government did not in any way attempt this sub-identity theory. The oleomargarine standard merely requires a statement that the product is either made with vegetable fat, or from animal fat, or from a mixture of the two. If the same thinking were followed in connection with mayonnaise and related dressings, and bearing in mind that such dressings contain only vegetable fats, then it becomes apparent that the proposal of the government in connection with dressings represents a marked departure over the past few years in the direction of further rigidity and restrictions.

Food standardization is a very important subject to all of us, and it warrants the constant and careful thought of those interested in or affected by it, including government and industry. It is understandable how, with a new statute, the government proceeded most cautiously and, as some feel, even leaned over backwards. Now that the Act is 10 years old, we have had an opportunity to observe how the standards have worked, in peace and in war. We submit that these experiences have proven, or should have proven, that at least some changes in thinking and approach should be made so as to prevent unnecessary strangulation of initiative and improvement and to permit the consumer to receive the benefits she might receive if some needed changes would be made.

REFERENCES

1. O. Salthe, "Legislative History of the Federal Food, Drug, and Cosmetic Act," 3 Food Drug Cosmetic Law Quarterly (1948) 148; C. W. Dunn, "The Federal Food, Drug, and Cosmetic Act and the Food Industry," 3 Food Drug Cosmetic Law Quarterly (1948) 166; J. F. Hoge, "The Federal Food, Drug, and Cosmetic Act and the Drug Industry," 3 Food Drug Cosmetic Law Quarterly (1948) 178; C. W. Crawford, "Ten Years of Food Standardization," 3 Food Drug Cosmetic Law Quarterly (1948) 243; P. B. Dunbar, "Administrative Progress of the Federal Food, Drug, and Cosmetic Act," 3 Food Drug Cosmetic Law Quarterly (1948) 5.

2. The Federal Food, Drug, and Cosmetic Act did not become fully effective until one year after it became a law.

3. The Food and Drug Administration was part of the U. S. Department of Agriculture and, accordingly, the Secretary of Agriculture was the chief enforcement official. This was true also for the Federal Food, Drug, and Cosmetic Act until the Food and Drug Administration and the enforcement of this Act were transferred to the Federal Security Agency and the Federal Security Administrator by a Presidential Reorganization Plan.

4. The original bill, S.1944, was introduced on June 12, 1933, in the 73rd Congress. After this and three succeeding bills all failed of passage in the 73rd and 74th Congresses, S.5 was finally passed on the 75th Congress on June 13, 1938, and signed by the President twelve days later.

5. For a very interesting article on this subject, see H. Thomas Austern, "The Formulation of Mandatory Food Standards," 2 Food Drug Cosmetic Law Quarterly (1947) 532.

6. Federal Security Administrator vs. Quaker Oats Company, 318 U. S. 218.

7. Many states, by state law, have adopted the federal standards. Accordingly, intra-state shipments, in such states, of foods which do not comply with the federal standards violate state law.

8. Libby, McNeill & Libby vs. U. S. 55 Fed. Sup. 725 (CCA-2, 1945) 148 Fed. (2d) 71.

9. Of course, this is purely hypothetical as to facts. Actually, both mayonnaise and salad dressing today are in the course of being standardized under the Act. Some government officials have for years felt that "salad dressing," for certain reasons, should not be standardized. However, many of these very same officials realize that if you standardize mayonnaise, you practically have to standardize "salad dressing" in order to legalize it and prevent there arising the hypothetical situation described above.

10. Section 701(e) of the Federal Food, Drug, and Cosmetic Act.

11. F. N. Peters, "Are Standards of Identity Assets or Liabilities in the Food Industry?" 1 Food Technology (1947) 583.

12. 3 Food Drug Cosmetic Law Quarterly (1948) 243,248. The writer urges all those interested in this subject to read Mr. Crawford's address, since it very well states the thinking of the government on the subject of food standards and explains, in most capable fashion, the reasons underlying the policies and approach of the government.

Testing of Colloidal Solutions by Dye Solubilization*

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THE theoretical and practical aspects of solubilization phenomena have been discussed extensively in recent literature. By the most general definition solubilization is the ability of solutions containing surface-active agents to bring into stable colloidal solution substances insoluble in the solvent alone. It has been established that the solubilized material is not present in suspended particles or emulsified droplets but is adsorbed onto or incorporated in the colloidal micelles formed by the surface-active agent in the solvent. A comprehensive article on the structure and the general physical properties of colloidal solutions was recently published by Ralston (19).

Solubilization in non-aqueous solutions of surface-active agents was described by McBain *et al.* (14), and its application in textile processing was discussed by Creely (1). The solvent action of aqueous detergent solutions for organic materials was reviewed some years ago by Hartley (3) and Lawrence (8), who included a number of references to earlier work. Recently, McBain and Richards (15) and Stearns *et al.* (21), have published solubilization data for a large number of organic liquids and hydrocarbons in aqueous solutions of various soaps and detergents.

The solubilization of water-insoluble dyes in soap, detergent, and other colloidal solutions has been studied extensively by McBain and collaborators (2, 9-13, 16) and also by Kolthoff and Stricks (5). These studies helped to elucidate solubilization phenomena which, in turn, gave valuable data pertaining to the formation and structure of colloidal micelles. Solubilization values were given also for various commercial surface-active agents with the implication that dye solubilization can be used in evaluating the relative efficiency of such compounds.

