signment and other molecular structure data, values of the free energy function, heat-content function, entropy and heat capacity were calculated by the methods of statistical mechanics for various temperatures up to 1500° K.

BARTLESVILLE, OKLA. RECEIVED OCTOBER 1, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CHICAGO]

Solubilization of Polar–Non-polar Substances in Solutions of Long Chain Electrolytes[1a]

BY WILLIAM D. HARKINS AND HANS OPPENHEIMER

I. Introduction

Earlier work in this Laboratory[1b,2] on the effects of long chain alcohols and amines on both the X-ray bands and the critical micelle concentration of soap solutions indicates that their effects are very different from those of the hydrocarbons. This suggests that the locus in which the alcohols dissolve is also different, and thus that the relations exhibited in the solubilization of the alcohols should be different from those of the hydrocarbons.

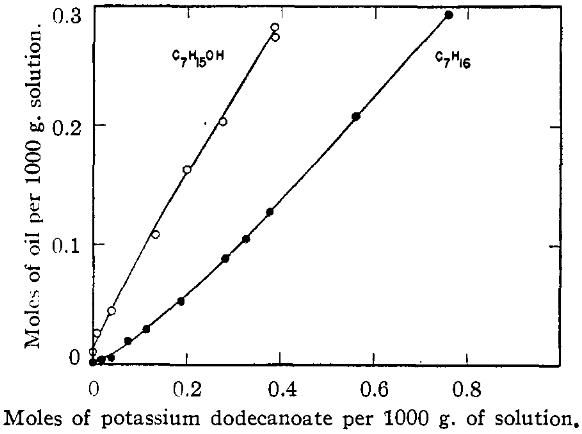

Fig. 1a.—Solubility of normal primary heptyl alcohol and of normal heptane in solutions of potassium dodecanate.

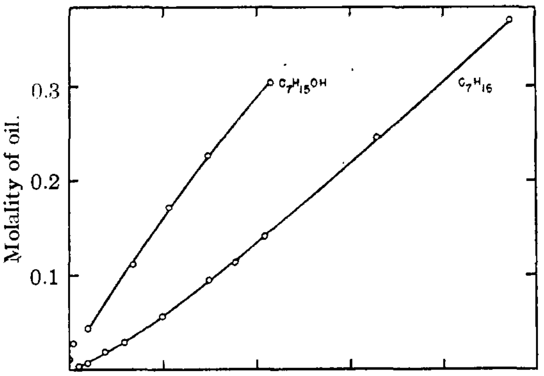

Fig. 1b.—Solubility of normal primary heptyl alcohol and of normal heptane in solutions of potassium tetradecanoate.

In Fig. 1a it is shown that the solubility in aqueous solutions of heptanol in aqueous solutions of potassium dodecanoate is twice as great as that of heptane at the higher soap concentrations. At low concentrations the ratio is much larger. In this figure the concentrations are given in moles per 1000 g. of the solution, but since the density of the soap solutions is, at all concentrations, very close to unity, these are very close to the molar concentrations. In Fig. 1b the concentrations are expressed in terms of molality, but the general relations remain as before.

The curve which represents the *non-polar* solubilization is, in both figures, convex toward the concentration axis. This is the usual relationship: the rate of increase of the non-polar solubilization with soap concentration, increases with soap concentration.

That which represents heptanol is concave toward the axis. Both curves are most highly curved just above the critical micelle concentration.

These curves indicate that, according to expectation, these two types of compounds exhibit two types of solubilization. These are considered further in a later section.

II. Experimental Methods

The solubility of the mercaptans was determined by an amperometric method, according to Kolthoff.[3]

That of the amines, alcohols and acids 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 increasingly turbid.

To determine the solubility of an alcohol 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

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[1a] 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.

[1b] M. L. Corrin and W. D. Harkins, *J. Chem. Phys.*, **14**, 640 (1946).

[2] W. D. Harkins, R. W. Mattoon and R. Mittelmann, *ibid.*, **14**, 763 (1947).

[3] I. M. Kolthoff and V. A. Stanger, "Volumetric Analysis," Interscience Pub., New York, N. Y., 1942, p. 264.

containing an increasing amount of the alcohol. The samples were shaken vigorously for forty-eight hours or more in order to attain equilibrium. That equilibrium was actually obtained was shown by approaching saturation from both undersaturation and supersaturation in enough instances to make certain that the times allotted were more than sufficient.

