

## Solubilization by Solutions of LongChain Colloidal Electrolytes

Richard S. Stearns, Hans Oppenheimer, Eric Simon, and William D. Harkins

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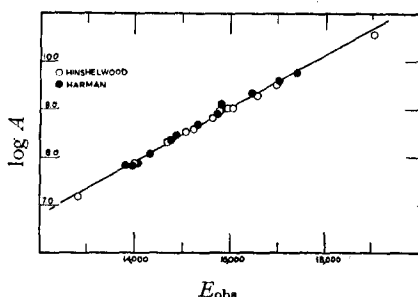


FIG. 18. Saponification of ethyl benzoate in water-acetone-ethyl alcohol mixtures.

ternary mixtures of acetone-ethanol-water<sup>20,21</sup> (cf. Fig. 8).

<sup>21</sup> R. A. Fairclough and C. N. Hinshelwood, *J. Chem. Soc.* **1937**, 538.

The existence of the correlation for the Arrhenius equation has, of course, been empirically known for some time (see, for example, references (19) and (21)), and it has been suspected that it was a solvent effect. It is quite satisfying to be able to derive it so simply from the concept of the quasi-crystalline liquid.

#### ACKNOWLEDGMENT

The authors wish to express their appreciation to Dr. R. Simha for his encouragement and many valuable suggestions during the course of this work. We also wish to thank Dr. H. Eyring for valuable suggestions as to the presentation of this material.

### Solubilization by Solutions of Long-Chain Colloidal Electrolytes\*

RICHARD S. STEARNS, HANS OPPENHEIMER, ERIC SIMON, AND WILLIAM D. HARKINS  
*George Herbert Jones Chemical Laboratory, University of Chicago, Chicago, Illinois*

Increase in the concentration of a soap or other detergent does not increase the solubility of an oil above that in water until the critical concentration for the formation of micelles (*cmc*) is attained. Above this the solubility, designated as solubilization, increases and, in general, more rapidly as the soap concentration increases; i.e., per mole of soap the solubilization is greater in a 25 percent than in a 5 percent soap solution. For a homologous series the volume of oil solubilized at a constant temperature is to a first approximation inversely proportional to the molar volume. The polarity and shape of the molecules solubilized also play a role. Salts increase the extent of the solubilization; at low concentrations to an extent which may be accounted for by the increase in micellar area resulting from the depression of the *cmc* by the salt. At higher soap concentrations the increase in solubilization is greater than can be accounted for in this way.

#### I. INTRODUCTION

ONE of the most outstanding properties of solutions of long chain colloidal electrolytes, inclusive of soaps and many other detergents, is their ability to solubilize various organic substances. This property, utilized commercially since 1874, is of fundamental importance both in their use as detergents and in emulsion poly-

merization.<sup>1</sup> Engler and Dieckhoff<sup>1c</sup> made very early, by the use of visual observations, a distinction between true solution and solubility in a detergent. Pickering,<sup>2</sup> in 1917, found that oils dissolve in concentrated soap solutions. Smith,<sup>3</sup>

<sup>1a</sup> G. Link in Friedlander's *Fortschritte der Teerfarbenfabrikation* (1877-88), Vol. I, p. 11.

<sup>b</sup> F. Von Heyden, D.R.P. 57842 (1890).

<sup>c</sup> C. Engler and E. Dieckhoff, *Arch. Pharm.* **230**, 561 (1892).

<sup>d</sup> G. A. Rappenstrauch, *Ibid.* **229**, 201 (1891).

<sup>e</sup> R. Otto, *Ber.* **27**, 2131 (1894).

<sup>f</sup> F. Nottbrack, *Chem. Ztg.* **32**, 100 (1908).

<sup>2</sup> S. U. Pickering, *J. Chem. Soc.* **111**, 86 (1917).

<sup>3</sup> E. L. Smith, *J. Phys. Chem.* **36**, 1401, 1672, 2455 (1932).

\* This investigation was carried out under the sponsorship of the Reconstruction Finance Corporation, Office of Rubber Reserve, in connection with the Government's synthetic rubber program.

McBain,<sup>4</sup> and others have determined the solubility of oils, dyes, etc., in soap solution as well as the effect of salts on solubilization. However, their work is concerned largely with the solubilization of water insoluble dyes, and apparently there exist no published data which give the solubility of an oil at various concentrations of the same soap solution. A general theory of the loci of emulsion polymerization had been developed by Harkins in 1942, and he requested the Rubber Director's Office to arrange that Professor W. B. Reynolds of the University of Cincinnati cooperate in obtaining evidence bearing on the theory. On account of the importance in this theory of the thin monomer layers in micelles, work on solubilization was begun by Stearns and Jura at Chicago on February 1, 1943, and similar work was begun at Cincinnati at about the same time.<sup>5</sup> The topics of the investigation as it proceeded were outlined in numerous conferences between Reynolds and Harkins, and it was decided that the former should study particularly the effect of salts in increasing the solubility of oils in soap solutions and polymerization in solutions of short-chain soaps such as the caprylate and caprate in the presence of electrolytes. The importance of salts in connection with solubilization was suggested by an experiment of Hartley<sup>6</sup> who discovered that sodium chloride increases the solubility of trans-azobenzene in solutions of pyridinium salts. The very extensive data on the solubilization of various oils in both the absence and the presence of salts as obtained by Reynolds and collaborators<sup>7</sup> will be published elsewhere.

At Cincinnati and in the initial work at Chicago, the procedure used for the determina-

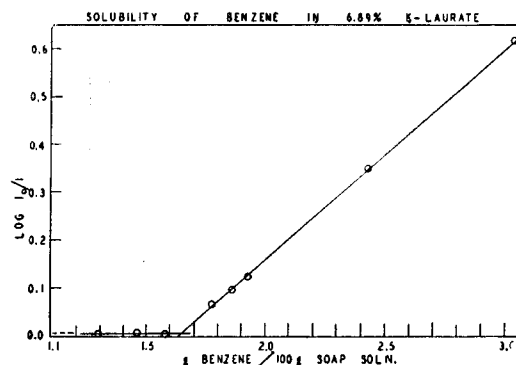


FIG. 1. Exhibits essential constancy in the optical density of a 6.89 percent potassium laurate solution with increasing amounts of dissolved benzene. The rapid increase of  $I_0/I$  begins where emulsion droplets first appear. The intersection of the two straight lines is considered to give the solubility of benzene in the soap solution.

tion of the solubility was the very old method of observing visually the appearance of turbidity as more and more oil is added. However, none of the results obtained by this method are included here, since the higher accuracy given by the use of a photometer is needed for a more careful consideration of the relations involved.