It might be well to point out that the performance of surface-active agents in a specific application can hardly be predicted on the basis of dye solubilization alone. In the case of detergency, for instance, it was stated by Hartley (3) and Preston (18) that solubilization plays only a secondary role in the usual washing process. Hartley and also Tomlinson (22) suggested, however, that in some instances—washing hands for example—soap is freely applied and the relatively high concentration will lead to the removal of certain soils by actual solubilization.

In any event, it appears that a quantitative solubilization test can be used as a measure of colloid formation in solutions containing surface-active agents. This property varies widely and is characteristic of each class of surface-active agent(e.g., wetting agents, detergents, emulsifiers, etc.). Hence,

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dye solubilization has been found to be a valuable complement to other conventional laboratory tests for the routine evaluation and comparison of surface-active agents. A brief outline of a simplified experimental procedure for dye solubilization tests and a few typical results obtained in this laboratory were given in a preliminary note (7).

The Nature of Dye Solubilization

An analysis of some data published by McBain and Johnson (11) shows that within certain limits a linear relationship exists between the logarithm of the amount of dye solubilized and the logarithm of the concentration of the surface-active agent in solution. As illustrated in Figures 1 and 2, the resulting linear "solubilization isotherms" show relatively simply the influence of molecular weight on dye solubilization as well as the effect of temperature and the addition of salts.

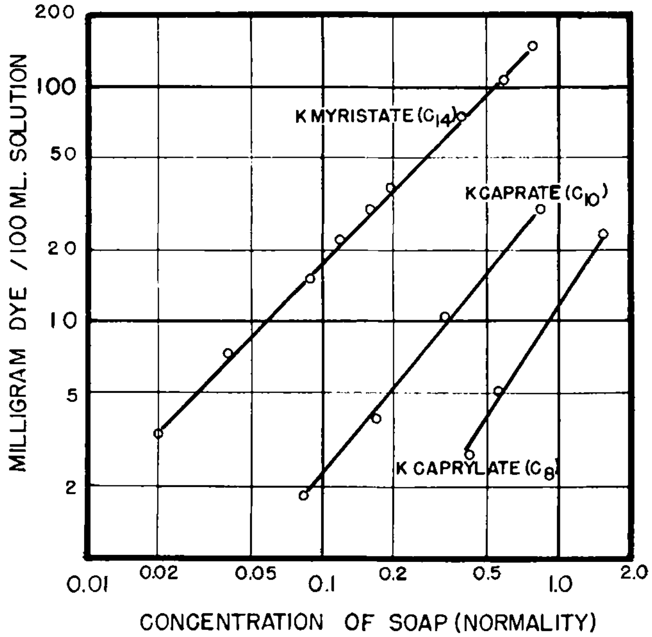

FIG. 1. Dye solubilization isotherms for various potassium soaps. (Plotted from data published by J. W. McBain *et al.*)

The experiments as described by the authors were made with pure potassium soaps and recrystallized Orange OT (Dye No. 2 in Table II). In order to obtain true solubilization, great care had been taken to eliminate any peptized or dispersed colloidal dye in the measurements. Under these conditions practically the same equilibrium solubilization values were obtained from undersaturation or oversaturation of the dye in the soap solution.

The dye solubilization characteristics at 25°C. of three homologous potassium soaps (containing 8, 10, and 14 carbon atoms respectively) are shown in Figure 1 which was obtained by plotting the values given by McBain and Johnson (11). In this and the following figures (2a and 2b) the values obtained from undersaturation were plotted. Some corrections published in a later paper by McBain and Green (10) were taken into account. The straight lines representing the solubilization isotherms change in position and slope with increasing molecular weight of the potassium soap. The influence of temperature is illustrated in Figure 2a. The solubilization isotherms of potassium myristate at 25° and 50° are parallel, the latter shifted toward lower concentrations indicating that within the whole concentration range about 30% less soap is required for solubilizing an equal amount of dye at the higher temperature. The addition of 1 mole KCl changes the position and the slope of the isotherm as shown in Figure 2b. At the lower concentrations there is about 50% less soap required for equal solubilization of the dye.

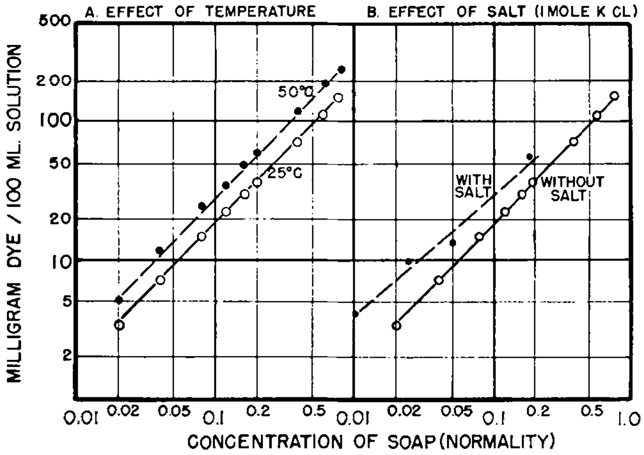

FIG. 2. Dye solubilization isotherms for potassium myristate. (Plotted from data published by J. W. McBain *et al.*)

