[Contribution from the Department of Chemistry, Stanford University]

The Solubilization of Water-insoluble Dye in Dilute Solutions of Aqueous Detergents*

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It has been abundantly proven[1] that thermodynamically stable colloidal solutions of otherwise insoluble materials are formed when the latter are presented to dilute aqueous or non-aqueous solutions of detergents. Thus it seems probable that any material may be dissolved in any solvent through the presence of a few tenths of a per cent. of a suitable solubilizing detergent.

This solubilization has therefore to be distinguished from other phenomena, such as the change in solvent power when *large* quantities of a second solvent are added; or from mere emulsification or suspension, or the protective action of surface active substances upon already preëxisting or mechanically formed particles or droplets.

A case of protective action unaccompanied by appreciable solubilization is afforded by 1% aqueous solution of methyl cellulose (Dow's medium viscosity Methocel). This dissolves only a minute trace of Yellow AB, but it suspends commercial finely powdered Yellow AB, carrying it completely through a #G3 Jena sintered glass filter of pore size 20 to 30 microns, to a less extent through Schleicher and Schüll filter paper #595, and practically not at all through a #G4 Jena sintered glass filter of pore size 5 to 10 microns. Moreover, most of the particles settle out on standing, whereas when solubilized they remain indefinitely in the solution.

The present communication is devoted to a study of the solubilization of a water-insoluble dye, supplemented by data on chlorophyll and organic solvents. No previous work has avoided all of the pitfalls which await the investigator of surface active materials. For example, previous work from this Laboratory on water-insoluble dyes[2] has not distinguished adequately between solubilization and peptization of colloidal particles in the commercial dyes, when used in solid form.

Some pitfalls that have been overlooked by various investigators have been (1) failure to distinguish between mechanically incorporated material and that truly solubilized, (2) sorption of detergent by the experimental apparatus or by filters or by excess of the dye itself, or (3) dye introduced by spontaneous emulsification[3] of a second liquid phase, left behind even when that phase has been largely removed again. In making measurements with commercial detergents another important influence is usually the presence of other materials such as salts, some of which enhance and some of which militate against solubilization by the detergent itself.

Four kinds of evidence support the conclusion that solubilization consists in the spontaneous stable formation of self-organized colloidal particles. First is the X-ray evidence of Kiessig and Philipoff,[4] who show that the spacings of the lamellar micelles in solutions of sodium oleate undergo an expansion in thickness when benzene is dissolved therein, the normal spacing increasing from 91 to 127 Å. The sheets of benzene are 36 Å. thick and those of water 42 Å. thick, each of the two separated layers of soap molecules contributing 24.5 Å., making a total of 127 Å. for the multilayered sandwich.

The second indication is the invariable presence of colloidal particles seen in the ultramicroscope when the detergent is not too concentrated or too lightly loaded with insoluble material (experiments with M. E. L. McBain).

The third proof comes from unpublished work of Dr. S. A. Johnston in this Laboratory, who found in exact measurements of the lowering of freezing point of potassium oleate solutions that the lowering is not affected when iso-octane is dissolved in the oleate, even in amounts sufficient to change the lowering by a high percentage if the iso-octane were in separate molecules.

A fourth indication is the inability of small amounts of good solvents to change the solvent power very greatly. For example, M. E. L. McBain[1a] found that it was necessary to add 30% of alcohol before water began to dissolve a notice-

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* A much more detailed account (120 pages, in addition to a review of previous literature) is available as microfilm copies of the Stanford University theses of Merrill and Vinograd, 1940, obtainable through the Department of Agriculture, Washington, D. C. Experiments with oleate and lauryl sulfonic acid by J. R. V., others by R. C. M.

[1] See, for example, (a) McBain and McBain, This Journal, **58**, 2610 (1936); (b) McBain and O'Connor, *ibid.*, **62**, 2855 (1940); (c) McBain, Merrill and Vinograd, *ibid.*, **62**, 2880 (1940).

