the cmc while those that enter by solubilization have little effect on cmc.

Another example of penetration (49) is that of polar dyes, such as Orange OT and Yellow AB, in potassium laurate solutions. These are said to show characteristic penetration by the dye molecule into the palisade layer of the soap micelles rather than solubilization into their hydrocarbon center. In the following discussion however no differentiation between these terms will be made.

Measurement

Opacity. The most common method for estimating the solubilization end-point used by American workers has been the evidence of opacity when an excess of solubilizate has been added. It is assumed that these droplets signify the beginning of emulsification, but Lawrence (44), by polarizing microscope methods, believes these "droplets" to be spherulites of a liquid crystalline phase and a continuation of the solubilization process.

Plots of measurement of optical density against concentration give a curve from which two lines may be drawn to fit the slope below and above the point of maximum solubilization, and their intersection is taken as the point of maximum solubilization. Since the greatest proportion of the recorded work has been based upon this procedure, considerable credence must be placed in it until a consistently more satisfactory operation can be developed.

Spectral Dye. McBain and Merrill (52, 58) demonstrated solubilization by the formation of thermodynamically stable colloidal particles of surfactant and insoluble dyes, such as Yellow AB and Orange OT. Their work proved the stable nature of the system by the passage of these dye-surfactant aggregates through semipermeable membranes, thus distinguishing them from emulsions and from suspensions.

Equilibrium is said to be attained quickly by operating at elevated temperatures (43), but on occasion this can give false results.

X-Ray Diffraction. Kiessig and Philipoff (26) by X-ray diffraction data showed that benzene was entrapped in the micelles; these become measurably larger, and the sidewise distance remains unchanged. Others (17), using other hydrocarbons, have shown measurable changes in the micelle structure depending upon the molecular shape of the solubilizate. Harkins and Mittleman (19) demonstrated changes in soap micelle size, increasing with hydrocarbon addition and decreasing with alcohol (C_{10} or less in molecule) addition.

Temperature Effect

Klevens (31) reviewed temperature effect and pointed out that any effect which will increase micelle formation should increase solubilization but that reported data give conflicting evidence. The spectral dye method is specific in showing decrease of cmc with increasing temperature. Considerable variation in results occurs with a homologous soap series (39) while data for nonionics are not uniform (46).

Surfactant Structure

Just as micelles presumably begin forming before the critical concentration is reached, so solubilization must also start. Ekwall (6, 8) has demonstrated that solubilization occurs at surfactant concentrations considerably below the cmc. The lowest point at which it occurs is called the limiting association concentration (L.A.C.). For a given surfactant the limiting association concentration does not vary with the chain length of the added alcohol.

A peculiarity of the dye solubilization method should be noted: Yellow AB is solubilized less by soaps than by other surfactants (53). Others (37) found differences for given solubilizers with solubilizates, such as dimethylaminoazobenzene, Orange OT, and trans-azobenzene.

Fatty Acid Soaps. Klevens (31), using data from several sources, drew the following generalizations for soaps.

a) The most marked changes with chain length are found for hydrocarbon solubilizates.

b) An inversion in solubilization occurs with long chain alcohols, but a general increase in alcohol solubility is found for increase in chain length of soap (21), which is almost linear between C_{12} and C_{18}.

c) A double bond appears to reduce degree of solubilization.

d) Cation type, *e.g.*, Na^+ or K^+, has only small effect on solubilization.

e) Free fatty acids combined with soaps seem to increase solubilization.

f) Increase in concentration of soap generally increases degree of solubilization.

g) Mixtures of soaps of differing chain lengths are beneficial. Lower chain lengths solubilize relatively insoluble higher chain lengths. While the combination may be a slightly less effective solubilizer than a "pure" long chain soap, there is improvement, often marked, over strictly lower chain length soaps (31).