As will be shown later, the mathematical expression for the proposed solubilization isotherm corresponds formally to the well known Freundlich adsorption isotherm. However, no claim is made here that the linear relationship demonstrated above has any far-reaching physical-chemical significance. Nevertheless, the potential usefulness of this method of presenting solubilization data for further theoretical interpretation can be illustrated by the derivation of a new mixture rule. It was deduced by examining the re-plotted solubilization values at 50°C., published by McBain *et al.*, for potassium laurate, potassium myristate, and a 50:50 mixture of these soaps. Since the solubilization isotherm of the mixture fell equidistant between the isotherms of the components, the solubilization values of the mixture (S_m) were computed from the values S_1 and S_2 reported for each component using the expression

$$\log S_m = \frac{\log S_1 + \log S_2}{2}$$

The above relation can be rewritten as $S_m = \sqrt{S_1 S_2}$ showing that S_m is the geometric mean of the individual solubilization values. Table I shows that the mixture rule employing the geometric means approximates the experimental values much closer than the arithmetic means mentioned by the authors in the above article. This mixture rule which appears to hold for soap homologues might also be applicable to certain other mixtures of surface-active agents. However, because of anomalies to be described later, this or any other rule becomes definitely invalid for mixtures containing dissimilar surface-active agents (e.g., an anionic agent and a cationic agent).

TABLE I

Illustration of Mixture Rule

Dye Solubilization Values for a 50:50 Mixture of Potassium Laurate and Potassium Myristate Compared With Calculated Values

(*Experimental* data published by J. W. McBain *et al.*)

Normality of Soap	Arith. Mean	Experimental Value	Geom. Mean
0.04	8.10	6.85	7.6
0.08	21.10	15.19	16.6
0.20	45.95	44.10	44.2
0.40	92.03	87.3	88.5
0.80	182.8	175.1	176.6

Dye Solubilization Tests

The experimental procedures which have been used by a number of investigators (5, 11, 16) appear rather tedious since the methods involve the attainment of equilibrium conditions requiring periods in the order of several days or even weeks. Additional time, from several hours to one day, is required for the settling out of the excess dye in the colloidal solutions. Furthermore, it is suggested that dye be added only in slight excess of the solubilization value in order to avoid any peptization effects; this requires, obviously, a number of preliminary tests with varying amounts of dyestuff. A relatively rapid, but only qualitative method utilizing dye solubilization for detecting surface-active agents was reported recently by Hoyt (4).

In view of the nature and simplicity of the isotherms in the log-log presentation of solubilization data, it became questionable whether the high degree of precision attempted in the past for quantitative determinations is actually required for obtaining useful results in comparative testing. Therefore, the first objective was to find a modified procedure which would more rapidly yield reproducible dye solubilization values approximating closely the equilibrium values.

A preliminary study was made to determine the gross influence of some experimental variables on the rate of dye solubilization. Solutions of Aerosol MA (1% and 16%), Igepon T (1%) and Nacconol NR (1%) were used for determining the effects of such variables as temperature, amount, and physical form of the dyestuff, type of agitation during solubilization, and method of removing excess dyestuff.

The above solutions gave solubilization values which fell within the range from 0.5 to 80 mg. dye/100 ml. Even large excess amounts of crystalline dyestuff did not affect appreciably the relative order of the respective solubilization values. The difference between amorphous and crystalline dye was more pronounced at room temperature than at 50°C. As expected, the amorphous dye showed a higher rate of solubilization at the lower temperature. Independent of the type of agitation (rolling, shaking, or stirring), the solubilization values after 15 minutes were at least 80% of the equilibrium values established after several days. The method of removing excess dyestuff (sedimentation, filtration, or centrifuging) had little effect on the final results, but it was found that filtering is least time-consuming.

These results suggested that a very much simplified procedure could be worked out for the comparative testing of colloidal solutions by dye solubilization. A new method was evolved, based on the above findings, that dye solubilization values sufficiently close to the equilibrium values could be attained within a short period of time, providing the tests were made at an elevated temperature and the amounts of dye solubilized did not exceed certain limits. Moreover, subsequent tests indicated that after dispersing the dyestuff by mild shaking, further agitation of the mixture during period of interaction was unnecessary.

Outline of Procedure

Eight to 12 different solutions can be readily handled for simultaneous testing. Furthermore, by selecting three or four concentrations over a range sufficiently wide to give solubilization values above 0.2 and below 50 mg. dye/100 ml., a fairly accurate isotherm can be obtained. Thus, as many as four different materials can be evaluated in any one run.