The present paper deals with the solubilization of various hydrocarbons in solutions of potassium laurate and potassium myristate and the effect of salts and of mixtures of soaps on solubilization. This effect has long been a matter of discussion, and in spite of the extensive work done on these subjects the problem is still far from its solution. However, it has been found in this laboratory that soap solutions contain aggregates each of which, designated as a micelle, contains soap molecules, varying in number but of the general order of 100. It also seems to be established that soap solutions exhibit a critical concentration below which no micelles exist.

In a recent paper<sup>8</sup> Harkins, Mattoon, and Corrin have discussed the structure of soap micelles as indicated by x-rays and the theory of molecular orientation. The x-ray work discussed in this paper, taken together with more recent work, indicates that each micelle consists of a double layer of soap molecules with their hydrocarbon chains oriented towards each other and with their polar ends toward the water. The effect

<sup>4</sup> J. W. McBain and M. E. Laing McBain, *J. Am. Chem. Soc.* **58**, 2610 (1936); J. W. McBain and J. J. O'Connor, *ibid.* **62**, 2855 (1940); J. W. McBain and R. C. Merrill, *Ind. Eng. Chem.* **34**, 915 (1942); J. W. McBain and K. E. Johnson, *J. Am. Chem. Soc.* **66**, 9 (1944); J. W. McBain and P. H. Richards, *Ind. Eng. Chem.* **38**, 642 (1946); J. W. McBain and Sister Agnes Ann Green, *J. Am. Chem. Soc.* **68**, 1731 (1946).

<sup>5</sup> The earliest work of Reynolds on styrene and of Jura on butadiene was reported in a private communication from the University of Chicago, March 19, 1943; and that of McBain from Stanford University on both materials on March 23, 1943.

<sup>6</sup> G. S. Hartley, *J. Chem. Soc., London* **1938**, 3970.

<sup>7</sup> W. B. Reynolds, P. J. Canterino, E. W. Cotten, R. E. Holland, and J. E. Wicklatz. Many private communications (University of Cincinnati, Cincinnati, Ohio, 1943-4).

<sup>8</sup> W. D. Harkins, R. W. Mattoon, and M. L. Corrin, *J. Am. Chem. Soc.* **68**, 220 (1946).

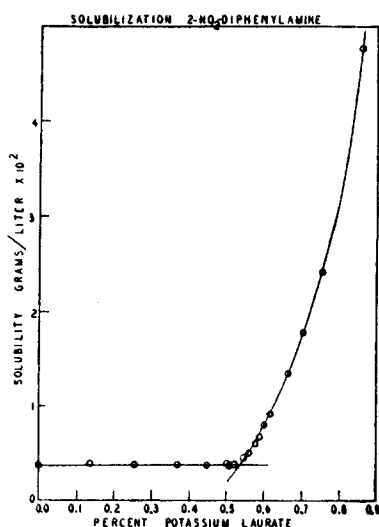


FIG. 2. Solubility of 2-nitrodiphenylamine in dilute potassium laurate solutions. The solubility remains constant until the critical concentration is passed after which there is a sharp increase due to solubilization in soap micelles.

of solubilized oil on the x-ray diffraction bands<sup>9</sup> seems to indicate that the oil is solubilized in the hydrocarbon interior of the micelle, presumably between the hydrocarbon ends of the soap micelles. The critical concentrations of the soaps considered here have been determined accurately by Corrin<sup>10</sup> as 0.393 for potassium caprylate, 0.100 for potassium caprate, 0.023 for potassium laurate, and 0.0059 for potassium myristate, as expressed in moles per liter.

## II. METHOD OF DETERMINING SOLUBILIZATION

The extent of solubilization of the hydrocarbons was found by use of a turbidimetric method, in which a photometer was used to determine the turbidity. It was assumed as a criterion of solubility that as the saturation point is exceeded, the excess oil is emulsified and the solutions therefore become turbid.

To determine the solubility of a hydrocarbon in a soap solution at one given concentration the following procedure was adopted. The soap solution was weighed into a glass ampule, a weighed amount of oil was added, and the ampule was

sealed. At a constant soap concentration a series of ampules was prepared, each successive ampule containing an increasing amount of oil. The samples were shaken vigorously for at least forty-eight hours in order to attain equilibrium. At the end of this time the turbidity of the solutions was measured by the use of a photometer. For those samples in which the amount of added oil was below the saturation value the turbidity was equal to that of the original soap solution. As soon as an excess of oil was present, the solutions exhibited a rapid increase of turbidity, caused by the appearance of emulsion droplets, with increase in the amount of oil. A plot was made of the turbidity against the amount of oil added, and the sharp break in the curve was considered as the saturation point. Figure 1 shows the type of curve obtained upon addition of benzene to a 6.89 percent solution of potassium laurate.

The turbidimetric method as described here works well if there is a large difference between the refractive index of the oil and that of the soap solution. It becomes less and less sensitive as the refractive index of the oil approaches that of the

TABLE I. Solubilization in potassium laurate.

Percent K-laurate ( $\frac{\text{Grams soap}}{100 \text{ g solution}} \times 100$ )	Moles K-laurate 1000 g solution	Grams oil 100 g soap solution
Benzene		
H <sub>2</sub> O	—	0.185
0.545	0.0228	0.187
0.769	0.0322	0.217
2.02	0.0846	0.472
3.34	0.1400	0.760
5.08	0.213	1.170
6.89	0.289	1.64
9.65	0.405	2.50
11.93	0.501	3.27
15.00	0.629	4.38
16.64	0.697	5.01
19.95	0.836	6.41
Ethylbenzene		
2.11	0.088	0.212
5.16	0.216	0.710
9.70	0.406	1.67
14.85	0.624	2.97
20.65	0.869	4.68
n-Heptane		
2.11	0.088	0.068
5.02	0.211	0.255
9.55	0.400	0.67
15.00	0.630	1.30
19.25	0.810	1.88
24.25	1.020	2.57

<sup>9</sup> W. D. Harkins, R. W. Mattoon, M. L. Corrin, J. Colloid Sci. 1, 105 (1946); R. W. Mattoon, R. S. Stearns, W. D. Harkins, J. Chem. Physics, 15, 209 (1947).

