hard, non-tacky wax fraction. Two procedures investigated consisted of removal of the oil from the tank settlings by washing with acetone, destruction of the phosphatides through hydrolysis or saponification, and subsequent purification by fractionation from isopropanol solution; another involved hydration of the tank settlings, followed by separation of the aqueous and oil phases, and fractionation of the oil phase from isopropanol solution; and two procedures used simple fractionation of the tank settlings with the aid of solvents.

Yield of the hard wax fractions from the typical sample of tank settlings varied from 8.3 to 13.7%, based on the weight of the original settlings. The iodine value varied from 11.1 to 17.6, the free fatty acid content from 2.1 to 7.3%, the phosphorus content from 0.01 to 0.15%. The lowest melting point observed was 75.3°C. and the highest was 79.9.

The samples of hard wax were almost black in color when in the liquid state and could not be bleached readily with activated clay or carbon. The waxes were bleached readily by hydrogen peroxide and by chromium trioxide in the presence of sulfuric acid solution, or by combinations of these reagents. Practically white waxes could be produced with 0.5 part of 29% hydrogen peroxide and 1 part of chromium trioxide per 1 part of wax.

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Solubilization of Orange OT and Dimethylaminoazobenzene

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SOLUBILIZATION, a fundamental phenomenon associated with colloidal aggregates, i.e., miscelles, has been investigated by numerous workers (2, 4, 7, 12). The measurement of solubilization by the dye solubility method appears to be convenient. However considerable variation is to be found in the results reported by different workers. For example, the earlier work reported by McBain and co-workers (2, 10) is found to be at variance with that reported by Kolthoff and Stricks (7). It is our purpose to reinvestigate the dye method with emphasis on the reported points of disagreement.

It was thought that departure from neutrality of the soap solution might account for the divergent results, hence the effect of a slight excess both acid and alkali in Na- and K-laurates was studied. The interesting possibility of the existence of micelles below the critical micelle concentration will be discussed in light of the present work.

Materials Used

Orange OT (F.D. and C. No. 2,1-o-tolyl-azo-2-naphthol), a Calco product, was purified according to directions given by McBain (10).

Dimethylaminoazobenzene (abbreviated as DMAB), a Merck technical product, was recrystallized according to Kolthoff's directions (7).

Potassium and sodium laurate solutions were prepared from Eastman Kodak white label lauric acid and KOH and NaOH solutions (carbonate free), respectively. Solutions were prepared with excess lauric acid (1.6% in Na-laurate and 1.2% in K-laurate) and with excess alkali (1.4% in NaOH and 0.74% in KOH).

Sodium oleate, Baker C.P. neutral grade, was used without further purification.

Dodecylamine hydrochloride (DDA.HCl) was prepared by neutralization of the free DDA (Armour product), dissolved in absolute ethanol, with concentrated HCl. After cooling to 0°C., the white mass of DDA.HCl crystals was filtered, washed first with ether and then with ethanol, and then dried *in vacuo* at room temperature. Analysis for ionizable chloride indicated 99% purity.

Span 20 and Tween 20 were obtained from the Atlas Powder Company and dried at 100°C. for 7 hours before use.

N-Dodecyl-β-alanine hydrochloride was prepared in the same way as DDA.HCl by neutralization of N-dodecyl-β-alanine (G. E. Goodrich product).

Tergitol 4 was obtained from the Union Carbide and Carbon Corporation.

Ultrawet K was obtained from the Atlantic Refining Company.

Technique and Experimental Method

Detergent solutions of varying concentrations were placed in 30-ml. vaccine bottles, with sufficient dye to

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ensure an excess. The bottles were mounted on a wheel 18 in. in diameter and submerged in a constant temperature (30° ± 0.05°C.) water bath. The wheel was modified by the addition of fins so that the current generated by the thermostat stirrer would rotate the wheel at about 20 RPM.

