[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, STANFORD UNIVERSITY]

Solubilization of Water-Insoluble Dye in Soap Solutions: Effects of Added Salts

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Solubilization consists in the spontaneous passage of molecules of a substance insoluble in a given solvent into a dilute solution of a detergent in that solvent, to form a thermodynamically stable solution.[1,2] This phenomenon is characteristic of solutions of colloidal electrolytes, and from a theoretical consideration of the probable mechanism any factor affecting the formation of colloidal particles would be expected to influence the solubilizing power.[3] The addition of salt containing a common ion to solutions of anion active or cation active detergents or colloidal electrolytes has been shown to affect the amount of insoluble material solubilized in dilute solutions.[4,5,6] Hartley found that sodium chloride enhanced the solubilizing action of cetyl pyridinium chloride[6]; McBain and Johnson found a similar effect when potassium chloride was added to potassium laurate and myristate.[5]

Using potassium laurate as a representative detergent of the anion active type, a series of measurements has been made on the solubilizing ability of soap over a wide range of concentrations in the presence of a constant amount, 1.0 *N*, of different salts. Salts greatly increase the solubilizing power of potassium laurate for dye. This increase extends over the whole range of concentration of soap. It is most striking in dilute solutions where the soap would solubilize but little if at all; but up to the highest concentration of soap the solubilizing power per mole of soap is still increasing. The quantitative relation does not vary greatly with the potassium salt used. In the concentration range between 0.25 and 1.00 *N* soap, with 1 *N* salt present, the solubilization of dye per mole of soap continues to increase with increasing concentration of soap. In the case of soap alone, where solubilization seemed to reach a nearly constant level in this range it increased again in still higher concentrations of soap. The physical and colloidal properties of potassium laurate which have already been studied add to the significance of these data. According to osmotic[7,8] and conductance[9] measurements, this soap reaches full colloidal form in about 0.2 *N* aqueous solutions. The nearly constant amount of dye solubilized per mole of soap beyond this concentration indicates almost no increase in the proportion of colloidal particles in the pure soap solution throughout most of the more concentrated range until much higher concentration is reached. The effect of salt which magnifies the solubilization and still produces a marked increase in all concentrations of soap points to either an increase in effectiveness or in amount of the effective colloidal micelles.

Experimental

Materials.—Orange OT (F. D. and C Orange No. 2; 1-*o*-tolyl-azo-2-naphthol) which had been recrystallized from boiling alcohol and dried at 80° was used. Treated thus, the dye was in crystalline form, bright orange-red in color, and insoluble in water and in inorganic salt solutions at room temperature.

Potassium laurate was prepared by Dr. M. E. L. McBain by neutralization of Kahlbaum "purest" lauric acid with carbonate-free potassium hydroxide. Stock solutions were prepared from this according to two methods. (a) For a conveniently weighed-out stock solution, 0.10 mole of soap was added to 100 g. of water, containing 0.004 equivalent of potassium hydroxide to suppress hydrolysis. The volume normality of this solution was then calculated to be 0.819 *N* by the formula

$$N_v = 1000 d_4^{25}/(1000 + MN_w)$$

by using the density reported by Bury and Parry,[10] where *d* is density and *M* is molecular weight. This method eliminated the tediousness of preparing a definite volume of such a substance with such foaming properties. (b) One-tenth mole of soap was placed in a 100-cc. volumetric flask and enough water added to dissolve it with only gentle rotatory agitation in a thermostat for five to six hours at 25°. This treatment did not produce foam, so that the solution could then be made up to the volume mark.

The potassium chloride, potassium hydroxide, and potassium thiocyanate were Baker C. P. products. The thiocyanate was fused at 120° for forty-eight hours, cooled, powdered and again dried at 120° for forty-eight hours.[11] This treatment produced a dry form sufficiently stable for weighing. The potassium sulfate was a Kahlbaum product.

Acetone of technical grade was distilled to obtain an optically clear liquid for dilutions in making dye concentration measurements in the Lumetron (Photovolt's photoelectric colorimeter Model 402E). Equal volume mixtures of acetone and water were used in making dilutions for colorimetric measurements to prevent the precipitation of the dye, salt, and soap.