<sup>10</sup> M. L. Corrin, W. D. Harkins, and S. H. Herzfeld (private communication).

soap solution. When the refractive index of the oil equals that of the soap solution, the solution no longer appears cloudy when excess oil is present, since there is no light scattering by the emulsion drops present. For some of the higher

hydrocarbons the emulsions formed are not at all stable, and in these cases also this method is of little value, since the turbidity changes during the period in which the measurements are being made.

For the solubilization measurements made with solid colored compounds the procedure was to shake the soap solution with an excess of the solid until equilibrium was reached, and then to measure the amount of solubilization by measuring the depth of color of the solution by standard spectrophotometric methods. The solubilization measurements were made at room temperature,  $25 \pm 3^\circ\text{C}$ . This variation of temperature introduced no appreciable error into the solubilization determinations.

### III. SOLUBILITY BELOW THE CRITICAL CONCENTRATION

It has been assumed that below the critical concentration micelles do not exist. If solu-

TABLE II. Solubilization in potassium myristate.

Percent K-myristate (Grams soap 100 g solution $\times 100$ )	Moles K-myristate 1000 g solution	Grams oil 100 g soap solution
<i>n</i> -Heptane		
H <sub>2</sub> O	—	0.007
0.506	0.019	0.039
1.043	0.0392	0.058
2.03	0.0763	0.192
3.025	0.114	0.29
5.04	0.189	0.53
7.47	0.280	0.886
8.69	0.326	1.05
10.00	0.376	1.275
14.9	0.560	2.10
20.15	0.757	2.95
Benzene		
H <sub>2</sub> O	—	0.186
0.50	0.0189	0.275
1.01	0.0379	0.42
2.01	0.0755	0.70
3.05	0.115	1.05
4.02	0.151	1.36
5.03	0.189	1.75
7.27	0.273	2.7
10.05	0.378	4.04
15.03	0.566	6.70
Ethylbenzene		
2.6	0.097	0.57
5.0	0.188	1.32
7.5	0.282	2.15
10.0	0.376	3.06
12.5	0.470	4.10
15.0	0.563	5.10
<i>n</i> -Propylbenzene		
H <sub>2</sub> O	—	0.012
1.01	0.038	0.15
5.00	0.188	1.06
10.15	0.381	2.75
15.08	0.567	4.30
Iso-propylbenzene		
H <sub>2</sub> O	—	0.017
1.025	0.0385	0.20
3.01	0.113	0.75
4.98	0.187	1.40
7.46	0.280	2.37
9.95	0.373	3.30
14.98	0.563	5.10
<i>n</i> -Decanol		
H <sub>2</sub> O	—	0.005
0.985	0.037	0.195
2.00	0.075	0.438
3.485	0.131	0.85
5.25	0.197	1.35
9.85	0.370	2.75
14.85	0.556	4.30

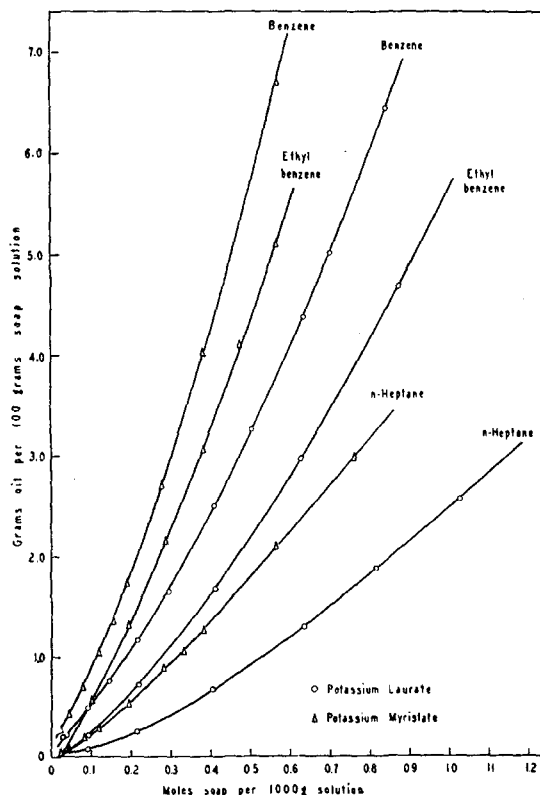


FIG. 3. Solubilization of *n*-heptane, benzene, and ethylbenzene in aqueous solutions of potassium laurate and potassium myristate. The magnitude of the solubilization is much greater in the 14 carbon atom than in the 12 carbon atom soap.

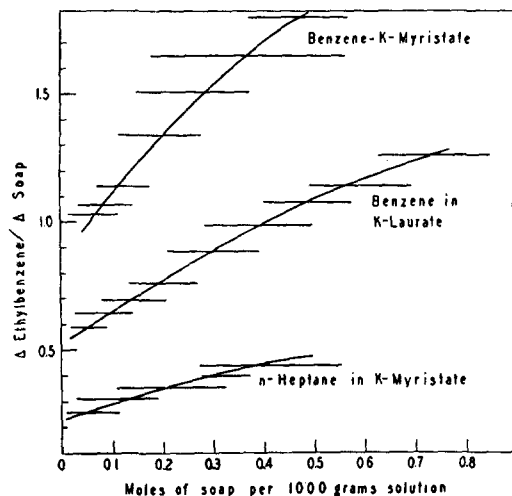


FIG. 4. Chord plots from the data of Fig. 3 illustrate the increment in the number of moles of solubilized oil per unit increment in the number of moles of soap as a function of soap concentration.

bilization is the result of incorporation in or adsorption on the micelle, then in the absence of micelles there should be no solubilization.

The solubility of 2-nitrodiphenylamine, a yellow solid compound, was determined in dilute solutions of potassium laurate. It was found that within the limits of accuracy of our measurements the solubility remained constant until the concentration of soap reached  $2.26 \times 10^{-2}$  mole per liter, after which there was a sharp increase in the solubility (Fig. 2). It may be noted that the dye method of Corrin and Harkins gave  $2.3 \times 10^{-2}$ , and from this excellent agreement it seems that there is no solubilization, above the solubility in water, below the critical concentration for those soaps which exhibit a sharp break at this point.