Two 20-ml. portions of each solution are poured into separate test tubes, one to be used for dye solubilization, the other as photometric control, if necessary. One set of solutions (i.e., eight to 12 test tubes) is preheated for 5 minutes in a constant temperature bath at 50 ± 1°C. The test tubes are removed from the bath and 100 ± 5 mg. of recrystallized dye No. 2 is added to each. Each test tube is then corked tightly, inverted slowly 10 times and replaced in the bath for 15 minutes. Using No. 50 Whatman paper, the solutions are filtered into another set of test tubes placed in the bath. The first 2 or 3 ml. that filter through is discarded. The color of the filtrate is compared with a set of reference solutions of dye No. 2 prepared in 20% Aerosol MA* (Concentration of dye: (a) 1, (b) 2, (c) 5, and (d) 20 mg./100 ml.). The filtrates are diluted with 0, 1, 4, or 9 parts of a 50:50 acetone-water mixture, the amount of the dilution being that required to get an approximate visual match to the reference solutions (a) or (b). Using a Fisher Electrophotometer with micro cells (blue filter 425B and range C) density readings of the solution, in 100 × density (100 × D) units, are taken on Scale A after the instrument had been set at zero with distilled water. The other set of solutions is now pre-heated in the constant temperature bath for 20 minutes and filtered following the same procedure as for the dye-containing solutions. Every filtered control solution which gives a photometer reading higher than 3 is diluted in the same manner as the corresponding dye solution and its density recorded. The difference between the density of the dye solution and that of the control is converted to mg. of dye per 100 ml. of solution. For this purpose a previously-prepared calibration curve is used which was obtained by measuring in the photometer dye solutions of known concentrations with Aerosol MA as the solubilizing agent. Finally, depending on the dilution used, the results are multiplied by the factor 1, 2, 5, or 10 respectively.

Materials

The surface-active agents were all commercial products excepting Lauric-Igepon T (a medium molecular weight methyl tauride) which had been prepared experimentally at this laboratory. The commercial surface-active agents used are described as follows: the *wetting agents* included esters of sodium sulfosuccinic acid (Aerosol MA and Aerosol OT, American Cyanamid and Chem. Co.) and sodium salts of organic sulfonates (Nekal BX and Nekal NS, General Aniline and Film Corp.—GDC). *Emulsifying*

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* Aerosol MA at this relatively high concentration gives a clear and stable solution having the required solubilizing power.

agents were organic ethers of a long chain fatty acid and a fatty alcohol respectively (Emulphor ELA, Emulphor ON, General Aniline and Film Corp.—GDC), sulfonated castor oil (Monopol Brill. Oil, General Aniline and Film Corp.—GDC) and a sulfonated ethylene formaldehyde condensation product (Tamol NNO, Rohm and Haas). The *detergents* used were fatty alcohol sulfates (Gardinol WA and Dupanol ME, E. I. duPont de Nemours Co.), a substituted phenol ethylene oxide condensation product (Igepal CA, General Aniline and Film Corp.—GDC), high molecular weight methyl taurides (Igepon T and Cyclopon A, General Aniline and Film Corp.—GDC) and an alkyl aryl sulfonate (Nacconol NR, Allied Chemical and Dye Corp.—National Aniline Division). The *soaps* tested were Lux (Lever Bros.) and sodium oleate (Baker Chemical Co.). The *hydrotropic agents* were sodium xylenesulfonate (Wyandotte Chemicals Corp.) and sodium-p-toluene sulfonate (Eastman Kodak Co.).

Some of the dyestuffs and azo compounds which are described in more detail in Table II were available as commercial products, and some were synthesized especially in small experimental quantities. The following commercial dyes were obtained as amorphous powders: Sudan Orange RA and another Sudan Orange equivalent to Orange OT [General Aniline and Film Corp.—General Dyestuff Corp. (GDC)]; FD&C Yellow No. 3 (Allied Chemical and Dye Corp.—National Aniline Division). Orange OT (Dye No. 2) was used in crystalline form for most experiments. It was prepared by recrystallizing the dye from ethanol after dissolving about 45 g./liter at the boil under reflux. After vacuum filtration the dye was dried at 50°C. in a vacuum. Two experimental azo compounds (Nos. 4 and 5) were obtained in essentially amorphous form as prepared in the dye section of this laboratory. The available amounts were insufficient for recrystallization. Another experimental compound (No. 6 in Table II) was purchased from Republic Laboratories, Chicago, Ill. The product was crystalline but exhibited at first considerable water solubility; after being washed several times in distilled water, the residual material appeared to be essentially water-insoluble.

Specificity of Various Dyestuffs

Some consideration was given to the selection of a suitable type of water-insoluble dyestuff. The data presented by Merrill and McBain (17) had shown that slightly different dyestuffs vary greatly in their solubilization values. For instance, it was found that certain surface-active agents solubilize 10 times as much Yellow AB (Dye No. 3) as Orange OT (Dye No. 2). The authors attributed this phenomenon to the more hydrophilic character of Yellow AB. Hartley (3) offered an explanation for the relatively high solubility of dimethylaminoazobenzene (Dye No. 7); his concept of "amphipathy" suggests the possibility of a specific and varying interaction between dyes having polar groups and the colloidal micelles formed by the different surface-active agents.

Before selecting Orange OT for the testing of colloidal solutions, the solubilization characteristics of four oil soluble dyestuffs and two unsubstituted azo compounds of similar structure were studied. The chemical constitution, wave length of maximum light absorption, and other properties of the dyes and compounds are given in Table II, where some literature data for dye No. 7 are included for comparison. The spectral absorption curves of the compounds Nos. 1 to 6 in solution, as shown in Figure 3, were determined in a GE and Cary recording spectrophotometer for the visible and ultraviolet spectral range respectively. The solutions were prepared in 8×10^{-3} g./liter concentration in acetone and were measured in a 1-cm. absorption cell. The absorption curves are characteristic of the compounds in the organic solvent but some changes of absorption characteristics, accompanied by slight shifts in the absorption maxima, can be expected in aqueous solutions containing surface-active agents.