Cationic Type Surfactants. Cationic surfactants are convenient to work with since they lend themselves to synthesis of well-defined homologous series.

a) The cationic type of surfactants appear to have greater solubilizing power than soaps (38, 54). Indications are that for the same alkyl chain length, cationic compounds are of larger volume hence accommodate larger quantities of solubilizate (18).

b) Solvent power varies with the anion:

$$Br^- > Cl^- > SO_4^{--} > OCOCH_3^- \quad (22)$$

Sulfates and Sulfonates. Chain length data (31, 35, 52, 58) show that increasing carbon chain length of soaps, alkyl sulfates and sulfonates, alkylbenzenesulfonates, and cationics increase solubilization of a number of solubilizates. For compounds with equal equivalent carbon chain lengths, the degree of solubilization is the same. An exception is the cationic type, which seems to provide an increased degree of solubilization over anionics (31, 43, 52, 58).

Polar Group Position and Branching. Some very interesting relationships are found for tetradecane sodium sulfates, where the $-SO_4$ position is moved progressively from the terminal position [the solubilizate was a mixture of cyclohexane dissolved in cyclohexanol (76)].

a) Solubilization increases as the position of the sulfate is moved from the 1- to the 7-position (even though the cmc increases in the same order, contrary to n-alkyl soaps and surfactants).

b) Branched chain compounds are better solubilizers than equivalent chain-length normal compounds.

Mixtures of Sulfates. It is seldom that commercial products are chemically pure, generally representing mixtures of a homologous series. The extent of the series content depends upon purification.

a) Solubilizing power and cmc are inverse functions, but branched chain sulfates give exceptions.

If the impurity to be removed is a surfactant of longer chain length, then cmc will increase with its removal and solubilization will decrease. If the impurity is of lower chain length, the reverse is true.

b) Mixtures of two surfactants of the same cmc but of different structure produce no observable change in solubilization (36).

Complexes. Ekwall (7) suggested that the solubilities of 1-decanol and other long-chain alcohols cannot be compared to those of hydrocarbons because with the former, when maximum solubilization had been passed, a substance composed of the alcohol, surfactant, and water separated. Hydrocarbons separated as pure materials.

Acid soaps have long been known (55); the potassium acid dioleate is a good example. More recently (70) stearic acid and sodium stearate were shown to exist in several isolatable states. The formulas corresponding to those isolated were 1 NaSt:1 HSt, 2 NaSt:3 HSt, and 1 NaSt:2 HSt.

Wilson (75) found two intermolecular complexes with sodium lauryl sulfate and lauryl alcohol which had molar ratios of the two components of 1:1 and 2:1, and crystalline precipitates of these were isolated. These data suggest the possibility that other surfactants might also form complexes with their unreacted hydrophobe base materials.

Nonionics. Comparatively speaking, very little work has been done with nonionic surfactants, undoubtedly because they are the least well known but also because purification of them to a single compound is extremely difficult (47). Nonionic products are comprised of compounds with a rather wide distribution of alkylene oxide chain lengths.

The fact that nonionics exhibit cloud-point can interfere with the usual solubilization procedures. Various fatty acid esters of polyoxyethylene sorbitan (27) as solubilizers for benzene and octanol exhibited two limits of solubilization by turbidity determination. The first maximum was associated with micelle formation and the second to a polar-nonpolar solubility, possibly explainable (74) as separation of a surfactant-rich phase. Other measurements have been made (46, 50, 68), but insufficient data exist to form any general conclusions concerning nonionics as solubilizers.

Solubilizates

Solubilizates in these systems can be gaseous, liquid, or solid, and no attempt will be made to recount all the numerous references on this subject. Only a few representative examples of liquid and solid types will be discussed.

Liquids. Klevens (31) has excellently summarized results with the variety of solubilizates, including liquids. Chain length, cyclization, unsaturation, and branching all affect solubilization, and some generalizations can be deduced from their action with a single solubilizer, from a homologous series, or from various types.