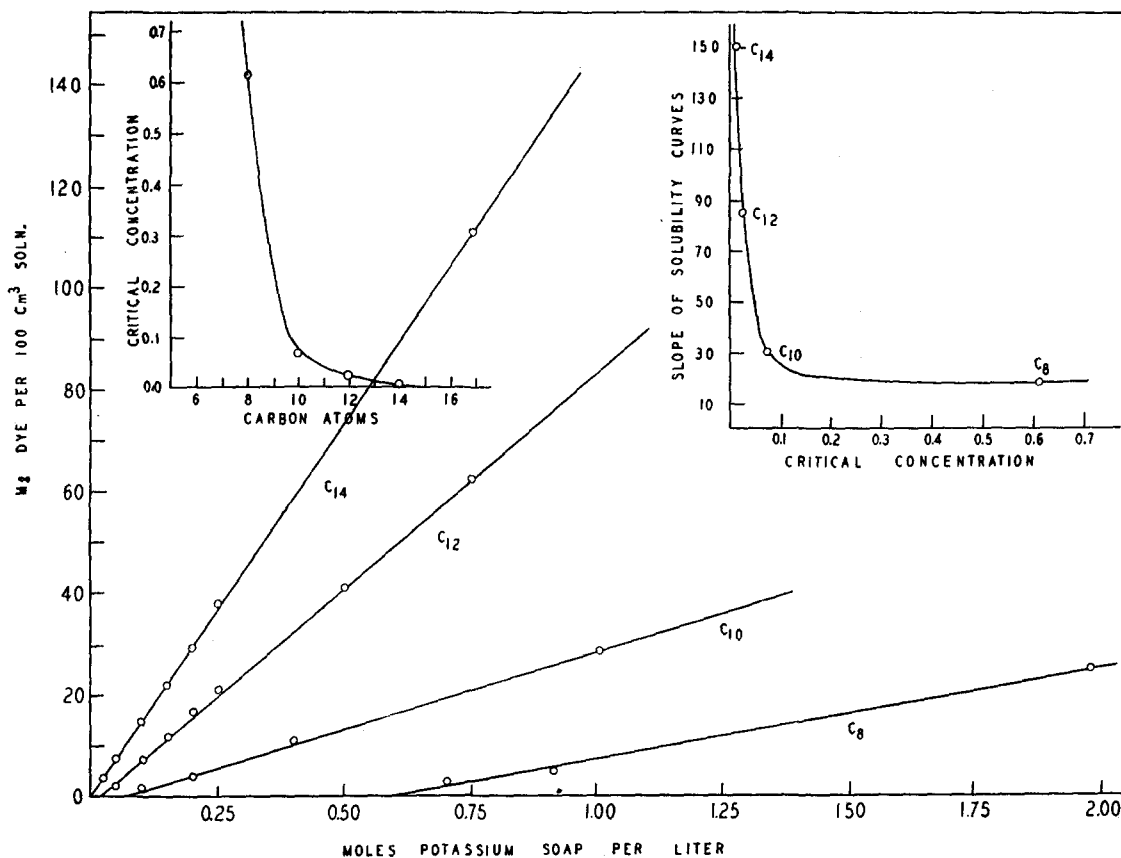


FIG. 5. Weight of dye (1-o-tolylazo- $\beta$ -naphthol) solubilized as a function of soap concentration and chain length from the data of McBain and Johnson [J. Am. Chem. Soc. 66, 9 (1944)]. The intercepts of the straight lines with the x axis should give the critical micelle concentrations of the soaps which are the potassium salts of the normal long chain acids. The critical concentration given for potassium octoate is 0.6, whereas the correct value is 0.4 molar. The other critical concentrations are more accurate. McBain and Johnson plotted moles of dye per mole of soap as a function of soap concentration, which obscured the linear relation, the value of the critical concentration, and the other relations shown here.

#### IV. SOLUBILIZATION IN SOLUTIONS OF POTASSIUM LAURATE AND POTASSIUM MYRISTATE AS A FUNCTION OF THE SOAP CONCENTRATION

The extent of solubilization of benzene, ethylbenzene, and *n*-heptane was determined in solutions of potassium laurate (Table I), and that of benzene, ethylbenzene, *n*-heptane, *n*-propylbenzene, isopropylbenzene, and *n*-decanol in solutions of potassium myristate (Table II). In Fig. 3 the extent of solubilization at equilibrium, expressed as grams of oil per 100 grams of solution, for benzene, ethylbenzene, and *n*-heptane in solutions of potassium laurate and potassium myristate is plotted as a function of the soap concentration expressed as moles of soap per 1000 grams of solution. The curves of Fig. 3 show that the solubility is not a linear function of soap concentration and that the solubility of a given oil is greater in the myristate than in the laurate. These data are of the greatest value when employed to find the variation in the number of moles of oil solubilized per mole of soap.

However, a false impression may be obtained from the ratio of the total number of moles of oil to soap present. In order to find correctly the variation in the moles of oil solubilized per moles of soap, i.e., the solubilizing power of the soap, the derivative of the curves in Fig. 3 should be found. This may be done by the chord-area method as illustrated in Fig. 4 for benzene in potassium laurate, and heptane and benzene in potassium myristate. This method of plotting the data shows clearly that the solubilizing power of the soap solution per unit amount of soap increases as the soap concentration increases.

An exception appears in the results of Kolthoff<sup>11</sup> and in the earlier much more extensive results of McBain and collaborators.<sup>5</sup> These show (Fig. 5) that "insoluble" dyes exhibit, in the range investigated by them, a linear increase in the amount solubilized with increase of soap concentration. That this is true was not shown by McBain and collaborators, since their method of plotting obscured this relation. They plotted molar ratios, and this has a deceptive effect, as considered in the paragraphs which follow. In order to determine whether the linear relation is

<sup>11</sup> I. M. Kolthoff and W. F. Johnson, J. Phys. Chem. **50**, 440 (1946).

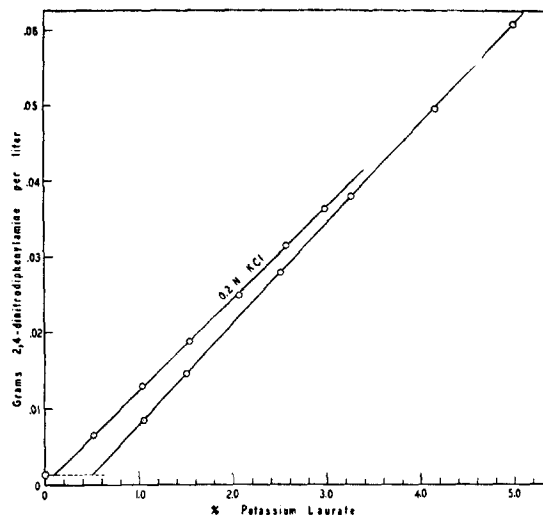


FIG. 6. Solubilization of 2,4-dinitrodiphenylamine in aqueous solutions of potassium laurate. The upper line shows the increase due to 0.2 normal salt.

valid for "insoluble" substances, the writers investigated the solubilization of 2,4-dinitrodiphenylamine in solutions of potassium laurate (Fig. 6). The linear relation exhibited here and in the work of McBain seems to be in disagreement with that of Fig. 2 for 2-nitro-diphenylamine, which is highly non-linear just above the critical concentration ( $2.34 \times 10^{-2}$  molar) of the soap.