While preliminary tests indicated that equilibria (maximum values) were usually obtained after 24 hours of rotation, agitation cannot be too violent since a greater degree of suspension will result. In these experiments equilibrium was approached from the side of undersaturation. In the case of supersaturated solutions the available evidence indicated that a considerably longer time is required for the dye particles to settle.

After rotation for a given period of time the bottles were placed in an upright position in the thermostat (for 24 hours) to allow the dye particles to settle. Two ml. of the supernatant solution were removed by pipette. A short rubber tube, packed with cotton, was attached to the tip of the pipette so that removal and filtration was accomplished at the same time.

The 2 ml. filtered sample was placed directly into a 20-ml. dry vial and diluted with 2 ml. of ethanol (U.S.P. 95%). For highly colored solutions an additional quantity of 1:1 ethanol-water was added to the vial.

The extinction of the solutions was measured with the Beckman Model DU Quartz Spectrophotometer, using 1-cm cells. The wave lengths of maximum absorption of DMAB and Orange OT were found to be 419 and 497 mμ, respectively, in agreement with Kolthoff's findings (7). However the calibration curves (optical intensity vs. concentration of dye) obtained for both DMAB and Orange OT were found to be about 5% lower than Kolthoff's curves. For comparison with Kolthoff's data all experimental values were corrected for this 5% difference.

Experimental Results

The solubility of Orange OT and DMAB in pure water at 30°C. was found to be 0.2 mg. and 0.4 mg., respectively, which was subtracted from all experimental values to obtain the amount solubilized. The results are compared with those of McBain and of Kolthoff. The effects of different experimental conditions on the solubilization of Orange OT and DMAB in the soap and detergent solutions are presented in Tables I to III.

Discussion

Considering the various sources of experimental errors, such as pipetting, dilution, incomplete sedimentation of the dye, and incomplete filtration of suspended dye, the results reported in this work indicate a fair degree of reproducibility (Table I). The experiments indicate that the experimental techniques used by different workers may account for some of the discrepancies in the values reported in the literature. Previous workers have indicated that it is difficult to attain the true equilibrium value from supersaturated solutions. High values have been attributed to the suspending action of the detergent or to incomplete settling of the dye. Lambert and Busse (9) have reported a rapid semi-quantitative method for the estimation of the solubilizing power of detergents, in which the detergent solutions were heated at 50°C. for five minutes, Orange OT added, and the tubes rotated 10 times. The solutions were allowed to stand at 50°C. for 15 minutes before cooling to 25°C. The results appeared to be quite consistent. However from Table I it can be seen that a settling time of four days was not sufficient in this work since the results are high for DMAB and irregular for Orange OT.

It is generally believed that solubilization occurs only in the presence of micelles and that no solubilization should be noted below the critical micelle concentration since the detergents are thought to exist as non-solubilizing molecules or ions. Kolthoff (7) noticed a slight solubilization at low concentrations and was led to the conclusion that even below the C.M.C. there are a few micelles present.

The results of this work indicate that below the C.M.C. there is no measurable solubilization of either Orange OT or DMAB. In those cases in which a small solubilization value was obtained below the C.M.C., the results obtained in different samplings differed widely from each other, and, in general, this slight solubilization disappeared entirely after the solutions were allowed to stand for longer periods of time. Thus it would appear that the apparent solubilization below the C.M.C. is due either to the suspending action of the detergent or incomplete filtration. McBain did not use a filter in sampling the dye-detergent solution. However he admitted that his values at low concentrations were too high and attributed them to the above reason. Kolthoff used a glass wool filter in sampling the solution, but it is doubtful if this is very effective in removing the suspended dye since it is difficult to pack glass wool tightly. A cotton plug filter was chosen for use in this work because it is easier to obtain a tight pack. To test whether the cotton would adsorb the dye, the following experiment was performed. Ten ml. of the clear dye-soap solution were removed through a small cotton filter. Two ml. were

TABLE I

Solubilization of Orange OT and DMAB in Na-laurate Solutions* at 30°C.