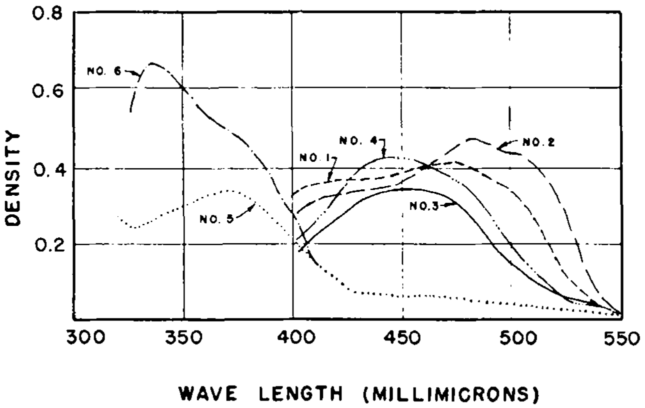


Fig. 3. Spectral absorption curves of various dyes and azo compounds. (See Table II.)

The extinction coefficient (k) listed in Table II, is defined as

$$k = \frac{1}{cd} \log \frac{I_0}{I}$$

where I_0/I is the ratio of the light intensities after absorption in the solvent and in the solution respectively, c is the concentration of dye in the solution (g./liter) and d the cell thickness in cm. (in this case $d = 1$).

The compounds Nos. 1 to 6 were tested for relative solubilization in five solutions, each containing a different type of surface-active agent. The experimental procedure followed was essentially as outlined above except that amorphous dyes and compounds were used; furthermore, photometric density readings were employed for the comparison below without further conversion to actual dye concentrations.

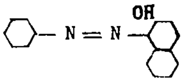
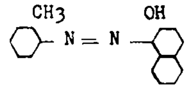
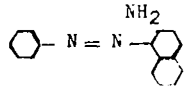
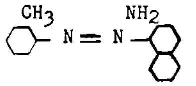
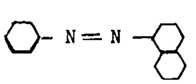
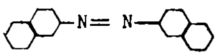
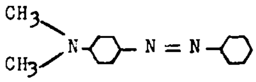
The results obtained in this experiment with compounds Nos. 1 to 5 are summarized in Table III. Relative amounts of solubilized dye were obtained by setting the maximum photometric value in each column at 100 and calculating the other values in proportional units. For the testing of colloidal solutions these relative solubilization values for the various compounds with different types of surface-active agents seemed of greater importance than the absolute amounts solubilized. However, the maximum photometric value for each dye is included at the bottom of the table to give an approximate index of the absolute amounts.

The data confirmed the contention that slight structural changes in the water-insoluble material influence greatly the solubilization values obtainable with different types of surface-active agents. On a relative basis, compounds Nos. 1 and 2 are solubilized

TABLE II

Chemical and Physical Data for Various Azo Compounds

Light Absorption Data Determined in Acetone Solutions (8×10^{-3} g./liter)

Azo Dye or Compd. Exp. No.	Trade Name or Designation in Literature	Chemical Name	Chemical Structure	Abs. Max. (λmax.) mμ	Approx. Extinction Coefficient (k) at λ max.	Photometer Readings (100xD)
1	Sudan Orange RA	1-phenylazo-2-naphthol		472	51	38
2	F.D.&C.Orange #2 or Orange OT	1-o-tolylazo-2-naphthol		481	56	37
3	F.D.&C.Yellow #3 or Yellow AB	1-phenylazo-2-naphthylamine		450	44	24
4	Experimental	1-o-tolylazo-2-naphthylamine		445	53	28
5	Experimental	1-phenylazo-naphthalene		372	43	6
6	Experimental	2,2'-azo bis naphthalene		336	83	8
7	DMAB	dimethylamino-azo benzene		406*	127*	-

* Value reported by Kolthoff and Strickd (5) for DMAB in theanol(10^{-2} g./liter).

TABLE III

Solubilization of Various Oil Soluble Dyestuffs in Solutions of Surface-Active Agent

(1.0 g./liter active material in distilled water)

Surface-Active Agent	Dye or Compound Number				
	1	2	3	4	5
	Relative Amounts of Dye Solubilized (Arbitrary Units, Different for Each Dye)				
Cyclopon A	100	100	99	96	62
Igepal CA	44	64	100	100	100
Lux Flakes	54	40	17	14	35
Nacconol NR	27	41	12	10	10
Nekal BX	18	9	6	4	5
Distilled Water—Control	9	1	0	0	0
	Maximum Photometric Values (100×D)				
Cyclopon A	110	136	......	......	......
Igepal CA	......	......	286	201	46

to a higher degree by Cyclopon A than by the other agents, while compounds Nos. 3, 4, and 5 are solubilized preferentially in Igepal CA. The specificity becomes particularly obvious in the case of Lux Flakes and Nacconol NR; this is in contrast to the solubilization obtainable with Nekal BX (a typical wetting agent) which is relatively low for all compounds tested.

In view of the possibility of a specific interaction between the more polar molecules and the surface-active agents in solution, it would have been desirable to investigate further the unsubstituted compounds Nos. 5 and 6 for dye solubilization tests. However, the spectral absorption curves given in Figure 3 show that the absorption peaks of compounds Nos. 5 and 6 fall in the ultraviolet. In this range simple filter photometers have no response and this fact explains the low photometer readings shown in Table II for these compounds. It follows that the values given for compound No. 5 in Table III are uncertain. Moreover, in the case of compound No. 6, which gave still lower solubilization values, erratic photometer readings were obtained and the results had to be discarded. Further work with compounds Nos. 5 and 6 is contemplated using spectrophotometric equipment extending into the ultraviolet.