However, there is no real disagreement, since the amine exhibits a solubility of  $1.72 \times 10^{-5}$  molar in water, whereas the dye used by McBain is very much less soluble. When plotted in the simple way chosen by us, McBain's data show

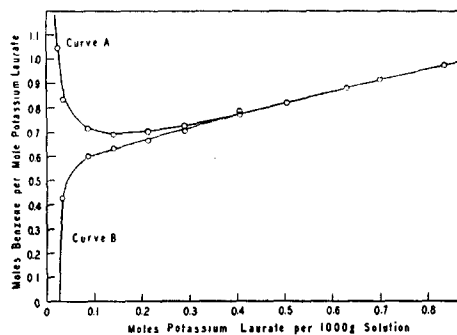


FIG. 7. In curve A the solubility data for benzene solubilized in potassium laurate are plotted as the moles of oil per mole of soap. This curve illustrates the incorrect way of plotting solubility data used by some authors and leading to incorrect conclusions. In curve B the solubility of benzene in water has been subtracted from the total solubility.

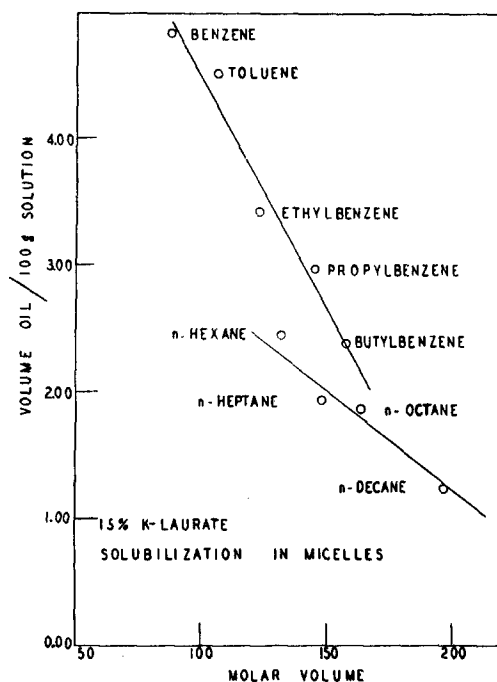


FIG. 8. Effect of molar volume on the solubilization of hydrocarbons in a 15.0 percent solution of potassium laurate at 25°C. Obviously the relations would be different if vapors of the liquids were solubilized at constant pressure.

that the constant rate of increase of solubilization with soap concentration:

1. Decreases rapidly with decrease in the number of carbon atoms in the soap molecule;
2. Decreases rapidly with increase of critical concentration, extremely rapidly as the number of carbon atoms decreases from 14 to 12 to 10, and very much more slowly in the further decrease to 8.

The general relations found by the writers are

TABLE III. The effect of molar volume on solubilization.

Oil	Molar volume	Grams oil 100 g soap solution	Solubility, oil in water	Volume of oil in micelles per 100 g soap solution
15% K-Laurate (0.630M)				
n-Hexane	131.5	1.60	0.014	2.44
n-Heptane	147.8	1.31	0.005	1.93
n-Octane	163.1	1.30	0.002	1.85
n-Decane	196.1	0.89	—	1.22
Benzene	88.5	4.38	0.186	4.82
Toluene	107.0	3.93	0.050	4.50
Ethylbenzene	123.0	2.95	0.015	3.40
n-Propylbenzene	140.5	2.54	0.010	2.95
n-Butylbenzene	157.0	2.03	0.005	2.37
15% K-Myristate (0.564M)				
Benzene	88.5	6.70	0.186	7.46
Toluene	107.0	6.00	0.050	6.90
Ethylbenzene	123.0	5.10	0.015	5.90
n-Propylbenzene	140.5	4.30	0.010	5.00
(Iso-propylbenzene) (140.4)	(5.10)	(0.017)	(5.92)	

the same, with the exception that the straight lines are changed to curves when organic substances much more soluble in water are used.

In Fig. 7, Curve A,<sup>12</sup> the solubility data for benzene in potassium laurate are plotted as moles of oil solubilized per mole of soap against the soap concentration. It will be noted that this curve exhibits a minimum. This minimum is a mathematical necessity, since the curve must go to infinity at zero soap concentration, and its position and depth depend upon the solubility of the oil in water. The solubility of benzene in water is rather large (0.186 grams per 100 g water). If it is assumed that the solubility of the benzene in water is not affected by the amount of soap present and if this is subtracted from the total, the "solubilization in the micelles" thus obtained exhibits no minimum. If the ratio of this value to the total number of moles of soap is plotted, Curve B, Fig. 7, is obtained. Both curves (A and B) coincide at higher soap concentrations when the total solubility is so large that the solubility in water is no longer an important part of the whole.

There is one more deceptive feature in plotting solubilization as the ratio of total moles of oil to total moles of soap. It has been shown that below the critical concentration there is no solubilization, and the amount of soap present in the form of micelles, supposedly responsible for solubilization above the critical concentration, is presumably zero. The chord-area method of finding the solubilizing power eliminates the ambiguity resulting from the mole ratio method of describing solubility data.

A theory of the increase in the solubilizing power of the soap solutions with concentration and the increase in solubilization at constant concentration with increase in the chain length of the soap will be discussed in a later paper.

<sup>12</sup> W. Heller and H. B. Klevens in a letter on solubilization, J. Chem. Phys. **14**, 567 (1946), state that the minimum in this type of curve gives the critical concentration of the soap, "providing thereby a new method for determining  $c_{cr}$  from solubilization measurements." However the minimum for Curve A is at 0.14 molar potassium laurate, whereas the value of the critical concentration of this soap as given by Corrin and Harkins and cited by them is 0.023 molar. Thus the minimum does not give the critical concentration. However, it approaches the critical concentration as the solubility of the solubilized substance decreases. However, a direct plot of solubility gives the critical concentration in a much better way.