[2] McBain and McBain, *ibid.*, **58**, 2610 (1936); McBain and Woo, *ibid.*, **60**, 223 (1938); *J. Phys. Chem.*, **42**, 1099 (1938); *Kolloid-Z.*, **87**, 74 (1939).

[3] McBain and Woo, *Proc. Roy. Soc.* (London), **A163**, 182 (1937).

[4] *Naturwissenschaften*, **27**, 593 (1939).

able amount of yellow dye. Five per cent. aqueous solutions of acetone or saturated solutions of ether dissolve no appreciable amount of Yellow AB or of chlorophyll. Similarly in non-aqueous solvents a large amount of ordinary polar solvent has to be added before the effects of very dilute detergents begin to be imitated. In studies of hydrotropy[5] it is customary to put in from 25 to 150% of hydrotropic agent or solvent. A small amount of good solvent does not appreciably change the thermodynamic environment and other properties within a non-solvent. It would indeed be inexplicable if less than 1% of solvent could cause molecules to dissolve separately in a 99% diluent. Solubilization as here defined can only proceed through association of molecules of solute and detergent.

Soluble substances can have their solubility enhanced by sorption within or upon detergent micelles, as was suggested for example by McBain and Bolam.[6] Indeed this is the basis for one of the best methods of studying solubilization.

Numerous examples of solubilization are evident in biological and industrial literature. For example, some of the bile salts are excellent detergents, although this has been explained by biochemists on the so-called "choleic acid" principle. However, a very recent study by Roepke and Mason[7] departs from this point of view and classifies them as colloidal electrolytes. We have found in experiments with Dr. Eloise Jameson which will be reported elsewhere that the fractionated γ serum globulins solubilize Yellow AB in aqueous solutions.

The solubilization which we wish here to study is characterized by reversible equilibrium. A detergent solution containing less will spontaneously take up more, and any excess will spontaneously separate out.

Experimental

Materials.—Yellow AB (F. D. & C. Yellow #3)(phenyl azo-β-naphthylamine) (containing about 2% of water-soluble material) was dissolved in the minimum amount of boiling alcohol, the solution was allowed to cool until crystallization began, the clear solution decanted and allowed to crystallize overnight. The remaining mother liquor was poured off and the crystals dried in an oven at 60°. These crystals were again dissolved in the minimum amount of hot alcohol and distilled water added very slowly, drop by drop, into the cooled solution (which was being stirred rapidly by motor-driven stirrer) until a large excess was present. A small amount of alcohol was then added to dissolve any small nuclei present[8] and the crystals dried in an oven at 60° overnight. The resulting crystals were of fairly small size (but *not* colloidal) and were a glistening dark red, in contrast to the amorphous orange powder of the technical material. The dye was insoluble in water and did not color warm solutions of electrolytes even faintly. All experiments were carried out at 25.0°. All *p*H measurements were made with a Beckmann glass electrode.

The chlorophyll used was the pure research grade 5X of the American Chlorophyll Company.

Bile acids were pure Riedel-de Haen Company products. The cholate, deoxycholate and dehydrocholate were made by neutralizing those bile acids with sodium hydroxide free from carbon dioxide. It was noticed that these insoluble acids dissolve before sufficient alkali for complete neutralization has been added. Thus six equivalents of cholic acid dissolved in 94 equivalents of sodium cholate. The approximate solubility of sodium deoxycholate and sodium taurocholate at 25° is 500 (by R. D. Vold) and 546 g. per kilogram solution, respectively, as compared with the values "greater than 333 and 235 g. per liter of water," mentioned by Sobotka.[9]

The hexadecane was an especially pure sample as used by Professor G. S. Parks for heat capacity measurements.

The lauryl sulfonic acid ($C_{12}H_{25}SO_3H$) was a specially pure preparation made by Dr. Martin E. Synerholm.

The other detergents were commercial detergents, some of which were pure, but most had not been purified.

Observations with Dodecyl Sulfonic Acid and with Potassium Oleate

In these experiments only, the supernatant liquid was first centrifuged in a hand-driven centrifuge and decanted.