Hydrocarbon. Solubilization is affected as follows.

a) Decrease in solubility occurs with increasing chain length of normal hydrocarbons, or of an alkyl group on the benzene nucleus.

b) Increased solubility occurs with cyclization.

c) Increased solubility is found for unsaturated compounds over their saturated equivalents.

d) The same solubility occurs with branched saturated hydrocarbons and their normal isomers.

e) Polycyclic hydrocarbons do not necessarily follow observations a through d.

1. Polycyclics are less soluble than normal paraffins of the same molecular weight.
2. Ring closure causes marked decrease in solubilization, and relationships true for simple hydrocarbons do not hold for complex polyacenes.

f) Each molecule of polycyclic (dibenzanthracene) requires a critical volume of hydrocarbon atmosphere within the micelle for solubilization.

g) Volume of hydrocarbon solubilized (by 0.1 N potassium dodecanoate) is a linear function of molar volume (molecular weight/density). However, as solubility of hydrocarbon decreases, linearity no longer holds. In this case, linear plots are obtained with the log of solubility as a function of molar volume. For polycyclics, two linear plots are necessary, one for linear polycyclics and another for nonlinear polycyclics.

h) The apparent density of surfactant solutions (potassium dodecanoate) containing several hydrocarbons shows a linear change with increase in concentration of added hydrocarbon (17), but further verification is indicated for generalization.

i) The volume of oil solubilized at one soap concentration is said to decrease approximately linearly with molar volume (34).

Polar Compounds. As might be expected, the presence of a polar group modifies the solubilization characteristics of a system in change with the orientation of the compound in the micelle. McBain (50, 51) demonstrated that dimethylphthalate, poorly soluble in water or dodecane, has a solubility 20 times that in hydrocarbon when solubilized in a decinormal potassium laurate solution, suggesting that the polar groups are mutually attracted in the micelle structure.

Harkins and Oppenheimer (20) demonstrated the effect of polar grouping upon solubilization for derivatives of dodecane in 0.3 molar sodium lauryl sulfate solution, showing that the more hydrophilic the solubilizate, the greater the degree of solubilization, so much so that these authors suggested that beyond solubilization there exists a further phenomenon they called "film penetration" in explanation of the manner in which these compounds enter the micelle.

The work of McBain and Richards (54) shows that:

a) increase in molecular weight within any homologous series of solubilizates tested tends to reduce solubilization;

b) polar compounds are much more extensively solubilized than are the hydrocarbons; there is a negative effect for nitrogen-containing solubilizates;

c) molar volume does not determine solubilization and its use is not generally applicable to all types of compounds. (See contradiction, paragraph 9 under Hydrocarbons [34]);

d) a general increase in alcohol solubilization occurs with increase in chain length of soap;

e) solubility decreases with increasing length of alcohol carbon chain length (20);

f) insufficient data for amines exists; and

g) the mercaptan tested was considerably less soluble than the equivalent carbon-chain alcohol or amine.

Several generalizations for the effect of alcohols upon the cmc of dodecylammonium chloride were developed (15).

a) The cmc is a linear function of alcohol concentration for alcohols of from 2 to 11 carbons in chain length.

b) Rate of change in cmc with alcohol concentration is smaller for branched chain than for straight chain compounds of the same number of carbon atoms.

c) The log of the derivative of the cmc, with respect to the alcohol concentration, is a linear function of the chain length of the alcohol for alcohols of 3 to 10 carbon atoms.

Mixed Liquids. A field which has received relatively little attention is that of mixtures of solubilizates, and Klevens (32) appears to have done much of the published work. His conclusions were these.

a) For a series of solubilizates of given alkyl chain length, when the polar grouping of the solubilizate is changed as follows, enhancement of solubilization occurs:

$$\mathrm{COO} < -\mathrm{OH} < -\mathrm{NH_2} < -\mathrm{SH}$$

b) As the chain length of the polar group (*e.g.*, —OH) is increased, there is an increase in solubilizing power.