### V. EFFECT OF MOLAR VOLUME AND POLARITY OF AN OIL ON ITS SOLUBILIZATION

The solubilization was determined for compounds in the series benzene, toluene, ethylbenzene, *n*-propylbenzene, and butylbenzene; also for *n*-hexane, *n*-heptane, *n*-octane, and *n*-decane in 15.00 percent potassium laurate solutions and, in addition, for benzene, toluene, ethylbenzene, *n*-propylbenzene, and iso-propylbenzene in 15.00 percent potassium myristate solutions. In Table III the solubilization data and the molar volumes are tabulated. A plot of these data (Fig. 8) shows that the solubility in the micelles is to a first approximation an inverse function of the molar volume for a homologous series. Undoubtedly, the polarity and shape of the molecule, as well as its volume, determine the extent of solubilization in the micelles. The effect of polarity is well illustrated by comparing the solubility of *n*-decanol and *n*-decane. The former is soluble to the extent of 3.31 cc per 100 grams of 10 percent potassium myristate solution, and the latter only to 1.05 cc. That the solubility is to a first approximation inversely proportional to the molar volume is what is to be expected if solubilization is the incorporation of the oil in the micelles. The effect of a double bond on solubilization is illustrated by comparing the solubility of ethylbenzene and styrene (Fig. 9).

### VI. DENSITY OF POTASSIUM LAURATE SOLUTIONS CONTAINING SOLUBILIZED ETHYLBENZENE

In an endeavor to obtain knowledge which may be of use in determining the mechanism of solubilization of hydrocarbons by soap solutions, the density of a series of soap solutions with increasing amounts of solubilized ethylbenzene was determined.<sup>12b</sup>

The solutions of 15.0 percent potassium laurate which contained solubilized ethylbenzene were made up on a weight basis. The samples were shaken for forty-eight hours at room temperature to insure complete solubilization. The densities of the original soap solution and the soap solutions plus solubilized ethylbenzene were determined at a temperature of  $25 \pm 0.005^\circ\text{C}$  in a pycnometer of about 25 cm<sup>3</sup> capacity having a capillary neck

TABLE IV. Density of 15.000% potassium laurate solutions containing solubilized ethylbenzene.

Grams ethylbenzene 100 g soap solution	Density $25 \pm .01^\circ\text{C}$
0.0000	1.01062
0.6755	1.00949
1.0448	1.00885
1.5119	1.00802
2.3269	1.00676
2.8615	1.00578

2 mm in diameter. The height of the liquid in the capillary was read to  $\pm 0.01$  mm by means of a cathetometer.

The pycnometer was calibrated with boiled redistilled water. All weighings were made to  $\pm 0.005$  mg with calibrated weights and the corrected weights reduced to *vacuo*. The variation in the volume of the pycnometer was about 0.007 cm<sup>3</sup> per 1 mm on the neck of the capillary. A precision of one part in 10<sup>5</sup> was obtained in the density measurements. The concentrations of ethylbenzene and the densities of the solutions are given in Table IV, and the data are plotted in Fig. 10. The experimental points are best represented by a straight line, the "least square"

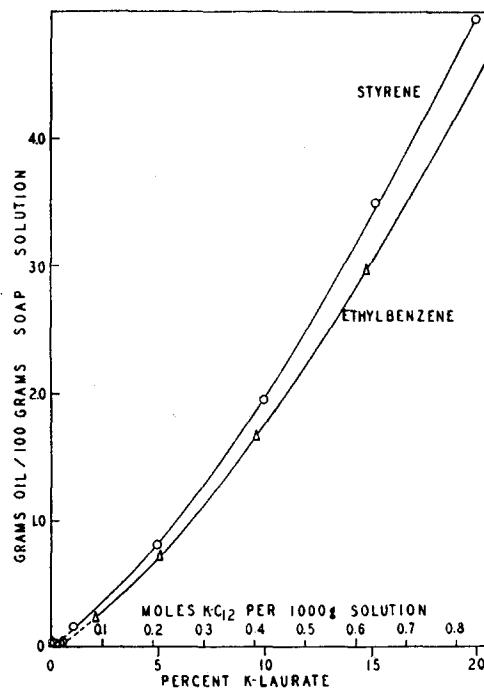


FIG. 9. Increase in solubilization of an oil by a double bond.

<sup>12b</sup> The density relations and apparent specific volumes of *n*-heptane and triptane are given by W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Colloid Sci. 1, 110 (1946).

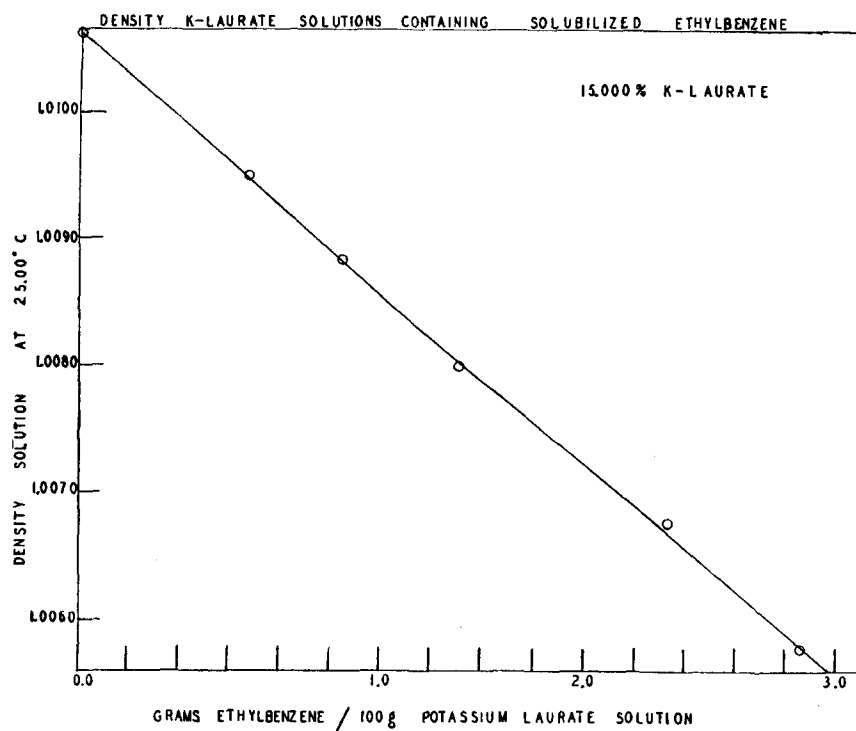


FIG. 10. Density of a 15.000 percent potassium laurate solution as a function of the amount of solubilized ethylbenzene.

equation for which is:

$$\rho = 1.0106128 - 1.68124495 \times 10^{-3}C,$$

where  $\rho$  is the density of the solution and  $C$  is the concentration of ethylbenzene expressed as grams per 100 grams soap solution.