As indicated in the Outline of Procedure, dye No. 2 was ultimately chosen for this investigation. Different lots of recrystallized dye gave solubilization values which were, with few exceptions, reproducible within the experimental error. Although dye No. 2 might give some specific interaction with certain surface-active agents, it appeared preferable to other, more soluble dyestuffs. Moreover, a cursory examination of some data published by Kolthoff and Stricks (5) seemed to indicate that the simple method, presenting solubilization data by plotting linear isotherms, fails with a more soluble dyestuff, such as No. 7.

Effects of Salts

As is known, the solubilization characteristics of surface active agents are influenced considerably by the presence of electrolytes. Since commercial products usually contain varying amounts of inorganic diluents, it will be in general more useful to compare such products on an active material basis.

In order to illustrate the order of magnitude of the salt effects which one encounters in practice, the solubilization isotherms for Gardinol WA (assumed activity: 40%) and Duponol ME (assumed activity: 100%) are shown in Figure 4. The solubilization values for the salt-containing detergent are consistently higher; over a wide concentration range only about half of the amount of active material is needed to obtain the same solubilization values.

A similar effect is shown in Figure 4 for an experimental Lauric-Igepon T sample which was prepared in distilled water and in a solution containing 0.25% sodium sulfate. Figure 5 shows the solubilization obtained with the same product in presence of calcium chloride. The values are first increasing rapidly with the addition of calcium ions, but become fairly constant beyond a concentration of 0.15% calcium chloride hydrate in the solution. In comparative tests it might, therefore, be advisable to add varying amounts of salt to samples to be tested in order to determine the optimum solubilization value for each surface-active agent.

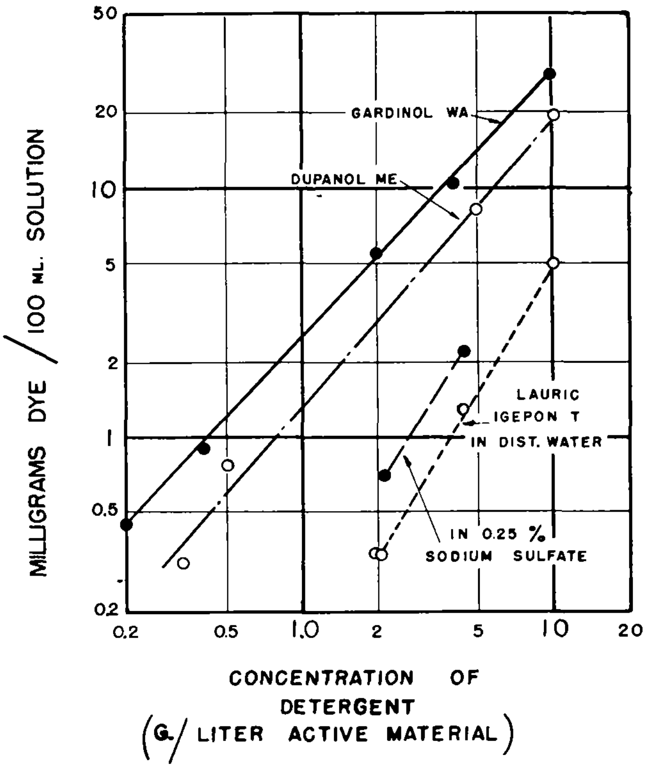


FIG. 4. Effect of salt on solubilization of dye No. 2.

Solubilization Data for Various Agents

Some typical results obtained for various commercial surface-active agents tested with Dye No. 2 are shown in Figure 6. Straight lines were drawn through a number of experimental points determined in several runs made at different times. The scattering of data as indicated is typical for this type of solubilization test. The overall precision is illustrated by a standard deviation of 5% determined for 9 different tests with a 1 g./liter Igepal CA solution and the same lot of recrystallized dye. The advantage of the log-log plot becomes obvious considering the significance of equi-distant horizontal deviation from any isotherm; irrespective of the position on the graph, deviations of the same magnitude represent the same percentage variation in the amount of surface-active agent.

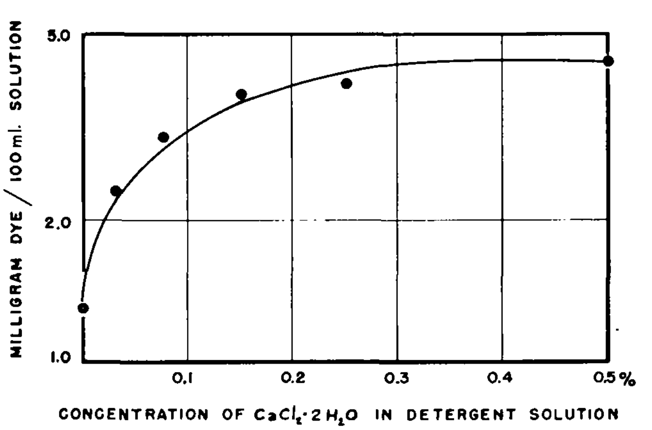


FIG. 5. Effect of calcium ions on the solubilization of dye No. 2 in Lauric-Igepon T solutions.