At the end of the time the turbidity of the solutions was measured by the use of a photometer. For those samples in which the amount of alcohol added was below the saturation value the turbidity was equal to that of the original soap solution. When an excess of alcohol was present, the solutions exhibited a rapid increase of turbidity, caused by the appearance of emulsion droplets, with increase in the amount of alcohol. A plot was made of the turbidity against the amount of alcohol added, and the sharp break in the curve was considered as the saturation point. Fig. 2 shows the type of curve obtained upon addition of benzene to a 6.89% solution of potassium laurate. The method works well if there is a large difference between the refractive index of the alcohol and that of the soap solution.

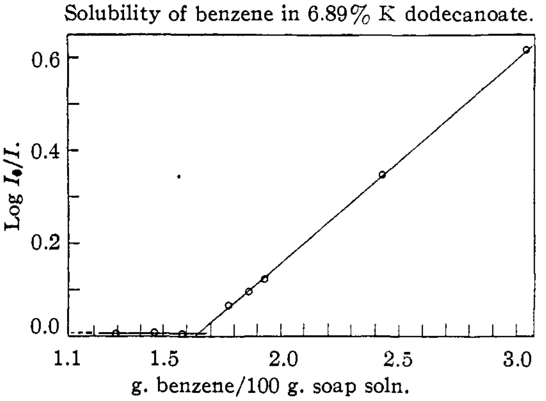


Fig. 2.—Turbidity of solutions of benzene in 6.89% potassium dodecanoate. The solubility is given by the intersection of the two straight lines.

The soaps were prepared as follows: No commercial soaps were used. The fatty acid (Eastman Kodak Co.) was dissolved in ethyl alcohol. This solution was slowly added to a hot solution of the base (usually KOH) in ethanol. The amount of base was about 10% more than the theoretical amount necessary for neutralization. On cooling, the soap crystallized. It was allowed to stand overnight and then was filtered off. It was purified by two or three recrystallizations from a mixture of ethyl alcohol and acetone. The final drying was done *in vacuo* over potassium hydroxide.

Sodium dodecyl sulfate (Procter and Gamble) was extracted with ether once or twice until it had lost its yellow appearance. Then it was recrystallized from 95% ethyl alcohol for two or three times. The crystals were very well formed. The drying was done *in vacuo* over potash.

The alcohols were obtained from Eastman Kodak Co. and Connecticut Hard Rubber Company, and were purified by fractional distillation, with the higher alcohols at a low pressure.

III. Effect of Length of the Hydrocarbon Chain.—The solubility of the *n*-long chain alcohols in solutions of potassium tetradecanoate is found to fall rapidly in the series, 7, 10, and 12 carbon atoms (Fig. 3). This is the general relation found for the hydrocarbons, but the solubilities exhibited here are in all cases much greater at the same chain length as pointed out earlier for heptane and heptanol.

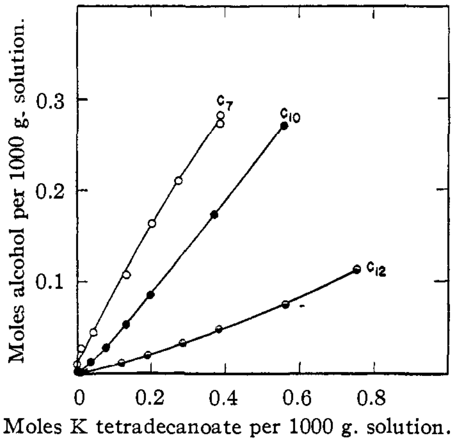
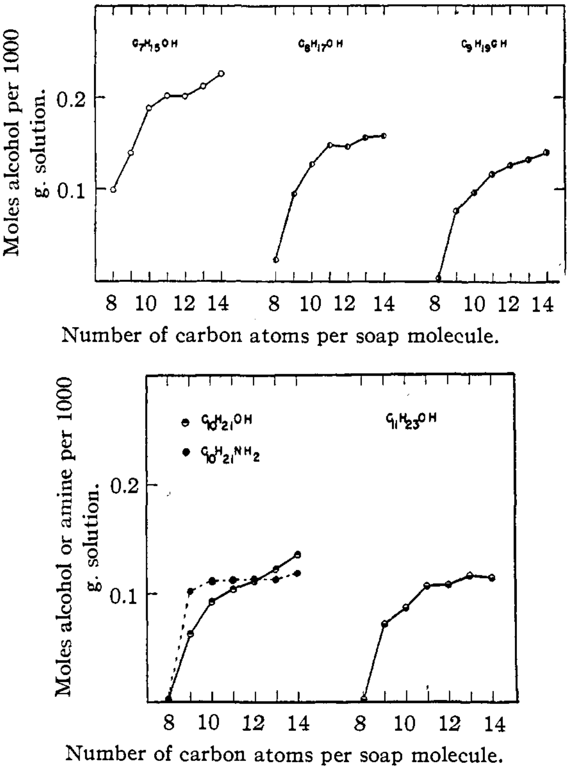