Method.—Series of solutions of varying soap concentration but with constant salt were made up by diluting a definite volume of the stock solutions of potassium laurate, after weighing the desired amount of salt into the volumetric vessel. These solutions were placed in 50 cc. glass bottles, with sufficient dye added to form a small amount of excess solid, sealed with plastic caps, lined with pure gold foil, and placed on an agitator in a 25° water thermostat. Solutions of concentrations below 0.2 *N* were found to require only two or three days to reach equilibrium value for maximum solubilization. The more concentrated solutions required from one to two weeks, depending on the concentrations. All solutions, including the dilute ones, were remeasured until constant.

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(1) McBain and McBain, THIS JOURNAL, **58**, 2610 (1936).

(2) McBain, Merrill and Vinograd, *ibid.*, **63**, 670 (1941).

(3) McBain, "Solubilization and Other Factors in Detergent Action," in "Advances in Colloid Science," Vol. I, Interscience Publishers Co., Inc., New York, 1942, pp. 99–142.

(4) McBain and Merrill, *Ind. Eng. Chem.*, **34**, 915 (1942).

(5) McBain and Johnson, THIS JOURNAL, **66**, 9 (1944).

(6) Hartley, *J. Chem. Soc.*, 1968 (1938).

(7) McBain and Bolduan, *J. Phys. Chem.*, **47**, 94 (1943).

(8) McBain and Brady, THIS JOURNAL, **65**, 2072 (1943).

(9) McBain, Laing and Titley, *Trans. Chem. Soc.* (London), **115**, 1282 (1919).

(10) Bury and Parry, *J. Chem. Soc.*, 625 (1935).

(11) Kolthoff and Lingane, THIS JOURNAL, **57**, 2129 (1935).

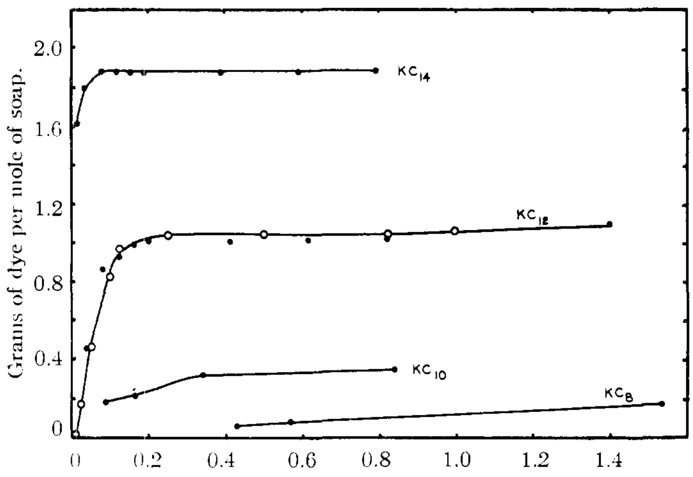

Fig. 1.—Solubilization of Orange OT in various concentrations of aqueous solutions of soaps at 25°: potassium myristate, KC_{14}; potassium laurate, KC_{12}; potassium caprate, KC_{10}; potassium caprylate, KC_8.

In order to measure dye concentration, the bottles were first placed upright in a stationary position in the thermostat for ten to twenty hours until the excess dye had settled, leaving clear, transparent colored solutions above. One-cc. portions were then removed by serological pipets, and diluted in volumetric flasks with 50% acetone in preparation for measurements of percentage transmission by the colorimeter. The B-420 blue filter (with transmission in the range 4000–5300 Å., was used, for which a calibration curve had been obtained by dissolving known amounts of dye in acetone and benzene. From the instrumental readings of percentage light transmitted, the dilution of the 1-cc. sample, and the concentration of the solution, the amount of dye solubilized by the soap was calculated. Three or four measurements made at different dilutions of the same solution were found to agree within 2% on the calculation of mg. of dye per 100 cc. of solution. For the very dilute solutions, no dilutions were made, and their transmission was compared directly with that of the pure soap solution of the same concentration.