Conc. of soap Moles/liter	Mg. OOT solubilized per liter solution				Mg. DMAB solubilized per liter solution			
	I	II	III	IV	I	II	III	IV
0.3573	385.4	379.4	374.9	378.0	412.7	478.7	457.8	620.6
0.1787	185.9	183.8	183.8	212.1	231.0	241.5	237.3	317.1
0.0893	85.4	75.6	79.0	77.4	94.8	105.0	105.0	152.3
0.0447	22.3	21.6	21.8	29.2	28.0	29.4	30.5	50.2
0.0223	0.6	0.2	0.2	0.2	0.6	0.6	0.5	1.9
0.0112	0.1	0.0	0.0	0.4	0.2	0.2	0.4	0.8
0.0056	0	0	0	0	0	0	0	0
0.0028	0	0	0	0	0	0	0	0

* Excess lauric acid 1.6% of the soap concentration.
I. Rotation for 1 day and standing for 1 day.
II. Further rotation for 3 days and standing for 1 day.
III. Further standing for 1 day.
IV. Standing for 4 days from solutions made supersaturated at 50°C.

TABLE II

Solubilization of Orange OT and DMAB in Detergent Solutions at 30°C.

Detergent	Conc. of detergent Molarity	Mg. dye solz. per liter solution	
		Orange OT	DMAB
K-Laurate with 1.2% excess acid	0.4962	556.5	593.3
	0.2481	222.6	300.6
	0.1241	118.7	161.7
	0.0620	43.3	51.4
	0.0310	9.3	10.1
	0.0155	0.0	0.2
	0.0078	0.0	0.0
K-Laurate with 0.71% excess alkali	0.5512	592.2	693.0
	0.2756	280.4	336.0
	0.1378	154.4	127.1
	0.0689	42.2	58.0
	0.0345	8.4	3.2
	0.0172	0.0	0.0
Dodecylamine Hydrochloride	0.5000	1649	1213
	0.2500	615.3	592.2
	0.1250	267.0	258.3
	0.0625	105.0	103.0
	0.0313	34.4	26.2
	0.0157	8.5	5.4
	0.0079	1.3	0.2
Tween* 20	0.0407	191.1	307.0
	0.0204	92.7	163.0
	0.0102	47.2	81.5
	0.0051	22.9	39.5
	0.00255	10.4	17.9
	0.00128	4.5	8.1
	0.00064	2.0	4.2
	0.00016	0.1	0.2
Span** 20	0.0704	308.1	306.0
	0.0352		138.6
	0.0176	50.9	47.2
	0.0088	34.4	23.9
	0.0044	16.8	
	0.0022	6.2	6.3
	0.0011	3.4	4.0
	0.0003	0.3	1.0
N-Dodecyl-β-alanine Hydrochloride	0.0638***	56.3	72.5
	0.0319***	19.2	32.8
	0.0160	8.5	18.1
	0.0080	0.6	2.2
	0.0040	0.4	00.4
Na-Oleate	0.0938	297.2	
	0.0469	132.3	
	0.0234	56.7	
	0.0117	24.1	
	0.0059	10.5	
	0.0043	6.1	
	0.0029	2.6	
	0.0015	0.5	
	0.0007	0.3	

* M.W. was assumed to be 1235.

** M.W. was assumed to be 355.

*** Supersaturated solutions, the excess detergent crystallized out during experiments.

TABLE III

Solubilization of Orange OT in Tergitol 4 and Ultrawet K Solutions at 30°C.

Conc. of detergent Gms/liter*	Mg. dye solz. per liter soln.	
	Tergitol 4	Ultrawet K
50		110.0
25	39.9	57.2
12.5	11.4	25.1
6.25	3.2	13.2
3.13	0.9	5.3
1.56	0.0	1.7
0.78	0.0	1.0
0.39		1.0

* Concentration for Tergitol 4 has been reduced to anhydrous basis.

pipetted from this filtered dye-soap solution, diluted with alcohol, and the extinction measured. The rest of the solution was agitated with cotton for two minutes. Then 2 ml. was withdrawn and similarly diluted. The extinction was identical with the former one, indicating that cotton does not adsorb solubilized dye. Another sample taken from the same solubilization bottle, without the use of the cotton filter, showed a much greater extinction, indicating that the cotton filter was effective in removing the suspended dye particles.