Kolthoff and Graydon (37) investigated cosolubilized combinations of alcohols and hydrocarbons upon the solubilization of dimethylaminoazobenzene (DMAB), Orange OT, and transazobenzene in solutions of potassium laurate. Variations in solubilization were noted with the different solubilizates. Cosolubilized amyl alcohol and octyl alcohol both increased the solubilization of transazobenzene and naphthalene, but the latter had little effect upon polar solutes. Cosolubilization of hydrocarbons (with the alcohols) increased the solubilizing power of potassium laurate for DMAB, Orange OT, and transazobenzene.

The solubilization by surfactant solutions of normally water-insoluble dyes has been used as one means for determining cmc (52, 58). These thermodynamically stable solutions readily passed through semipermeable membranes, thus distinguishing these systems from emulsions or suspensions. The dyes specifically used were Yellow AB (phenylazo-β-naphthylamine) and Orange OT (o-tolylazo-β-naphthol); dimethylaminoazobenzene and transazobenzene (39) have also been used.

Orange L (2,4-dinitrophenylazo-1-naphthol-2) was used by Mankowich (46) in a considerable series of experiments as more strongly polar than Orange OT or the other dyes already mentioned, and in general less soluble than Orange OT.

The mechanism of solubilization for dyes is not well defined. McBain (52, 58) suggested dye sorption on the micelle exterior as being only a minor factor and implied that there are cases of formation of uni- and multimolar layers within the lamellar micelle. Experience with other surfactants (69) suggested differences in mechanism of dye incorparation by micelles when the dyes differ in structure.

Herzfeld (14) showed that varying concentrations of water-soluble pinacyanol dye yielded differing cmc values for short-chain soaps. Klevens (31) reviewed this subject and indicated that, at below cmc, charged pinacyanol chloride and soap form a precipitate which is solubilized when the critical concentration is reached. Below cmc the dye molecules may be in dimer or higher form while upon solubilization they return to their monomer form when the soap molecules associate to form micelles. It was suggested that the dye molecule, because of its structure, penetrates into the water layer as does the soap molecule and the hydrocarbon end is oriented similarly to the hydrocarbon of the soap. However the penetration must be only slight since the dye molecule decreases the cmc no more than a few per cent.

Detergency Application

Removal of an oil from a solid surface in a surfactant solution held in a quiescent state has been suggested as attributable to the preferential sorption of surfactant molecules at the substrate surface to permit its wetting and subsequent rolling back of the oily soil. It is likely that preferential sorption of the surfactant by oil also ensues. In either event the substrate is cleaned and the oil removed. These suggestions have been made when a fiber (cotton or wool) was the substrate, in which considerable preferential sorption of surfactant can occur. It is suggested that, because nonionic surfactants have many-fold lower adsorption characteristics, the substrate-surfactant sorption mechanism for general explanation may be weakened. Certainly this would be true with substrates showing essentially no preferential sorption for surfactant. It is now suggested that sorption of the surfactant by the oil, and oil solubilization may be more reasonable explanations for this phenomenon though the substrate type is also important.

As McBain pointed out (48), detergency is a complex of many diverse factors, among which solubilization is only one. However he considered it of sufficient importance that it was discussed at length. McBain and Hutchison (56) in continuing his work, discussed the solubilization phenomenon and its applications at length and very briefly considered its relationship to detergency. Klevens (31) reviewed the many factors of solubilization, briefly considering its implications in detergency. Preston (67), in discussing the correlating principles of detergent action, concluded that a critical washing concentration is characteristic of each surfactant and that this closely coincided with critical concentration for micelle formation but relegated solubilization of foreign matter as a function of the colloidal micelle to a secondary role in the usual washing process. Goette (11) concluded that detergency is more greatly affected by the interfacial potentials (*zeta* potential), electrostatic forces, and of ion charge than by solubilization.