Experimental Data

The solubility of Orange OT in various concentrations of pure potassium laurate was measured in order to extend previous data to a wider range of concentration, and to establish a reference for the interpretation of the effects of salts. The results given in Table I were at first sight higher than those obtained by McBain and Johnson.[5] This was found to be due to a systematic error entering into their method of calculating the amount of dye solubilized by one mole of soap in a molal solution for which the amount of dye per 100 cc. volume had been correctly measured and published. The necessary recalculation was made after careful consideration of their methods of preparing each solution, and the resulting values for potassium laurate (Table IV) agree with those observed in the experiments reported in this paper. Tables II to VIII present the recalculated values for grams of dye per mole of soap, and Figs. 1, 2 and 3 show the graphs of Tables I to VIII; these supersede Figs. 1, 2, and 4 of McBain and Johnson and the corresponding columns of their Tables II to VIII. Since the molecular weight of the dye is 262.3 the molar ratio between dye and total soap is obtainable by dividing the numbers given by 262.3. The values are low but not by any means negligible on account of the high molecular weight of the dye.[12]

Tables IX, X, XI and XII present the data for the effect of 1 *m* potassium salts, namely, the chloride, hydroxide, sulfate and thiocyanate. Table XIII gives the data for very dilute solutions of potassium laurate as affected by sulfate, chloride and thiocyanate. The results are shown graphically in Figs. 4 and 5. It is seen that in all cases the electrolytes greatly increase the solubilization of dye by the soap. In the graphs molar ratio of dye to soap is based upon the total soap. Several authors have recently suggested that it might be better to base the ratio upon that fraction of the soap which is in colloidal form if this were accurately known. Since above the critical concentrations simple fatty ions rapidly disappear from solution, the diagrams become identical with those here given and it would be quite erroneous to subtract the critical concentration from the total concentration of the soap.

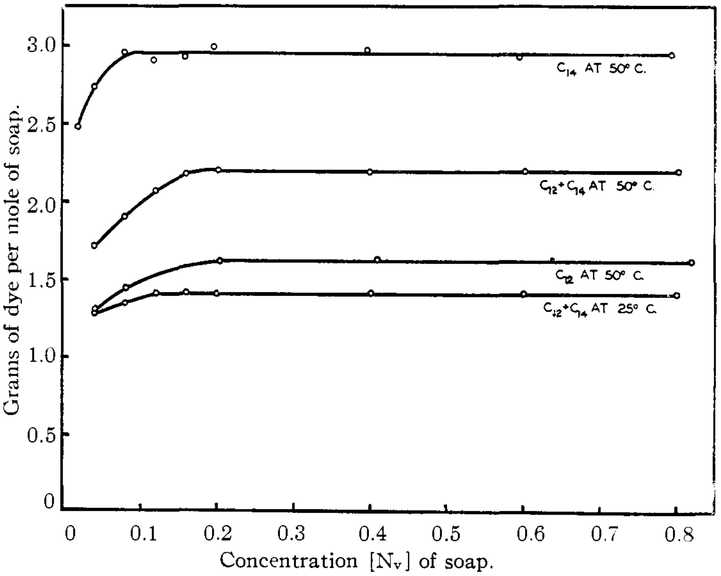

Fig. 2.—Solubilization of Orange OT in various concentrations of soaps: potassium myristate, KC_{14}; potassium laurate, KC_{12}.

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(12) McBain and Richards, *Ind. Eng. Chem.*, **38**, 642 (1946).

TABLE I

SOLUBILIZATION OF ORANGE OT IN AQUEOUS SOLUTIONS OF POTASSIUM LAURATE (KC$_{12}$) AT 25°

N vol. concn.	G. dye/mole KC$_{12}$
0.0001	. .
.001	. .
.005	0.02
.01	0.02
.025	0.176
.049	0.462
.098	0.833
.125	0.970
.250	1.038
.500	1.044
.820	1.041
1.000	1.076
1.500	2.167[a]

[a] From supersaturation. The viscosity of this solution may have kept it supersaturated, or have kept finely divided dye suspended.