As can be seen from Figure 6, both the position and the slope of the isotherm are characteristic of the type of surface-active agent. At low concentrations, detergents solublize more dye and have a lower slope than the other types of surface-active agents; wetting agents require higher concentrations for solubilizing an appreciable amount of dye and their isotherms have steeper slopes; and hydrotropic agents require the greatest concentration for solubilizing and their isotherms are the steepest.

The general equation for the solubilization isotherm is

$$S = Kc^n \text{ or}$$
$$\log S = n \log c + \log K$$

where S is the amount of solubilized dye (mg./100 ml. of solution), c the concentration of the detergent solution (grams/liter of active material) and where K and n are constants which are characteristic for each solubilizing agent. The values for n and K, determined experimentally for a number of surface-active agents (including the ones shown on Figure 6), are listed in Table IV. An additional column is included giving the concentration of each surface-active agent (g./liter active material) which is required for solubilizing 1 mg. of dyestuff. For the ready comparison of different surface-active agents, these values appear generally more significant than the absolute amounts of solubilized dye.

Anomalous Solubilization

In the course of this study it was of interest to determine the solubilizing characteristics of mixtures containing anionic and cationic agents. The anomalous behavior of such a mixture is illustrated in Table V. On the basis of active ingredients, considerably more dye is solubilized by the mixture than by either of the components separately.

Spectrophotometric tests were made using the GE recording spectrophotometer in order to determine whether changes of the absorption characteristics might have led to erroneous photometric readings and thus made the solubilization values appear abnormally high. It was found that an error was incurred by using the calibration previously pre-

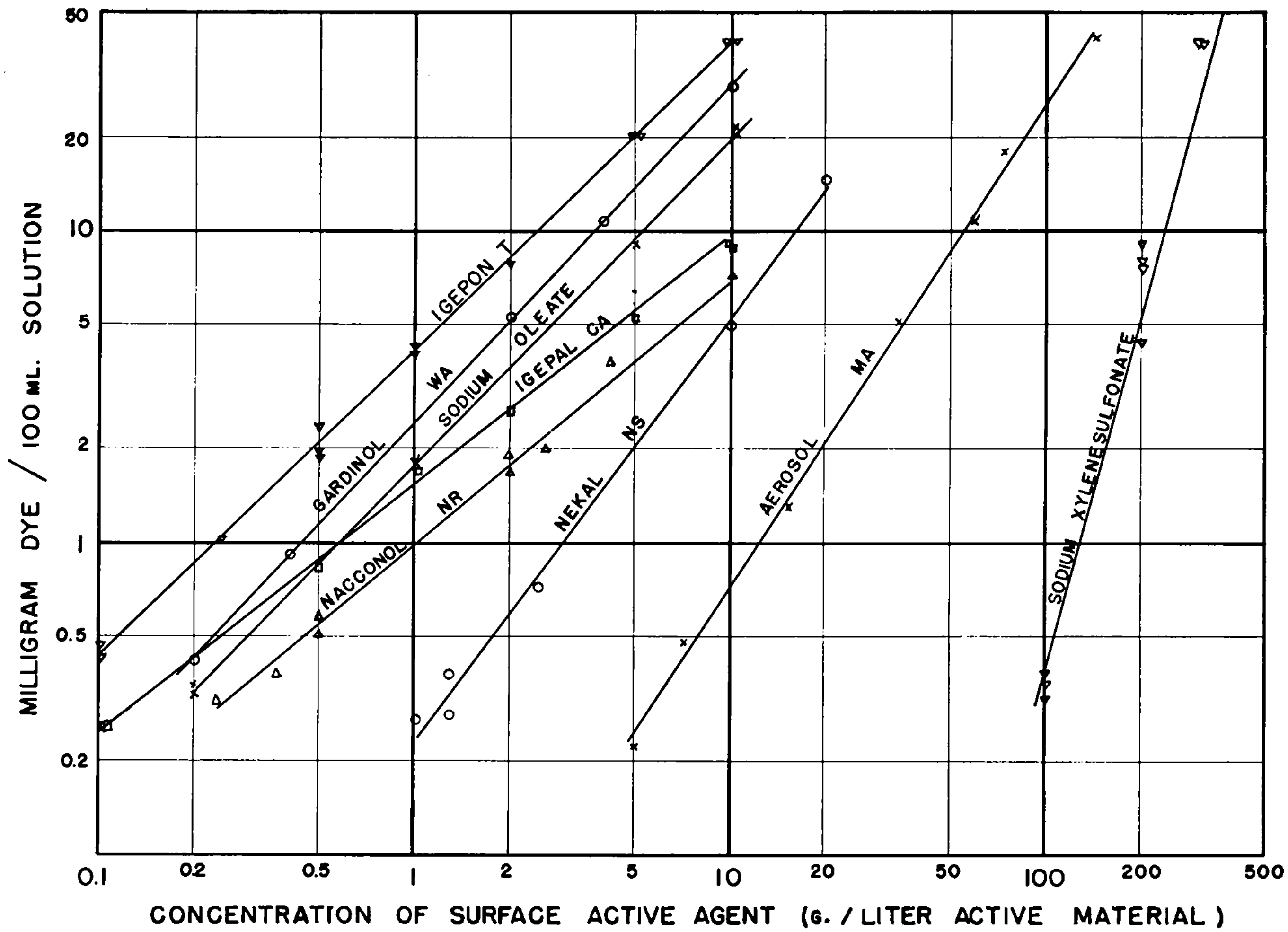


FIG. 6. Solubilization of dye No. 2 in aqueous solutions containing commercial surface-active agents.