It is quite apparent that a variety of beliefs exist concerning the importance of solubilization in the detergent process. It was pointed out (56) that though solid soils, such as lampblack and ferric oxide, are not subject to solubilization, solubilization can be quite important in applications where fats and the like are the contaminating substances.

Detergent Builder Effect. Materials such as electrolytes, which can affect cmc, should likewise have effect upon solubilization. Increase in micellar size or formation at lower critical concentration will increase solubilization, and a review of the principles governing electrolyte addition will apply to solubilization.

a) Critical micelle concentration is reduced by added electrolyte.

b) Influence of the valence of cation follows the Schulze-Hardy rule: the higher the valency, the less of the cation required to reduce cmc.

c) Cmc is essentially independent of the nature of the non-colloidal electrolyte ion and is a function primarily of the length of the surface-active ion (36).

d) Electrolytes which hydrolyze to yield alkaline or acid solutions are better builders than those providing essentially neutral solutions (12).

e) Cmc's of soaps depend upon the number of equivalents of added cations and are independent of the nature of the anion (4, 29). Goette (11) says however that cleaning activity (as apart from cmc) of neutral or alkaline salts is dependent upon the charge of their anions.

f) In contrast to electrolyte effect on cmc, solubilization of hydrocarbons is increased whereas polar solubilization is reduced by added electrolyte (33).

Just as surfactants may be classified as cationic, anionic, or ampholytic, so may the detergent builders be subdivided, and for essentially the same reasons. Additionally these may be acid, neutral, or alkaline in reaction upon solution. As indicated in previous discussion, much of the literature deals with anionic surfactants such as soaps, or with cationic surfactants, with little or none concerned with nonionic or ampholytic surfactants. Consequently the volume of data for effect of electrolytes upon solubilization is in essentially the same proportion. To simplify the discussion, the usual surfactant classification will be followed.

Neutral Electrolytes. Examples of these materials are the sodium and potassium chlorides and sulfates.

Orange OT was solubilized in potassium dodecanoate, and the order of effectiveness of electrolyte addition was

$$KOH > KCNS > KCl = K_2SO_4 > \text{no salt}$$

when added in equimolar quantities (49). For ethylbenzene in potassium tetradecanoate (71), the series was

$$NaCl > KCl > K_2SO_4 > K_4Fe(CN)_6 \cdot 3H_2O.$$

For n-heptane (33), the order was

$$KCl > K_2SO_4 > K_4Fe(CN)_6 \cdot 3H_2O.$$

However, when n-octanol was solubilized, the order was exactly reversed.

The solubilization of dimethylaminoazobenzene, Orange OT, and transazobenzene in surfactant solutions showed that the log of critical concentration of a detergent decreased linearly with increasing electrolyte normality (39) and that temperature appeared of little importance to this relation. Sodium (or potassium) ion concentration (57) reduces cmc to the same extent when calculated on the cation-equivalent basis. Common-ion effect was adduced as the cause of cmc reduction in accord with the law of mass action.

Data (56) measured at concentrations somewhat above criticality for micelle formation showed solubilization of Orange OT for several anionic surfactants with sodium sulfate, tetrasodium pyrophosphate, and carboxymethyl cellulose (NaCMC) as additives. In general, increases in dye solubilization took place with the electrolytes while carboxymethyl cellulose generally had little effect.

Klevens' review (31) of the effect of neutral electrolytes on cationic agents gives some valuable general information.

a) Addition of Na or K chlorides increases solubilization of azobenzene.

b) With hydrocarbons, solubilization increases with the increase in electrolyte concentration, followed by a decrease.

c) With an alcohol, a decrease in solubilization occurs with added electrolyte.

Cationic Electrolytes. The effect of these builders is controlled by the valence of the cation. Harris (12) demonstrated that soaps and other anionic surfactants show an initial increase in activity when very low concentrations of cationic electrolytes are used, followed generally by a marked reduction when the electrolyte concentration is increased. This effect follows the Schulze-Hardy rule: the higher the valency, the more marked the result.