Three methods of analysis were examined. The first, direct colorimetry of the detergent–dye solution with the Zeiss Stupho photometer using an S47 blue filter with an accuracy of about 0.5% of the total dye present, showed that each detergent required direct standardization. Thus potassium laurate and Turkey red oil with a blue filter, and sodium deoxycholate and Aerosol OT with a green filter, are similar and rather near to a solution of the dye in pure benzene. This is similar to the long recognized fact that the refractivity of a solute in the colloidal condition is also the same as when it is truly dissolved. On the other hand, potassium oleate and sodium deoxycholate with a blue filter are somewhat different, possibly arising from some absorption of light by the detergent. Laurylsulfonic acid has quite a different color, possibly due to salt formation. Each graph of per cent. transmission is linear when plotted on semilogarithmic paper against concentration of dye.

A second method of analysis was similar colorimetry, but after extraction of the dye with benzene, comparing with standard solutions in pure benzene. It is advisable

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[5] Neuberg, *Biochem. Z.*, **76**, 107 (1916); Lindau, *Naturwissenschaften*, **20**, 396 (1932), and von Hahn, *Kolloid-Z.*, **62**, 202 (1932), approach hydrotropy from the viewpoint of ternary phase rule systems.

[6] *J. Chem. Soc.*, 825 (1918).

[7] *J. Biol. Chem.*, **133**, 103 (1940).

[8] Precaution introduced by G. S. Hartley, *J. Chem. Soc.*, 1972 (1938).

[9] H. Sobotka, "Chemistry of the Sterids," Williams and Wilkins Co., Baltimore, Md., 1938.

first to precipitate the detergent by barium chloride or hydrochloric acid before extraction. Mere evaporation of the original mother liquor or of the extract is too inaccurate because it includes any extracted detergent or impurity in the residue.

A third method of weighing undissolved dye is trustworthy only if the dye is not finely divided or the solution too dilute and if the dilution necessary in washing does not cause precipitation of further dye. However, the filter itself sorbs dye and Merrill has shown that it may even clog up and then rob the solution mechanically. S. A. Johnston in this Laboratory has demonstrated, contrary to the experience of Hartley,[8] that the excess of solid dye sorbs appreciable amounts of detergent and thus diminishes the observed concentration of dye. Thus when two portions of 0.0034 *m* sodium lauryl sulfonate solution are shaken with 0.1 g. of crystalline and 0.3 g. of commercial amorphous Yellow AB, respectively, both turn yellow at first, but only that in contact with the crystalline dye remains so.

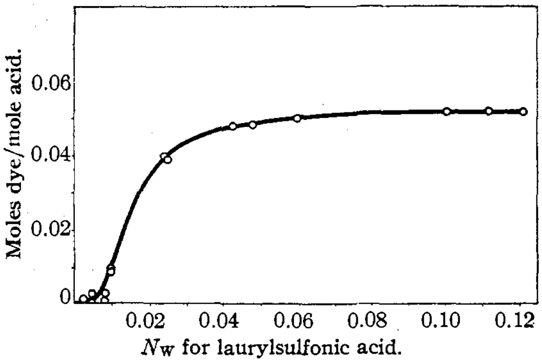

Fig. 1.—Solubility of recrystallized yellow AB in laurylsulfonic acid solutions at 25°.

In four experiments to measure solubility with 0.4 *m* potassium oleate, two were begun at 75° to supersaturate with crystalline Yellow AB, while two others were placed with the crystals in a thermostat at 25° for sixty-six hours. The first two gave 0.201 and 0.207 by the second and third methods of analysis, respectively, and the last two 0.197 and 0.197 g. of dye per 100 cc. This is proof that the same equilibrium has been obtained from both sides. A commercial dye unrecrystallized gave a result 12% higher due to preëxisting particles. The extra amount must of course depend upon the actual excess dye that was used, for if only just enough were used it would all be solubilized and here only slight excess was allowed. On the other hand, sufficient excess would give a value twice as great with technical as with recrystallized dye; this was actually found in a series with lauryl sulfonic acid. Great excess would deplete the detergent solution and hence lessen the amount solubilized, as in Johnston's experiment.