TABLE II

SOLUBILIZATION OF ORANGE OT IN VARIOUS CONCENTRATIONS OF AQUEOUS SOLUTIONS OF POTASSIUM CAPRYLATE (KC$_8$) AT 25°

N_v vol. concn. of soap	From undersaturation g. dye/mole KC$_8$	From oversaturation[a] g. dye/mole KC$_8$
0.426	0.064	0.075
.562	.087	. . .
1.532 (2.0 m)	.150	0.174

[a] In general results from undersaturation are nearer the equilibrium value than those from oversaturation because of the long persistence of oversaturation; the true values should be bracketed between them.

TABLE III

SOLUBILIZATION OF ORANGE OT IN VARIOUS CONCENTRATIONS OF AQUEOUS SOLUTIONS OF POTASSIUM CAPRATE (KC$_{10}$) AT 25°

N_v vol. concn. of soap	From undersaturation g. dye/mole KC$_{10}$	From oversaturation g. dye/mole KC$_{10}$
0.084	0.216	0.177
.168	.221	. . .
.335	.308	0.336
.839 (1.0 m)	.348	.345

TABLE IV

SOLUBILIZATION OF ORANGE OT IN VARIOUS CONCENTRATIONS OF AQUEOUS SOLUTIONS OF POTASSIUM LAURATE (KC$_{12}$) AT 25°

N_v vol. concn. of soap	From undersaturation g. dye/mole KC$_{12}$	From oversaturation g. dye/mole KC$_{12}$
0.041	0.473	0.476
.082	.842	.906
.123	.873	.989
.164	.954	1.024
.205	1.018	1.026
.410	0.964	1.043
.615	.969	1.058
.819 (1.00 m)	1.015	1.043
1.403 (2.00 m)	1.101	. . .

TABLE V

SOLUBILIZATION OF ORANGE OT IN VARIOUS CONCENTRATIONS OF AQUEOUS SOLUTIONS OF POTASSIUM MYRISTATE (KC$_{14}$) AT 25°

Vol. concn. of soap	From undersaturation g. dye/mole KC$_{14}$	From oversaturation g. dye/mole KC$_{14}$
0.020	1.63	. . .
.040	1.81	1.81
.079	1.88	1.92
.119	1.85	1.91
.159	1.84	1.91
.196	1.85	1.93
.396	1.85	1.92
.592	1.83	1.93
.793 (1.00 m)	1.86	1.92

TABLE VI

SOLUBILIZATION OF ORANGE OT IN VARIOUS CONCENTRATIONS OF AN EQUIMOLAR MIXTURE OF POTASSIUM LAURATE AND POTASSIUM MYRISTATE, AT 25°

N_v vol. concn. of soap	From undersaturation g. dye/mole soap	From oversaturation g. dye/mole soap
0.040	1.28	1.29
.080	1.32	1.36
.120	1.41	1.43
.160	1.41	1.44
.201	1.37	1.45
.401	1.37	1.43
.602	1.38	1.41
.802 (1.00 m)	1.40	1.42

TABLE VII

SOLUBILIZATION OF ORANGE OT IN VARIOUS CONCENTRATIONS OF SOAPS AT 50°

N_v vol. concn. of soap	g. Dye/mole soap	N_v vol. concn. of soap	g. Dye/mole soap	N_v vol. concn. of soap	g. Dye/mole soap
I. Potassium Laurate		II. Potassium Laurate and Potassium Myristate Mixed 50:50		III. Potassium Myristate	
0.041	1.29	0.040	1.71	0.020	2.47
.082	1.44	.080	1.90	.040	2.73
.205	1.62	.120	2.07	.079	2.96
.410	1.63	.160	2.18	.119	2.90
.819 (1.00 m)	1.62	.201	2.19	.159	2.92
		.401	2.18	.196	2.99
		.602	2.19	.396	2.96
		.802 (1.00 m)	2.18	.592	2.92
				.793	2.94

TABLE VIII

SOLUBILIZATION OF ORANGE OT IN VARIOUS CONCENTRATIONS OF POTASSIUM LAURATE AND POTASSIUM MYRISTATE AT 25° IN THE PRESENCE OF 1 m POTASSIUM CHLORIDE

N_v vol. concn. of soap	Laurate g. dye/mole soap	Myristate g. dye/mole soap
0.010	1.53[a]	3.90[a]
0.025	1.08	3.78[a]
.049	1.16	2.73
.191	1.09	2.84
.450	1.19	. .