Our results on solubilization in Na- and K-laurate agree more with Kolthoff's than with McBain's data. The large difference reported in solubilizing power between Na- and K-laurates cannot be attributed to the departure from neutrality of the soap solutions since an excess of either acid or alkali did not effect the amount solubilized to an appreciable extent. The effect of excess acid or alkali on solubilization of hydrocarbons in solutions of laurates has recently been published by McBain and Stissant (11). Their results seem to support this work.

It should be noted that McBain's data were obtained at 25°C. and should theoretically be lower than that which would be obtained at 30°C. However the difference in solubilization between 25° and 30°C. is probably small and may be neglected in the comparison.

The agreement between different workers on the solubilization of dyes in dodecylamine hydrochloride

TABLE IV

Critical Micelle Concentrations

Detergent	Temp. °C.	C.M.C. Molar	Method of Determination
Na-laurate	30	0.0275	Solz. with OOT (excess acid)
	30	0.0282	Solz. with OOT (excess alkali)
	30	0.0275	Solz. with OOT, our plot with Kolthoff's data (8)
	30	0.0253	Solz. with OOT, Kolthoff's data (7)
	25	0.027	Solz. with OOT, our plot with McBain's data (2)
	25	0.0195	Solz. with OOT, Kolthoff's plot with McBain's data (7)
	30	0.0282	Solz. with DMAB (excess acid)
	30	0.0250	Solz. with DMAB (excess alkali)
	30	0.0265	Solz. with DMAB, our plot with Kolthoff's data (7)
	30	0.0255	Solz. with DMAB, Kolthoff's data (7)
	17-70	0.028	Conductivity (1)
	60	0.026	pH measurement (14)
K-laurate	30	0.023	Solz. with OOT (excess acid)
	30	*0.0245*	*Solz. with OOT (excess alkali)*
	30	0.023	Solz. with OOT, our plot with Kolthoff's data (7)
	30	0.0235	Solz. with OOT, Kolthoff's data (7)
	25	0.0295	Solz. with OOT, our plot with McBain's data (2)
	25	0.028	Solz. with OOT, Kolthoff's plot with McBain's data (7)
	30	0.0250	Solz. with DMAB (excess acid)
	30	0.0325	Solz. with DMAB (excess alkali)
	30	0.0255	Solz. with DMAB, our plot with Kolthoff's data (7)
	30	0.0235	Solz. with DMAB, Kolthoff's data (7)
	30	0.022	Laurate-ion activity (6)
	25	0.0215	Spectral dye method (8)
		0.0235	
	35	0.0205	Spectral dye method (8)
		0.0220	
	25	0.0255	Interferometric method (5)
	35	0.0270	Interferometric method (5)
Dodecylamine Hydrochloride	30	0.0115	Solz. with OOT
	25	0.0156	Solz. with OOT, our plot with McBain's data (2)
	30	0.0115	Solz. with DMAB
	30	0.0124	Solz. with DMAB, our plot with Kolthoff's data (7)
	30	0.0134	Solz. with DMAB, Kolthoff's data (7)
	30	0.0129	Conductivity (13)
		0.0131	
	26	0.0124	Spectral dye method (8)
		0.0136	
Tween 20	30	0.0003	Solz. with OOT or DMAB
Span 20	30	0.0002	Solz. with OOT
	30	0.0000	Solz. with DMAB
N-Dodecyl-β-alanine Hydrochloride	30	0.004	Solz. with OOT or DMAB
Na-oleate	30	0.00237	Solz. with OOT
	25	0.00058	Solz. with OOT, our plot with McBain's data (2)
	30	0.0011	Solz. with DMAB, Kolthoff's data (7)
Tergitol 4	30	3 gms/1	Solz. with OOT
Ultrawet K	30	0.5 gms/1	Solz. with OOT

is also poor. Our data with DMAB gives a linear relationship with concentration whereas Kolthoff reported an increase in solubilization with increase in concentration. It is interesting to note that Orange OT is solubilized more than DMAB in DDA.HCl while the reverse is true in the case of N-dodecyl- alanine hydrochloride, suggesting a difference in mechanism by which micelles incorporate the dyes of different structures.