McBain and Woo's method of avoiding solid by extracting dye from toluene solution overlooked the fact that toluene itself is solubilized by aqueous detergents, and therefore a liquid so rich in dye carries an excess into the aqueous solution. Thus 100 cc. of 0.4 *m* potassium oleate can dissolve about 3.8 cc. of toluene, which in turn could have itself carried twice the amount of dye required for saturating the soap solution. Thus partition coefficients with concentrated solutions of dye can easily be too large. Furthermore, Engler and Dieckhoff[10] showed that often two insoluble materials are each more solubilized when simultaneously present. Finally, when toluene nearly saturated with dye is carefully placed upon solutions of lauryl sulfonic acid of concentrations between 0.05 and 0.075 *m* streamers of color project into the lower layer, showing spontaneous emulsification.

Each point in Fig. 1 is the mean of two determinations with recrystallized dye in lauryl sulfonic acid solutions, one from the side of supersaturation and the other from undersaturation, making thirty-two experiments. Although in 0.01 *m* detergent the solubilization was far less than at all higher concentrations, still more dilute solutions were nevertheless definitely colored by solubilized dye, although these are below the so-called "critical concentration for initial formation of micelles," namely, 0.008 from conductivity and 0.010 from freezing point.[11] The "critical concentration" for practical completion of formation of micelles is about 0.06 *m*. According to the mass law there can be no sharp critical concentration of micelles. A 0.002 *m* acid dissolved 9.2×10^{-5} g. of dye/100 cc., whereas water dissolves 1.6×10^{-5} g. of dye/100 cc.

It is a remarkable fact that the solubilization in soap solutions is greater at high temperatures than at room temperatures in spite of there being far less colloid at high temperatures. Likewise in paraffin oil methylene blue is solubilized only at higher temperatures.[1c] In every case the solutions of crystallized dye solubilized in lauryl sulfonic acid were full of ultramicroscopic particles, whereas the soap solution itself was clear.

Experiments with potassium oleate and slight excess of technical dye gave 0.025 mole of dye per mole of soap for concentrations between 0.2 and 0.5 *m* potassium oleate, falling to 0.020 for 0.05

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[10] Engler and Dieckhoff, *Arch. Pharm.*, **230**, 561 (1892).

[11] E. L. McBain, W. B. Dye and S. A. Johnston, This Journal, **61**, 3210 (1939).

m oleate, where $m = N_W$, weight normality or molality.

Solubility of the Water-Insoluble Yellow AB in Organic Solvents.—To test the suggestion of Hartley[8] and Lawrence[12] that the solubility of a water-insoluble substance in soap micelles is the same as in hydrocarbon solvents, recrystallized dye was rotated gently with organic solvents for four hours. In each case a duplicate was supersaturated by warming and then the excess dye allowed to crystallize out at 25°. A sample of clear supernatant liquid was then removed with a slightly warm pipet and analyzed by evaporation to dryness. Table I exhibits the results which show a great difference between solvents, the best tested being the polar oxygen compound, acetone. Hartley's suggestion must be regarded as doubtful and cannot be general.

TABLE I

THE SOLUBILITY OF YELLOW AB IN ORGANIC SOLVENTS AT 25° IN GRAMS OF SOLUTE PER 100 G. OF SOLUTION

Solvent	From supersatn.	From undersatn.	Mean	Moles dye / mole solvent
Acetone	60.3	60.2	60.25	0.49
Benzene	38.8	35.8	36.3	.17
Toluene	29.1	27.6	28.3	.15
Hexadecane	0.692	0.612	0.65	.061

Solubilities of Yellow AB in Aqueous Detergents

Final Experimental Method.—A small excess of crystallized dye was used for saturating the solution, and a duplicate experiment was simultaneously carried out from the side of supersaturation assured by a preliminary warming. Usually two or three days of gentle agitation, and occasionally as much as two weeks, was required to obtain identical results from both sides, proving equilibrium. It is noticeable that contrary to experience in measuring ordinary solubility, the supersaturated solubilized dye approaches equilibrium more slowly than the undersaturated system.