[a] Includes suspension; see later section of this communication.

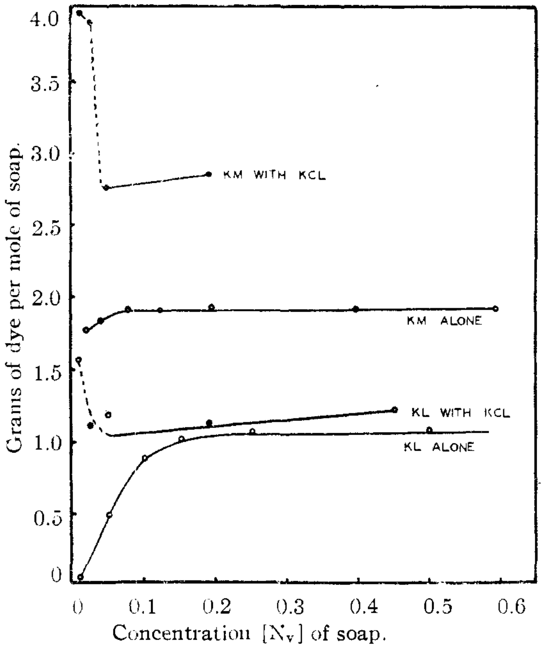

Fig. 3.—Solubilization of Orange OT in various concentrations of potassium laurate and potassium myristate at 25° in the presence of 1 *M* potassium chloride: M, myristate; L, laurate.

Discussion

Solubilization in Solutions of Soap and Detergents without Salt.—The graphs show that in sufficiently dilute solutions of detergents there is no solubilization, presumably because there are no colloidal particles in which the solubilized material can be incorporated. Then as suitable micelles form in the solution upon increase of concentration, the amount of dye solubilized by each mole of soap rises to a constant value, which increases again only in the highest concentrations. Comparing the constant values for the various soaps in the homologous series it is seen that the amount of dye solubilized per equivalent of soap rises very rapidly, being 162 mg. for KC_8, 347 for KC_{10}, 1050 for KC_{12} and 1880 for KC_{14}. This increase is out of all proportion to the increase in the amount or length of the hydrocarbon chain in the molecule of soap which is only in the ratio of 1:1.25:1.50:1.75, whereas the amounts solubilized are as 1:2.14:6.48:11.61. Hence the solubilization is obviously not proportionate to the amount of hydrocarbon in the soap molecules. Where practically all the soap is in the form of micelles, as in the higher concentrations, it must also be true that the solubilization is not proportionate to the amount of hydrocarbon in those micelles. Of course, some micelles may be incapable of solubilizing; the lack of proportionality between amounts of organic liquids solubilized and the increase in X-ray spacings clearly indicates that the different micelles differ in solubilizing power.

TABLE IX

SOLUBILIZATION OF ORANGE OT IN AQUEOUS SOLUTIONS OF POTASSIUM LAURATE IN THE PRESENCE IN 1 *m* POTASSIUM CHLORIDE AT 25°

N_v vol. concn. of soap	mg. Dye/100 cc.
0.0493	5.38
.0978	10.6
.145	15.7
.191	21.4
.236	27.0
.450	63.4
.643	95.3
.819	134.8

TABLE X

SOLUBILIZATION OF ORANGE OT IN AQUEOUS SOLUTIONS OF POTASSIUM LAURATE IN THE PRESENCE OF 1 *m* POTASSIUM HYDROXIDE AT 25°

N_v vol. concn. of soap	mg. Dye/100 cc.
0.0047	1.19[a]
.0094	1.10
.024	2.50
.047	5.95
.094	11.4
.142	20.4
.189	28.2
.236	36.9
.410	70.1
.615	124.1

[a] Includes suspension; see later section of this communication.