Anionic Electrolytes. These electrolytes are the ones most effective as anionic and nonionic surfactant builders. However their use in conjunction with cationic surfactants generally results in the loss of effectiveness of the surfactant by chemical interaction. Exceptions to this can be achieved by proper selection of both surfactant and builder.

Tetrasodium pyrophosphate combined in an amount equal to the surfactant generally exhibits no marked change while a 2½-fold addition either reduced the degree of solubilization or left it essentially unchanged. With nonionics, carboxymethyl cellulose either caused little change or lowered solubilization. Other work has shown considerable reduction in cmc as a result of electrolyte addition, but by using considerably different technics. It is probably this which accounts for differences in the apparent electrolyte effect. Considerable increase in solubilization of Orange L by nonionic surfactants was noted as the pH changed from 4 to 12 while weakly polar Orange OT showed no such trend. Increases in solubilization of both dyes occurred with temperature increases.

A minimal mole ratio of anionic electrolyte to calcium or magnesium soaps is necessary to prevent the formation of alkaline earth soaps (60).

Solubilization of Orange OT is improved by builders, such as polyphosphates and silicates, but the anions exhibit essentially no effect. Lowering is directly attributable to the cation and to mass action.

In textile practice, as in other detergent operations, solubilization almost certainly occurs in the early stages (the more effective the agitation or mechanical action, the more rapidly solubilization occurs). Then, if the solubility of the soil in the detergent solution is exceeded, emulsification ensues. In raw wool scouring the first several bowls certainly contain contaminant in excess of the ability of the detergent to solubilize, but in subsequent bowls this effect must occur. In the scouring of tops and of woven fabric prior to finishing, where the wool enters containing low proportions of added or natural oils, solubilization certainly occurs. Scouring of woven greige goods of other fibers prior to dyeing and finishing likewise utilizes solubilization as one factor in the detergent picture. In the kier boiling of cotton, removal of the natural waxes is undoubtedly partially accomplished by solubilization. Silk degumming, with the removal of natural sericin, undoubtedly involves solubilization.

Bast fibers can be degummed by soaking in a cosolubilized mixture of water, isopropyl alcohol, and turpentine containing alkylated aryl polyether sulfate as the surfactant (3).

In laundry practice, either home or commercial, the oily soils are solubilized, and the insoluble soils are suspended for removal. Oily matter, either of a sebaceous nature or of cosmetic or medicinal nature, represents the materials frequently encountered. Of course, oils or fats from meats, shortening agents, or butter on garments or kitchen towels are frequently encountered and are subject to this same factor in soil removal.

Metal Cleaning. Soils on metals almost invariably contain, or are, mineral, animal, or vegetable oils, present as a result of metal treatment. Hence aqueous detergency in metal cleaning almost invariably involves solubilization as a factor. When degreasing baths become overloaded, solubilization is followed by emulsification, and if the load becomes sufficiently high, oil phase separation actually occurs. Diphase metal cleaning approaches solubilization in that the aqueous phase contains surfactant and a cosolvent while the solvent phase contains some of the surfactant. Emulsion cleaning, as it implies, has exceeded the solubilization stage, and an emulsion of the cleaning solvent is used to dissolve oils. In metal cleaning, solubilization is the main initial factor, followed by emulsification as the oil solubility in the surfactant micelles is exceeded.

Fineman and Kline (9), in evaluating an oil-carbon black soil on a variety of substrates, showed that for a soil to be dispersed it must come off a substrate and that substrates varied widely in their ability to permit this soil to be dispersed. The amount of soil applied and the surfactant concentration ranges were such that solubilization could have occurred. These investigators speak of emulsification of this soil, observed under a microscope, so that solubilization very probably played only a small but nevertheless important part in these particular systems.

Hand dishwashing is cited (56) as an excellent example of solubilization because oils, fats, and fatty acids are almost invariably constituents of the soil, and cleaning proceeds by their solubilization. Once the solubility point has been exceeded however, emulsification occurs and the foam begins to fall because the surfactant is adsorbed in the process. If this process is continued long enough, cleaning ceases even though some foam may remain.