(a) **Procuring a Sample of the Saturated Liquid for Analysis.**—Proof that a sintered glass filter such as used by Hartley[8] can sorb an appreciable portion of dye was shown in four ways. One hundred cc. of approximately 1% sodium salt of dioctyl ester of sulfosuccinic acid saturated with Yellow AB and containing an excess of large crystals was allowed to stand undisturbed at 25° and then filtered through a Jena #4 sintered glass crucible. The first 15 cc. passing through the clean filter contained 13.5 mg. of dye/100 cc. The second similar volume contained 15.0 mg./100 cc., while the clear supernatant liquid carefully removed with a medicine dropper so as to avoid agitation contained no less than 18.6 mg./100 cc.

In a similar experiment with chlorophyll the impoverishment of the filtrate was noticeable to the eye.

The effect of sorption by the filter was noted with a solution of chlorophyll in alkaline sodium cholate. The first 14 cc. of filtrate had a *p*H of 10.91, whereas the next was 11.10.

The sorbed dye blocks the filter, greatly reducing the rate of filtration. For example a saturated solution of Yellow AB in 5% sodium cholate passed 14 cc. of solution in the first 30 sec., only 3.5 in the next 30 sec., and during 90 sec. more only 4.5 cc.

It is evident that for accurate work the solutions cannot be filtered and that the best method is to use a small excess of large crystals and obtain a clear supernatant layer by quiet standing for one hour or more in a thermostat, and then very carefully pipetting off a sample. The same solubility was obtained whether the solution stood one, twenty-four or sixty hours or more, which also excludes the possibility of isomerization to a more soluble form in this time. This procedure of securing a sample avoids any alteration in the solution and in the detergent through taking up of carbon dioxide from the air. Hence solutions must be kept in sealed vessels or with glass stoppers well vaselined and protected from the thermostat by a tight rubber cap or a thin film of nitrocellulose.

(b) **Analysis.**—The extraction method was abandoned because a quick method of preparing a whole series of known concentrations of dye in the aqueous detergent itself was hit upon. Instead of requiring some weeks to ensure complete solution, if the weighed dye is dissolved in the minimum amount of alcohol or acetone (2–3 cc.) and added slowly to the aqueous detergent (100 cc.) the standard solutions for calibration are rapidly made, and are readily diluted with water or detergent solution as required. It was found that warming off most of the acetone or alcohol and then restoring to the original volume with water did not appreciably change the Cenco-Sheard photelometer reading and was therefore unnecessary. Most determinations for Yellow AB were made with a green filter and for chlorophyll with a blue filter.

Results

The true reversible solubility of Yellow AB in colloidal solution of various aqueous detergents is given in Table II. There is no satisfactory name in general use for these substances. Clearly the term paraffin-chain salts is a misnomer for ring compounds and other complicated derivatives, and for proteins and bile salts, which yet closely resemble the typical soaps. The term colloidal electrolytes is certainly very much more general for it includes, for example, sodium silicates which have no solubilizing power. The word "detergent" which we have frequently used here has been given a much looser and inapplicable tentative definition by the American Society for Testing Materials as "any material

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(12) A. S. C. Lawrence, *Trans. Faraday Soc.*, **33**, 815 (1937).

which aids in washing." Probably the best generic expression for this subclass of the colloidal electrolytes is soap and soap-like detergents. However there is but little point in leaving out the modern nonelectrolytic detergents which likewise are solubilizers, but cannot possibly be classified as salts or colloidal electrolytes, and which in some cases contain no paraffin chain. Hence we are thrown back upon the generic term solubilizers or solubilizing detergents. We should have preferred to have shortened this simply to the word detergents.

Those which are at least moderately free from other compounds are given their chemical name in Table II, whereas several of the commercial materials are unknown mixtures and contaminated with salts. In each case 1% solution was made from the material as given. The Merck sodium oleate was impure, and the dye fades in the solution. Four different Turkey red oils of different types are included.