From the above equation the apparent volumes and apparent densities of the solubilized ethylbenzene have been calculated from the formula:

$$\phi = (V_T - v_s/C)$$

where  $\phi$  is the apparent specific volume of solubilized ethylbenzene,  $V_T = 1/\rho$  is the specific volume of the soap solution plus the solubilized

benzene,  $v_s$  is the specific volume of the soap solution, and  $C$  is the concentration of ethylbenzene expressed as grams per 100 grams soap solution. The data are tabulated in Table V and plotted in Fig. 11.

The solubility of ethylbenzene in 15.000 percent potassium laurate solution is 3.00 grams oil/100 grams soap solution as determined by turbidity measurements. The bulk density of ethylbenzene was determined by us to be 0.86205 g/cm<sup>3</sup> at 25.00°C. From Fig. 11 it will be noted that at saturation the apparent density of the solubilized ethylbenzene equals the bulk density within experimental error.

The significance of the decrease in the apparent density of the solubilized ethylbenzene as satura-

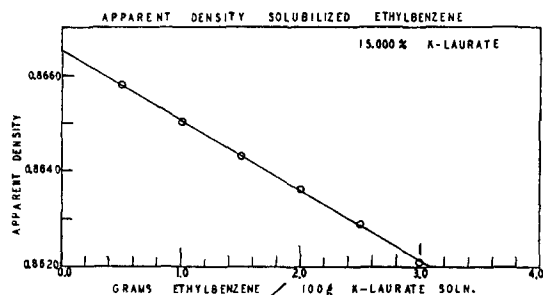


FIG. 11. Apparent density of ethylbenzene solubilized in a 15.000 percent potassium laurate solution.

TABLE V. Apparent volumes and densities of ethylbenzene solubilized in 15.000% potassium laurate solutions.

Grams ethylbenzene 100 g soap solution	Apparent volume	Apparent density
0.500	1.15507 cm <sup>3</sup> /g	0.8657 g/cm <sup>3</sup>
1.000	1.15603	0.8650
1.500	1.15700	0.8643
2.000	1.15796	0.8636
2.500	1.15893	0.8629
3.000	1.15990	0.8621

tion is approached is difficult to interpret, even when the assumptions inherent in all calculations

TABLE VI. Solubilization of ethylbenzene in soap+salt solutions.

Moles salt 1000 g water	Grams ethylbenzene 100 g soap solution
A. 10% K-laurate+KCl (0.42 m $KCl_2$ )	
0.00	1.70
0.025	1.81
0.050	1.89
0.075	1.96
0.100	2.02
0.150	2.14
0.200	2.24
0.300	2.43
0.500	2.83
B. 2.6% K-myristate+KCl (0.1 m $KCl_4$ )	
0.00	0.570
0.0187	0.656
0.0396	0.723
0.0810	0.840
0.1465	0.930
0.2445	1.08
0.347	1.18
0.638	1.42
1.503	1.79
2.00	1.87
C. 2.6% K-myristate+NaCl (0.1 m $KCl_4$ )	
0.000	0.570
0.00557	0.610
0.0204	0.706
0.0319	0.776
0.0479	0.812
0.0705	0.909
0.0989	1.005
D. 2.6% K-myristate+ $K_2SO_4$ (0.1 m $KCl_4$ )	
0.0000	0.57
0.0577	0.81
0.1622	0.96
0.3645	1.19
0.5735	1.35
E. 2.6% K-myristate+ $K_4Fe(CN)_6 \cdot 3H_2O$ (0.1 m $KCl_4$ )	
0.0000	0.57
0.02875	0.70
0.1030	0.94
0.2028	1.08
0.2868	1.10
0.4988	1.10
F. 2.6% K-myristate+ $K_3PO_4$ (0.1 m $KCl_4$ )	
0.4783	1.12
G. 2.6% K-myristate+1.383 molal salt (0.1 m $KCl_4$ )	
No salt	0.57
KF $2H_2O$	1.43
KCl	1.76
KBr	1.37
KI	1.31
KSCN	1.52

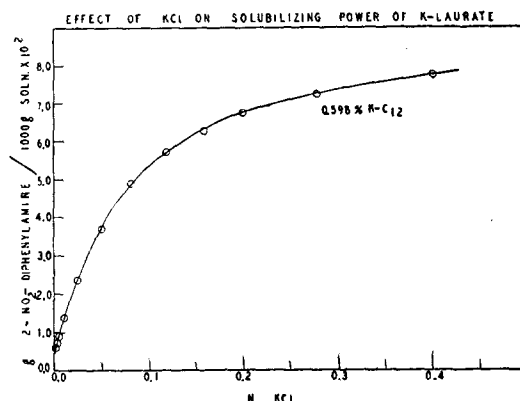


FIG. 12. Effect of added salt on the solubilization of 2-nitrodiphenylamine in a 0.598 percent solution of potassium laurate.

of apparent values of the density are taken into account.

## VII. THE EFFECT OF SALTS ON SOLUBILIZATION

The addition of salts, such as potassium chloride, to soap solutions greatly increases their solubilizing power. The effect of potassium chloride on the solubilizing power of a dilute potassium laurate solution was investigated by the use of 2-nitro-diphenylamine. At a constant soap concentration of 0.59 percent potassium

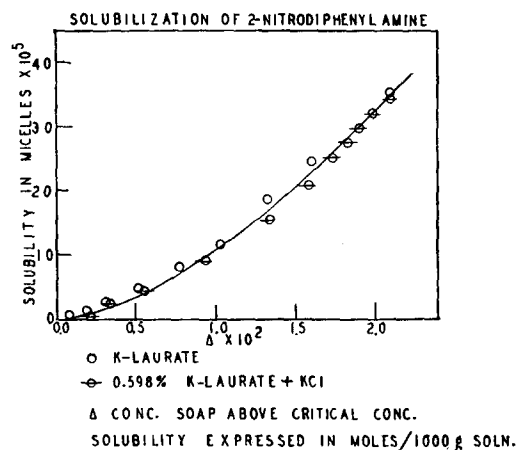


FIG. 13. In this figure  $\Delta$  is the increase between the critical concentration and the total soap concentration. At a constant soap concentration when increasing amounts of salts are added, the value of  $\Delta$  is increased, since the critical concentration is lowered. The solubility of 2-nitrodiphenylamine is expressed in moles solubilized in the micelles per 1000 g solution. The open circles (O) represent the solubilization in potassium laurate with increasing soap concentration. The circles with lines ( $\otimes$ ) represent the solubilization in a 0.598 percent potassium laurate solution containing increasing amounts of salts.