TABLE IV
Solubilization Data for Various Surface-Active Agents
(Dye No. 2; Interaction: 15 min. at 50°C.)

Surface-Active Agent	n	Log K	Conc. of S. A. Agent for Solubilizing 1 mg. dye/100 ml. sol. (g./liter active material)
Wetting Agents			
Aerosol MA	1.56	—1.71	12.0
Aerosol OT	1.26	—0.70	3.6
Nekal BX	1.46	—0.68	2.8
Nekal NS	1.34	—0.62	3.0
Emulsifying and Dispersing Agents			
Emulphor ELA	0.83	0.31	0.46
Emulphor ON	0.95	0.11	0.76
Monopol Brill. Oil	1.05	0.29	0.54
Tamol NNO	0.83	—0.33	2.5
Detergents			
Gardinol WA	1.09	0.38	0.44
Igepal CA	0.80	0.19	0.58
Igepon T	1.00	0.61	0.25
Nacconol NR	0.83	0.01	1.0
Soaps			
Lux Flakes	1.24	0.19	0.70
Sodium Oleate	1.06	0.24	0.58
Hydrotropic Agents			
Sodium Xylene-sulfonate	3.86	—4.27	140
Sodium-p-Toluene-sulfonate	5.21	—7.47	270

pared with Aerosol MA solutions containing known amounts of dye. Such errors in filter photometry were reviewed in detail by States and Anderson (20). However, an estimate made on the basis of the spectral absorption curves for the various solutions indicated that the effect of stray light could have increased the values given in Table V by not more than 10%. The anomalous solubilization effect shown is definitely of a different magnitude.

TABLE V
Anomalous Solubilization of Dye No. 2 in Aqueous Solutions Containing Mixtures of Surface-Active Agents

Surface Active Agent	Concentration in g./liter Active Ingredients	
	0.2	1.0
	mg. dye/100 ml.	
1:2 Mixture of Cetyl Pyridinium Chloride and Igepon T	1.0	4.2
Cetyl Pyridinium Chloride	0.5	2.6
Igepon T	0.5	2.2

A possible explanation of the enhanced solubilization in the above mixtures might be the incorporation into the micelles of water-insoluble complexes which were described in detail by one of the authors (6). It appears that the expanded micelles solubilize considerably more dyestuff.

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Report of Cellulose Yield Committee 1948-1949

FOUR sets of samples of cotton linter pulp, of three different grades, were checked by 10 different laboratories during the past year. One laboratory, number 9, reported only three sets of results so these are not included in the over-all average for the year. The average yield results for the three types of linters sent out are given below:

Lab. No.	No. Sets Samples Tested	Samples			Over-all Average for Year
		A Linters	B Linters	C Fiber	
1	4	79.8	73.8	69.7	74.4
2	4	80.1	73.1	69.4	74.2
3	4	79.5	73.5	68.7	73.9
5	4	79.9	73.4	69.4	74.2
6	4	80.5	73.7	68.4	74.2
7	4	79.6	72.9	68.2	73.6
8	4	80.2	74.7	70.1	75.0
9	3*	79.0	72.5	69.1	73.5
10	4	80.2	73.5	68.9	74.2
11	4	80.0	74.0	69.9	74.6
Avg.	....	80.0	73.6	69.2	74.3

* Not included in average.

Another laboratory, number 4, which had been checking samples for the past 12 years, dropped out of the checking group due to not having time to make the tests and also stated that since practically identical yields were obtained by all laboratories, they did not think it worthwhile to continue running the routine check samples.

During the year one of the laboratories had to replace the screens in their washers, which were giving low yields; another had to replace the spray pipes. It should be mentioned that both of these conditions should be watched closely and possibly should be changed every two or three years as the holes in the screens and spray pipe increase in size. These should be checked first if low results are obtained.

Considering the fact that cotton linter pulp is very non-uniform in composition and therefore in the cellulose yield, the above results are excellent checks. It has been suggested by some that these check samples be omitted due to the good check results which are obtained. However, the fact remains that during each year there are at least one or two laboratories whose results get out of line but are immediately brought back after finding the trouble, which is usually not too hard to find. For this reason, it is thought that these checks are very valuable in keeping all of the equipment in good working condition as some of this equipment is not used too often in some of the laboratories.

It should be pointed out that this method is not applicable to low hull fiber yields, i.e., below 55%. Hull fiber of this very low grade has very little value and should not be made in the first place. It can be estimated close enough by visual inspection by the purchaser so that agreement can be reached on price without yield test. About one such incident occurs in the country per year. Work will be done next year to see if the method can be amended to include these isolated cases.

Recommendations: It is recommended that samples be sent out to all members of the Cellulose Yield Committee and to laboratories which have been participating in the past in these check samples. Also to any other laboratory which requests in writing, to the Cellulose Yield Committee Chairman, that they would like to be included in this check group. Four sets of samples should be sent out during the next year: one in August, one in October, one in December, and one in February.

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