Table II

The Solubility of Yellow AB in 1.0% Aqueous Solutions of Various Pure and Commercial Solubilizing Soap-Like Detergents at 25° in Mg. of Dye/100 Cc. of Solution

Soap or detergent	From super-satn.	From under-satn.	*p*H	Moles dye / Mole solubilizer
Merck sodium oleate	3.6	3.4	10.1	0.0042
Sodium laurate[a]	3.0	3.6	12–13	.0034
Na salt of dioctyl ester of sulfosuccinic acid	12.2	11.8	7.1	.022
Lauryl pyridinium iodide	32.4	31.5	6.8	.048
A Na naphthenate	3.4	2.8	8.0	....
Commercial detergent of the type $RCONHCH_2CH_2N(C_2H_3)_2 \cdot HCl$	54.0	53.0	2.5	....
Commercial non-electrolytic detergent	62.5	58.0	5.0	....
Mixture of C_8 to C_{12} sulfonates	21.2	20.5	9.1	About 0.02
Sulfonated castor oil 75% pure	83.8	77.5	7.0	....
Sulfonated castor oil 4.3% SO_3, 29.6% H_2O	65.0	59.0	6.0	....
Sulfonated castor oil 30% water	75.0	75.0	6.5	....
Sulfonated castor oil 32.5% SO_3, 48% pure	37.2	36.5	5.1	....
Sodium cholate	2.5	2.3	10.7	0.0042
Sodium deoxycholate	6.2	6.0	8.0	.011
Sodium deoxycholate + excess NaOH	7.4	7.3	9.0	.012
Sodium dehydrocholate	0.0	0.0	9.0	.00
Sodium taurocholate	6.0	5.2	6.3	.011

[a] From pure Eastman Kodak Co. lauric acid (0.0361 g. excess NaOH per 40.0 cc.).

It is noteworthy that there is such disparity in the solubilizing power for Yellow AB of the various detergents listed in Table II. The most remarkable observation is that sodium dehydrocholate completely lacks the solubilizing power which makes the other closely similar bile salts so important in biology, physiology and medicine. Another communication appearing in *Chemical Products* shows that some commercial non-electrolytic detergents owe at least part of their action to the hitherto unrecognized factor of ion exchange by virtue of the salts which they contain.

The effect of concentration was studied with the pure bile salt sodium deoxycholate and the results are contained in Table III. The so-called critical concentration for initial formation of micelles is 0.005 *m*; the "critical concentration" for practically complete formation of micelles is about 0.08 *m*. The solubility is measurable down to the lowest concentration of bile salt, although it changes 10,000 fold over the range studied.

Table III

The Solubility of Yellow AB in Aqueous Sodium Deoxycholate Solutions at 25° in Mg. of Dye/100 Cc. of Solution

Concn. NaDe, *m*	From supersatn.	From undersatn.	Moles dye / Mole NaDe
0.45	335.5	335.5	0.0302
.225	165.0	165.0	.0297
.090	54.9	51.6	.0239
→ .063	32.6	31.9	.0207
.045	15.1	15.0	.0135
.027	8.6	6.0	.0109
.0090	0.60	0.60	.0027
.0063	.38	.36	.0024
→ .0045	.24	.22	.0020
.0036	...	.13	.0014
.0027	.095	...	.0014
.0018	.07	.06	.0013
.0009	.03	.027	.0012

Next, the solubility as influenced by the addition of salts, none of which have any solubilizing action of themselves, but all of which in small concentration enhance the solubilizing action of 0.009 *m* bile salt, was given careful measurement in Table IV. It will be observed that urea had no such action. In this concentration, 0.009 *m*, the sodium deoxycholate is not yet wholly colloidal and the effect of any sodium salt would be to form more colloid. Here, except for trisodium phosphate, all of the 0.025 *N* sodium ion solutions practically double the effect; however, the anions show some influence. Hartley[8] found that down to extreme dilution sufficient addition of salt developed the full solubilizing power of cetyl pyridinium salts.