TABLE XI

SOLUBILIZATION OF ORANGE OT IN AQUEOUS SOLUTIONS OF POTASSIUM LAURATE IN THE PRESENCE OF 0.5 *m* POTASSIUM SULFATE AT 25°

N_v vol. concn. of soap	mg. Dye/100 cc.
0.0205	2.26
.0410	4.70
.082	10.4
.123	16.0
.164	22.1
.205	27.7
.410	57.2
.615	91.3
.819	136.2

TABLE XII

SOLUBILIZATION OF ORANGE OT IN AQUEOUS SOLUTIONS OF POTASSIUM LAURATE IN THE PRESENCE OF 1 *m* POTASSIUM THIOCYANATE AT 25°

N_v vol. concn. of soap	mg. Dye/100 cc.
0.0236	2.55
.0472	6.10
.0944	12.25
.142	17.5
.189	24.0
.236	31.2
.410	62.2
.615	103.5

TABLE XIII

SOLUBILIZATION OF ORANGE OT IN DILUTE AQUEOUS SOLUTIONS OF POTASSIUM LAURATE IN THE PRESENCE OF POTASSIUM SALTS AT 25°

N_v vol. concn. of soap	With 0.5 *m* K_2SO_4 mg. dye/100 cc.	With 0.5 *m* K_2SO_4 mg. dye/100 cc.
0.0250	3.29[a]	0.26
.0100	1.09[a]	0.05
.0082	0.85[a]	...
.0050	.55[a]	0.025
.0025	.25[a]	...
.0010	.02[a]	0
.0001	..	0
	With 1 *m* KSCN	With 1 *m* KCl
0.0250	2.72[a]	0.25
.0100	1.15[a]	.10
.005	0.60[a]	.05
.0025	.20[a]	..
.001	.02[a]	0
.0001	..	0

[a] Includes suspension; see a later section of this communication.

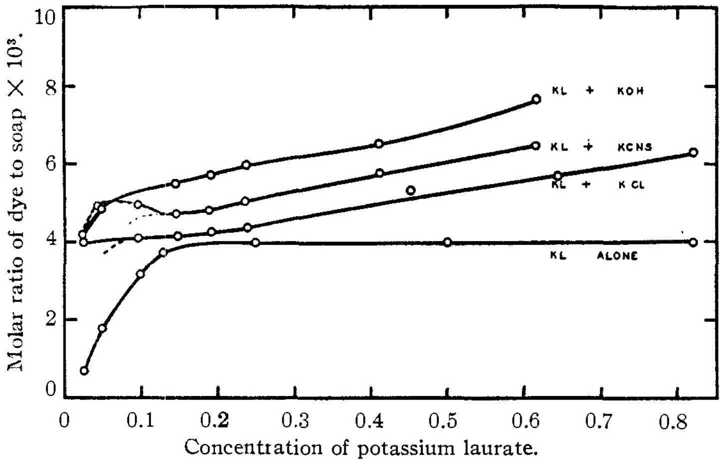

Fig. 4.—Effect of 1 *M* potassium hydroxide, thiocyanate and chloride on solubilization by potassium laurate, at 25°.

Since the previous publication[5] several papers have appeared in this country corroborating the X-ray evidence first put forward by Krishnamurti, then by Hess and Thiessen and their collaborators in their 13 papers published in Germany. These have come from the laboratories of Chicago University,[13] the Shell Development Company[14] and Stanford University.[15] All of these agree in showing that some at least of the micelles in detergent solution are lamellar in organization, the molecules being arranged normal to parallel sheets, and taking up water and solubilized material between these sheets, as revealed by the expanding Bragg's spacings.

McBain and Palit[16] have shown that the same forces which are operative in producing the lamellar micelles of the solubilizing detergents in aqueous solution result in enhancing the true solubility of substances in high concentrations of mixtures of co-solvents. This is in addition to any solubilization through formation of colloidal micelles in such solvents.