Lime Soap Dispersion. The ability of certain surfactants to solubilize either their own insoluble calcium salts or the insoluble calcium salts of other surfactants is a commercially valuable asset. Lindner (45) demonstrated that Igepon T had the unusual ability to disperse insoluble calcium soaps; at the near boil almost clear solutions were obtained, which could be successfully filtered.

Tartar and Cadle (72) investigated the solubility of calcium dodecyl sulfonate in aqueous solutions of the corresponding sodium salt. The increase in solubility of the calcium salt was accompanied by an increase in both the Ca and Na ions with a decrease in sulfonate ions. The calcium salt solubility increase was explained by the formation of micelles, and the calcium ions because of their high valence were considered as held more readily on the micelle surface as gegenions than the Na ion. The solubility of calcium dodecyl sulfate in aqueous solutions of the sodium salt were more than 10 times that of the corresponding sulfonate, and complex micelle formation was used to explain the solubilization. An attempt was made to measure the solubility of calcium laurate in solutions of sodium laurate but was too insoluble even in concentrated solutions to measure.

Miles and Ross (59) investigated mixtures of the sodium and calcium salts of laurate soaps and lauryl sulfate. The mixed salt Ca laurate-lauryl sulfate was definitely characterized.

The foregoing suggest that optimum lime salt solubilization can occur within a homologous series with optimum hydrophobic length, that for a given hydrophobe the polar ending can have marked effect upon solubilization, and that complexes of mixed salts can be formed and isolated.

Compositions. Many preparations are compounded initially to involve blending or hydrotropy to provide clear, nonsettling concentrates, which, on dilution, produce clear solutions. The latter stage, during application, involves solubilization.

Germicidal compositions have long used solubilization as a function, in which ordinarily water-insoluble active germicides are solubilized in dilute or concentrated surfactant solutions. Stable 4% solutions of thymol or chlorothymol can be obtained in soap solutions (25). Hexachlorophene is used in germicidal soaps in 1 to 3% quantities (42). A clear, homogenous pine oil solution is obtained by using rosin soap as an emulsifier and water to form a solution (2). This can be further diluted for use, providing a clear aqueous solution (solubilized system).

Selection of the most effective soap or surfactant for solubilization of germicidal agents is important to germicidal potency. Much work has been done in the solubilization of ortho-benzyl-para-chlorophenol (61); and soaps, surfactants and cosolubilizates are discussed in attaining the most effective formulation of this compound.

Dyes ordinarily insoluble in water have been solubilized by surfactant solutions. A practical application of this phenomenon is the solubilization of an optical brightening agent by surfactant solutions for use in cleaning and simultaneously brightening nylon (13).

Representative of concentrated hand dishwashing compositions is one containing oleyl methyl tauride as the surfactant, diethyleneglycol monobutyl ether as a coupling agent, and a lime sequestrant (1). Another contained the ammonium salt of alkylphenol polyglycol ether sulfate, water, and ethanol (40). Another variety for the same purpose contained a dialkylol amide, alkanolamine salts of dodecyl sulfate and dodecylbenzene sulfonate, water, and alcohol (73). While the initial concentrates involve hydrotropy and blending, the use concentrations involve solubilization.

An acid cleaner for painted surfaces which entails blending and solubilization comprised phosphoric acid, aryloxypolyalkylene ether sulfonate, and minor amounts of triamylamine (10).

Cosolubilization. This term signifies the effect of one solubilizate in a surfactant system upon the solubilization of yet another. In a practical manner the initial solubilizate can increase the solubilization effect where the last added material has only minor solubility. Such systems might comprise as the least soluble agent, a germicide, optical brightener, or corrosion inhibitor in detergent compositions, and in soil removal, gums, oils, or waxes to be removed from substrates to be cleaned.