TABLE IV

THE SOLUBILITY OF YELLOW AB IN MG. OF DYE PER 100 CC. OF SOLUTION IN 0.009 *m* AQUEOUS SODIUM DEOXYCHOLATE AS AFFECTED BY THE ADDITION OF SALTS WHICH ARE BY THEMSELVES NON-SOLUBILIZING

Salt, concn. equiv. *N*	*p*H	From supersatn.	From undersatn.
NaDe alone	7.2	0.60	0.60
NaCl, 0.0250	..	1.16	1.16
NaCl, 0.050	7.6	1.81	1.80
Silicate, 0.025 Na_2O/SiO_2 = 0.310	10.4	1.07	1.07
$NaNO_3$, 0.025	6.8	..	1.14
NaBr, 0.025	7.0	1.07	1.04
NaI, 0.025	7.1	1.18	1.18
Na_2SO_4, 0.025	8.2	1.17	1.12
Na_2CO_3, 0.025	10.5	1.20	1.25
Na_3PO_4, 0.025	10.9	0.74	0.84
Urea, 0.025	7.0	.56	.53

Experiments with Chlorophyll

Finally, on acccount of its possible interest in plant physiology the solubilization of chlorophyll by aqueous bile salts also was measured over a range of concentrations as shown in Table V. The range between "critical concentrations" for initiation and complete formation of micelles, 0.005 and 0.08 *m*, is indicated by arrows in the table.

TABLE V

THE SOLUBILITY OF CHLOROPHYLL IN AQUEOUS SOLUTIONS OF SODIUM DEOXYCHOLATE AT 25° IN MG. PER 100 CC. OF SOLUTION

NaDe, *m*	From supersatn.	From undersatn.	Moles Chl. / Mole NaDe
0.090	4.0	3.84	0.00048
→.063	2.02	1.98	.00035
.027	0.32	0.28	.00012
.009	.09	.09	.00011
.0063	.04	..	.00007
→.0027	..	.01	.00004

Ultramicroscopic Particles in the Solution

Solubilizing solutions that are originally clear in the ultramicroscope in most cases become filled with colloidal particles visible in the ultramicroscope after dissolving water-insoluble material. Here this has been shown for solutions of Yellow AB in 3 and 5% potassium oleate containing excess alkali, 0.001 *N* lauryl sulfonic acid, 0.003 *N* sodium deoxycholate supersaturated by warming and allowed to cool and stand, 5% sodium deoxycholate, concentrated sodium taurocholate, and for solutions of chlorophyll in 1 and 5% sodium deoxycholate. Solutions of both 5% sodium oleate containing excess alkali to prevent hydrolysis and 5% sodium deoxycholate after being in contact with a true molecularly dispersed solution of the dye in toluene were also found to be full of myriads of colloidal particles visible in the ultramicroscope. All the particles were definitely twinkling which is proof that they are not spherical. No colloidal particles were seen in the ultramicroscope in a saturated solution of dye in 1.0% Aerosol OT which had been allowed to stand for three and a half months, a solution (3.5 mg./100 cc.) of chlorophyll in 0.1 *N* sodium deoxycholate, nor in a saturated solution of Yellow AB in 0.45 *m* deoxycholate which had been standing in the thermostat for two and a half months.

Dialysis of Solubilized Yellow AB

It has been suggested that the water-insoluble material is wholly contained within the interior of micelles whether these be of the globular or lamellar types and that in the former case they were merely in solution in the hydrophobic interior. It was therefore of interest to see whether solubilized Yellow AB could pass through pores which would hold back all such aggregates, and permit only true ions and small molecules to pass. The following experiment proves that this is indeed possible, showing the true equilibria involved.

Untreated cellophane swollen in 64% zinc chloride solution[13] was wrapped tightly over the head and around the neck of a small bottle, containing only solid recrystallized Yellow AB, which was inverted in a beaker containing 5% potassium oleate solution plus excess alkali. Within two days the outer solution became distinctly yellow. The experiment was repeated after applying a coat of label varnish so as to leave a nitrocellulose film around the sides of the bottle and make doubly sure that no dye could pass out except through the membrane. Within one-half hour at 60° the dye had diffused into a concentrated solution of a commercial mixture of C_8 to C_{12} sulfonates.