Comparison of the Effects of Salt.—In all concentrations, salts (which by themselves are non-solubilizing) greatly increase the amount of solubilization by a given amount of soap. This is especially striking in the lower concentrations of soap where no solubilization is observed until the salt is added. Evidently the salt promotes the formation of colloidal soap except in excessively dilute soap solution. In the second place, keeping the salt in constant concentration, the amount of dye per mole of soap increases steadily with increasing concentration of soap over the whole range, showing that the kind of colloidal micelles formed in the more concentrated solutions of soap are far more effective as solubilizers than those in lower concentrations. This was already noted for the highest concentrations of soap alone.

The greatest effect is produced by potassium hydroxide, followed by that produced by potassium thiocyanate. Still somewhat less, but equal to each other, are potassium chloride and an equivalent amount of potassium sulfate. It is evident from the latter fact that these results bear no relation to the Donnan equilibrium where valency is a preëminent factor. Neither are these results related to the Hofmeister or lyotropic series or to the order of concentration required to salt out sodium palmitate.[17]

As in Hartley's experiments,[6] the first addition of salt has a much greater effect than later additions though the effect continues to increase as further salt is added. It may be noted that while the color of the dye was normal in the soap solutions with or without salt, strong hydroxide made dilute solutions below 0.05 *N* definitely more yellow.

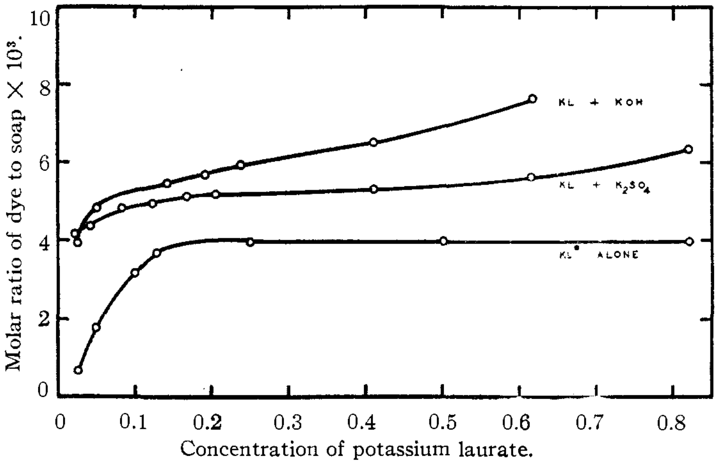

Fig. 5.—Effect of 1 *M* potassium hydroxide and sulfate on solubilization by potassium laurate solution, at 25°.

Solubilization and Suspending Action in Very Dilute Solutions of Soap.—Tables VIII, X and especially XIII, include dilute soap solutions but in the presence of 1 *m* salts. Here a maximum total effect per mole soap was observed at approximately 0.005 *N* soap. The effect was even higher during the first twenty-four hours, but fell off gradually to the approximately constant values observed at the end of a week and

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(13) W. D. Harkins, R. W. Mattoon, M. L. Corrin and R. S. Stearns, *J. Chem. Phys.*, **13**, 534 (1945); W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Coll. Sci.*, **1**, 105 (1946).

(14) E. W. Hughes, W. M. Sawyer and J. R. Vinograd, *J. Chem. Phys.*, **13**, 131 (1945).

(15) S. Ross and J. W. McBain, THIS JOURNAL, **68**, 296 (1946).

(16) S. R. Palit and J. W. McBain, *Ind. Eng. Chem.*, **38**, 741 (1946).

(17) J. W. McBain and A. V. Pitter, *J. Chem. Soc.*, 893 (1926).

given in the tables. This maximum thus varied in such a way as to indicate that it was not an equilibrium. Furthermore, it occurred at a dilution far too low for the soap to be in colloidal form. This sharp peak of effect occurred over a very narrow range and rapidly fell off to zero on still greater dilution.