Results of Na-oleate agree fairly well with those of McBain (10).

Results using Span 20 indicate that solubilization characteristics are shown by detergents that are dispersible but not soluble in water. However the solubilization is slow, showing only two-thirds of the maximum values after one day of rotation. It is also interesting to note that Tween 20 solubilizes about twice as much DMAB as Orange OT (on molar basis) whereas Span 20 solubilizes the two dyes to about the same extent.

Solubilization data has been used to determine the critical micelle concentration of detergents, by plotting the amount of solubilized dye against detergent concentration. In general, the C.M.C. found by solubilization is of a magnitude comparable to that obtained by other methods, such as pH measurements and the spectral dye procedure. However it is difficult to obtain accurate C.M.C. values because, first, solubilization is not linearly proportional to concentrations above the C.M.C. and a straight line cannot legitimately be drawn to find the intersection on the abscissa or concentration axis, and secondly the nature of solubilization below the C.M.C. is doubtful. Assuming no solubilization below the C.M.C., the C.M.C. found by using data in this work agree well with the values obtained by plotting both Kolthoff's and McBain's data. The C.M.C. for Na-laurate from this work is 0.0275 or 0.0282 M, and our plot of the data of Kolthoff and of McBain gives 0.0275 and 0.027 M, respectively. In contrast, Kolthoff reported a C.M.C. of 0.0253 M from his data and 0.0195 from McBain's data (Table 4).

Summary

1. Solubilization data have been obtained for aqueous solutions of Na-laurate, K- laurate, dodecylamine-HCl, Tween 20, Span 20, N-dodecyl- -alanine-HCl, Na-oleate, Tergitol 4, and Ultrawet K, using the water insoluble dyes, Orange OT, and dimethylaminoazobenzene as the solubilized substances. Results indicate that the dye solubility method is fairly reproducible. Filtration of samples was found to be an important part of the technique.

2. A slight excess of fatty acid or of alkali in Na- and K-laurate solutions was found to have no appreciable effect on solubilization.

3. In agreement with Kolthoff's but not with McBain's findings, the Na- and K-laurates were found to yield the same solubilization of either DMAB or Orange OT, indicating that the solubilizing species in solution depends upon the nature of the long chain ion.

4. Agreement on solubilization for dodecylamine-HCl with previous workers is poor.

5. The present work indicates no solubilization below the critical micelle concentration. The apparent solubilization reported by Kolthoff was attributed to suspended dye.

6. The use of solubilization data in the determination of critical micelle concentration is examined, and values are compared with previous works.

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Preparation of Peroxide Concentrates from Autoxidized Fatty Acid Esters[1,2]

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ALTHOUGH the first relatively concentrated hydroperoxides of fatty materials were isolated by molecular distillation (4), there are several objections to the use of this method for the separation of peroxides from autoxidized fatty acid esters, especially from autoxidized linoleates and linolenates. First, a portion of the peroxides is destroyed by decomposition or other alterations during distillation (10). This, coupled with the difficulty of obtaining good fractionation by molecular distillation, makes it almost impossible to obtain a high yield of the original peroxides in concentrated form.

Swift, Dollear, and O'Connor (11) isolated hydroperoxides from autoxidized methyl oleate in 85 to 90% concentration by a low temperature fractionation procedure in which the unoxidized oleate was segregated by crystallization from acetone at —80° C. The peroxides were recovered from the filtrate and

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