Discussion

The experimental data here given show that a true reversible equilibrium solubility is attained with water-insoluble substances in the presence of dilute aqueous solutions of solubilizers. This is shown by the correspondence obtained in each case by approaching equilibrium from supersaturation and from undersaturation. This solu-

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[13] J. W. McBain and R. F. Stuewer, *J. Phys. Chem.*, **40**, 1157 (1936).

bilizing action is quite apart from the properties of these same materials as emulsifiers or as protective agents for suspensions. The solubilizers include anion and cation active, as well as non-electrolytic solubilizers. For example, in an experiment with J. J. O'Connor, a polyglycerol ester which originally had a specific conductivity of 1.42×10^{-4}, after repeated electrodialysis to remove all ions, still dissolved about 30 mg. of Yellow AB in 100 cc. of 2% solution.

It is of real interest and probable significance that the freezing point curves (values of $1\text{-}g$ against concentration) obtained by S. A. Johnston can by suitable choice of scale be made almost to coincide with the graphs of moles of dye solubilized per mole of detergent over the same range of concentration. This indicates that solubilization is closely connected with presence of colloid, an interpretation that is supported by the effect of added salts. Our experience here agrees with that of Hartley.[8]

Nevertheless, some chlorophyll or dye is definitely solubilized at concentrations below the so-called critical concentration for initial formation of micelles. It is conceivable that the dye can promote the association with molecules of detergent causing solubilization. Likewise it is conceivable that the effect may be due to the great surface activity of these detergents which is often fully developed in these extremely dilute solutions.

The mechanism of solubilization needs further study and it is highly probable that it differs in different cases or even in different concentrations of detergent and of solubilized material. Hartley[8] and Lawrence[12] speculated that the insoluble material merely formed an ordinary solution in the paraffinic interior of the colloidal particle. This suggestion is evidently oversimplified and cannot be generalized, especially when one surveys the extremely different cases met with in non-aqueous[1c] as well as aqueous solutions of the most varied character. For example, although methocel solubilizes so slight an amount of Yellow AB, this is greatly increased by the addition of ordinary salts. Certainly there are no paraffinic or similar micelles involved here. Kiessig and Philipoff's[4] multilayered sandwich micelle has been rather definitely proven for one particular case with sodium oleate, but it has not been tested for any other system, either aqueous or non-aqueous.

Neither of these suggestions accounts for the increasing turbidity of these stable solutions when the detergent is dilute and heavily loaded and full of ultramicroscopic particles and yet exhibits a permanent reversible equilibrium attainable from both sides. It appears that solubilization must in some cases involve mere association of detergent with the molecules of solubilized material. This point of view has been emphatically accepted by all organic and biochemists for the so-called choleic acids. These are regarded as coördination compounds between bile derivatives and representatives of most varied assortment of organic substances. However, solutions of so-called choleic acids need reëxamination in view of the phenomena of solubilization, here described. Solubilizing detergents are effective in dilute aqueous and non-aqueous solutions with a remarkable variety of chemical materials.

Lester Smith's explanation[14] of solubilization has been repeatedly misquoted[15] in recent years. His actual words are, "The results are explained by postulating adsorption of the dye on the colloidal soap," and "the solvent powers of soap solutions can only be accounted for by postulating adsorption of the organic solute on the colloidal soap particles." He cites on page 1682 our reference 6 as an example of this.

Summary

The solubility of several water-insoluble materials, such as Yellow AB, chlorophyll and bile acids, has been critically measured from the side of both supersaturation and undersaturation using solubilizing detergents, such as bile salts, soaps and commercial cation and anion-active as well as non-electrolytic detergents. This solubilization has been separated and distinguished from protective action, such as emulsification or peptization, and also from the change in solvent medium brought about by substantial additions of a second solvent.

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[14] E. L. Smith, *J. Phys. Chem.*, **36**, 1675, 1684 (1932).

[15] Hartley, "Aqueous Solutions of Paraffin-Chain Salts," Hermann et Cie, Paris, 1936, p. 41; also article in "Wetting and Detergency," Harvey, London, 1937, p. 153; Lawrence, *Trans. Faraday Soc.*, **33**, 325 (1937).