Since a very minute absolute amount of suspension would be sufficient to cause a large effect relative to the soap in this dilution, the following experiments were devised to eliminate suspension of solid dye by avoiding the presence of any solid dye. A saturated solution of dye was prepared in hexadecane and then excess hexadecane was added to reduce the concentration to 90% of saturation. Hexadecane is a hydrocarbon which is not itself solubilized in dilute potassium laurate. Two cc. of this solution was placed on top of 20 cc. of the dilute soap solution containing salt. These were then placed on a rotating plate in a thermostat at 25° in such a manner that the interface between soap and hydrocarbon was not broken, but the liquids were kept very gently stirred. After a week of such treatment the aqueous soap layer was removed, and the concentration of dye in it was measured. The maxima had entirely disappeared, showing that those observed with solid dye were due to suspension of residual fine fragments from dye crystals. These would be too small to play any role in comparison with the very much larger amounts of soap in greater concentrations.

Solubilization of a Non-electrolytic Detergent with and without Added Salt.—It is of great interest to compare the behavior of a non-electrolytic detergent such as X with that of the colloidal electrolytes so far investigated. X is an alkylated aryl poly ether alcohol derived from polymerized ethylene oxide and it cannot ionize in aqueous solution. Hence there can be no common ion effect. Nevertheless addition of salt in general might be expected to promote association. Measurements of the solubilization of Orange OT in 2% solution of X alone at 25° gave 9.25 mg./100 cc. Addition of 10% potassium chloride raised this to 11.15 mg./100 cc., a result 20% greater. This is almost half as great an effect in increasing solubilization as if the salt had been added to a colloidal electrolyte such as potassium laurate This may be taken as an indication that non-electrolytic detergents are associated in aqueous solution.

Summary

The solubilization of water-insoluble dyes has been measured in aqueous solutions of soaps at 25°. Whereas the amount of hydrocarbon chain in the molecule of soap or in the soap micelle increases from the caprylate to the myristate only in the proportion 1:1.25:1.50:1.75, the solubilization increases disproportionately as 1:2.14:6.48:11.61. In all concentrations of potassium laurate above $N/1000$ the addition of potassium hydroxide or of potassium salts greatly increases the amount of solubilization. This solubilization occurs at dilutions of soap far below those in which soap alone can be solubilized, owing to the absence of colloidal micelles, but it increases rapidly and steadily with increasing concentration of soap showing that the kinds of micelles existing in higher concentrations are more effective than those formed in lower concentrations.

Extremely dilute soap solutions, especially in the presence of salt, exhibit a powerful suspending action for any minute particles of dye, a phenomenon quite distinct from solubilization.

Solubilization by a non-electrolytic detergent is also enhanced by the presence of potassium chloride, indicating increased association of the detergent.

STANFORD UNIVERSITY, CALIF. RECEIVED MARCH 22, 1946

The Kinetics of the Reaction of Hydroxyl Ion with the Meso and Racemic Di-*p*-toluenesulfonates of Butylene Glycol-2,3[1]

BY FREDERICK C. FOSTER[1a] AND LOUIS P. HAMMETT

The substitution of methyl for hydrogen has an effect upon the reactivity of alkyl halides, toluenesulfonates, and the like which is consistent and well-known. For nucleophilic displacements such

$$Y + R_3CX \longrightarrow R_3CY + X \qquad (1)$$

as the reactions with hydroxyl, halide, or acetate ions or with ammonia and amines, the rate of reaction drops rapidly in the series CH_3, CH_3CH_2-, $(CH_3)_2CH$- $(CH_3)_3C$-.[2] For the kinetically first order solvolytic reactions and the reactions with silver ion and the like, the rate of reaction increases in the same order.[2] A less thoroughly explored series is offered by the substitution of $-CH_2X$ for hydrogen, where X is hydroxyl, toluenesulfonate, halogen, or similar substituents. This has particular practical interest in the reactions of the sugar toluenesulfonates, where a distinction is frequently drawn between "primary" and "secondary" groups, *i. e.*, between the first

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(1) Dissertation submitted by Frederick C. Foster in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science Columbia University.

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(2) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 152–155.