Solvents have been used with soaps for many years, but realization of their relationship to solubilization has been neglected. That they are very useful for many specific purposes is apparent. Hetzer (16) discussed this at length. Palit (64) investigated solvents in soap systems with particular emphasis on their use to dissolve alkali metal soaps. Mentioned as particularly effective were mixtures of mono- and polyhydric alcohols, and an extensive table of what he calls latent solvents is given.

That cosolubilization is beneficial is indicated. In wool scouring, clear compositions were superior to those which were emulsions (41). Contrarily laboratory and commercial laundry tests (63) showed no advantage for solvent-containing detergents in removing fatty material from fabric.

Solubilization, because it is a complex phenomenon and difficult to measure in the detergency process, remains an intangible which nevertheless undoubtedly occurs to a greater or lesser extent in most detergent operations.

Summary

The ability of dilute surfactant solutions to solubilize water-insoluble substances to form stable systems is termed solubilization. Reviewed are the mechanism, methods for measurement, and temperature effect. Discussed in detail are surfactant structure and solubilizates, and the principles of solubilization involved. The application of solubilization to detergency operations is discussed broadly.

It is concluded that solubilization is a minor, difficultly measurable factor in the large majority of aqueous cleaning operations.

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[Received February 10, 1958]

Lecithin in Oil-in-Water Emulsions[1]

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OIL-IN-WATER EMULSIONS have been undergoing extensive clinical investigation for intravenous alimentation. The stabilizing agent in most of the emulsions that have been tested was a purified preparation of soybean phosphatides (3). These preparations, even after so-called purification, are complex mixtures of phosphatides and other materials. The presence of such impurities and the variation in their composition from one preparation to another may contribute at times to some of the adverse reactions observed on administration of these emulsions (9). This study was undertaken therefore to investigate the use of highly purified phosphatides, principally lecithin, in emulsion preparations. A small scale emulsion stability test was developed for the small quantities of highly purified fractions made available for this purpose. Highly purified lecithin was found to be an inefficient emulsifier producing emulsions particularly unstable to autoclaving, a requisite procedure in the sterilization of emulsions for use in intravenous alimentation.

Various materials were added back to the purified lecithin to determine their influence on emulsification. Such materials included fatty acids, carbohydrates, other phosphatides, and combinations of these materials. Addition of fatty acids improved considerably the emulsification properties of the lecithin preparations, but in no instance did any of the emulsifiers equal in their emulsification properties that of the soybean phosphatide preparations ordinarily used in emulsification.

Experimental

Purified Lecithin

Lecithin fractions were obtained from egg yolk by chromatographic purification procedures using an alumina column as described by Hanahan *et al.* (4, 5). These were found to contain trace impurities which were indicated to be in part lysolecithin (2, 7) and probably also sphingomyelin (1, 6). In subsequent purification employing silica column procedures similar to that described by Lea *et al.* (7), lecithin fractions were obtained which, by the chromatographic strip technique (2), analyzed as only one component having the same R_f value as an authentic sample of synthetic lecithin.[3]

Emulsion Evaluation Procedure

A small-scale test was developed to evaluate lecithin and mixtures as emulsifiers. The procedure consisted of dispersing in a Virtis homogenizer (Model No. 6-105) the requisite amount of emulsifier formulation in 85 parts (42.5 g.) of 5% dextrose solution containing 0.3 parts (0.15 g.) of Pluronic F-68[4] for about one minute at one-half full setting on the Virtis variac. Then at slow speed 15 parts (7.5 g.) of Wesson Oil[5] (15 wt.-% of the total emulsion) were added, and the speed was increased over a three-minute period to maximum for the homogenizer (about 13,000 r.p.m.). After five minutes at this speed a sample of about 10 ml. was transferred to a 15-ml. centrifuge tube, stoppered, mechanically

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[1] This investigation was supported in part by funds from the Office of the Surgeon General.

[2] One of the laboratories of the Southern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.