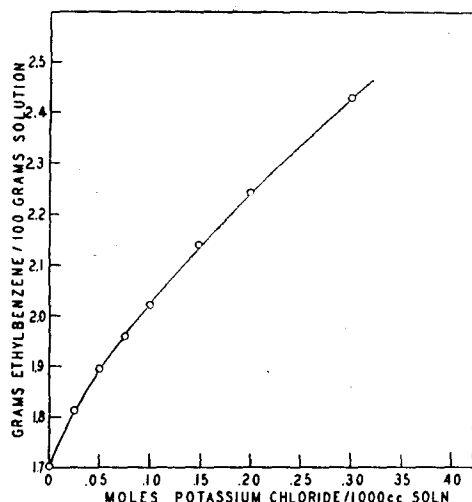


FIG. 14. Increase in the solubilization of ethylbenzene in a 10 percent solution of potassium laurate when KCl is added.

laurate, a concentration very slightly above the critical concentration, the solubility of 2-nitrodiphenylamine was determined as a function of the amount of potassium chloride present. The very large increase of solubility caused by the added salt, particularly at such a low soap concentration as that used here, is well illustrated by Fig. 12 as well as in Fig. 6.

The lowering of the critical concentration of potassium laurate in the presence of added salts was determined.<sup>18</sup> It is very interesting to combine the data on the lowering of the critical concentration with the data on the increase in

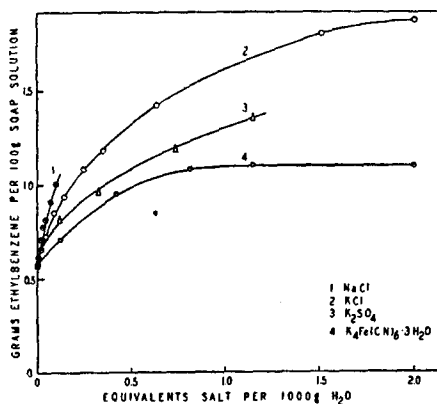


FIG. 15. Effect of various salts on the solubilization of ethylbenzene in a 2.6 percent (0.1 m) potassium myristate solution.

<sup>18</sup> M. L. Corrin and W. D. Harkins, J. Am. Chem. Soc. 69, 683 (1947).

TABLE VII. Solubilization of ethylbenzene in 0.1 molal solutions.

Mole fraction K-myristate	Grams oil / 100 g soap solution
A. Of K-laurate and K-myristate	
0.000	0.23
0.260	0.31
0.500	0.38
0.733	0.48
1.00	0.57
B. Of K-caprylate and K-myristate	
0.000	0.025
0.101	0.10
0.246	0.22
0.500	0.39
0.740	0.48
1.000	0.57

solubilizing power of potassium laurate in the presence of potassium chloride. The assumptions are made that no "solubilization" takes place below the critical concentration, that above the critical concentration there is always an amount of "free" molecular soap present, the concentration of which is given by the critical concentration, and that the amount of solubilization in the micelles is the total amount of material solubilized minus the solubility in water. At constant soap concentration the addition of increasing amounts of salt lowers the critical concentration, thus increasing the amount of micellar soap. This difference between the total soap concentration and the critical concentration is designated as  $\Delta$ . In Fig. 13 are plotted values of

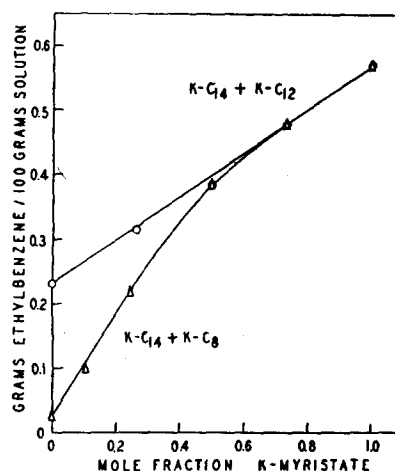


FIG. 16. Effect of mixtures of soaps on the solubilization of ethylbenzene.

the solubility of 2-nitrodiphenylamine in the micelles as a function of  $\Delta$ , both for solutions of increasing concentrations of potassium laurate and for solutions of a constant soap concentration but increasing salt concentrations. Within the accuracy of the experiments it is seen that the solubilization is determined by the amount of micellar soap at the low soap concentration employed. Since there is a pronounced curvature in the plot presented in Fig. 13 the amount of solubilization must be a function of the state of aggregation of the micelles as well as the amount of material in the micellar form.

At higher soap concentrations the effect of added salts on solubilization is not as large as that observed near the critical point. The effect of potassium chloride on the solubilization of ethylbenzene in 10.00 percent potassium laurate solutions and the effect of a number of salts on the solubilization of ethylbenzene in 2.60 percent solution of potassium myristate were investigated. The solubilization data are presented in Table VI and plotted in Figs. 14 and 15. At these higher soap concentrations the increase in solubility in the presence of added salts cannot be accounted for by the decrease in critical concentration with the resulting increase in micellar soap. The addition of sodium chloride to a potassium soap changes the nature of the soap, and therefore it is difficult to correlate the effect of this salt with that of potassium salts.

While the change in the critical concentration

has been shown to be dependent only on the total equivalents of the cation in the case of anionic soaps,<sup>13</sup> the data given here show that the change of solubility on addition of salts is dependent on both the nature of the cation and anion. Thus, KCl is more effective in increasing solubilization than is  $K_2SO_4$ , which in turn is more effective than  $K_4Fe(CN)_6 \cdot 3H_2O$ . That this effect is in some way connected with the size of the anion is shown by the fact that in the series of salts, KCl, KBr, and KI, the KCl has the greatest effect and KI the least effect in increasing solubilization. Unfortunately, KF and KSCN do not fall in the proper order as seen from the data in Table VI. These results are similar to those reported by McBain.<sup>4</sup>

#### VIII. SOLUBILIZATION IN MIXTURES OF SOAPS

Data for solubilization of ethylbenzene in mixtures of potassium laurate and potassium myristate and in mixtures of potassium caprylate and potassium myristate are given in Table VII and represented by Fig. 16. It is interesting to note that in mixtures of potassium laurate and myristate the solubility is a linear function of the mole fraction of soap present. For mixtures of potassium caprylate and myristate this linear relation no longer holds, which is presumably because of the fact that the critical point of the potassium caprylate is high, and this results in its action as a salt in its effect on the potassium myristate.