Fig. 3.—Solubility of heptanol, decanol and dodecanol (normal primary alcohols) in solutions of potassium tetradecanoate.

A general increase in the solubility of alcohols with chain length of the soap is exhibited in Figs. 4a and b, with soaps of from 8 to 14 carbon atoms. All alcohols, except heptanol, show by far the greatest increase between the 8 and the 9 carbon atom soap.



Figs. 4a and b.—Solubility of normal primary alcohols of 7 to 11 carbon atoms in solutions of soaps from 8 to 14 carbon atoms at 0.3 molar concentration.

A decrease in solubility with length of the hydrocarbon chain of the alcohol is brought out in

TABLE I

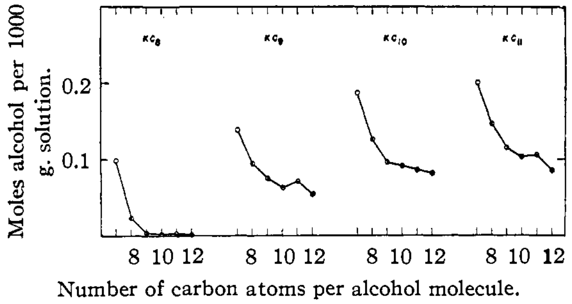
NON-POLAR SOLUBILIZATION OF n-HEPTANE IN POTASSIUM TETRADECANOATE

% K-tetradecanoate $\left(\frac{\text{Grams soap}}{\text{100 g. soln.}} \times 100\right)$	$\frac{\text{Moles K-tetradecanoate}}{\text{1000 g. solution}}$	Soap molality	$\frac{\text{Grams oil}}{\text{1000 g. soap soln.}}$	n-Heptane molality
H_2O	...	...	0.07	0.0007
0.50	0.019	0.019	.39	.0039
1.04	.039	.040	.58	.0059
2.03	.076	.078	1.92	.0196
3.02	.114	.118	2.9	.0298
5.04	.189	.199	5.3	.0557
7.47	.280	.303	8.8	.0956
8.69	.326	.357	10.5	.115
10.0	.376	.418	12.7	.141
14.9	.560	.658	21.0	.246
20.1	.757	.948	29.5	.369

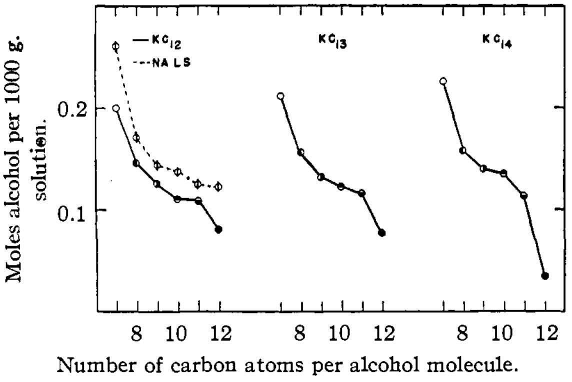
POLAR SOLUBILIZATION OF n-HEPTANOL IN POTASSIUM DODECANOATE

% K-dodecanoate $\left(\frac{\text{Grams soap}}{\text{100 g. soln.}} \times 100\right)$	$\frac{\text{Moles K-dodecanoate}}{\text{1000 g. solution}}$	Molality	$\frac{\text{Moles alcohol}}{\text{1000 g. soap sol.}}$	Molality alcohol
....	0.0	....	0.0103	0.0103
0.206	.0077	0.0077	.026	.026
1.056	.0397	.0401	.044	.044
3.511	.132	.137	.108	.112
5.32	.200	.211	.163	.172
7.315	.275	.297	.210	.227
10.268	.386	.430	.273	.304

Figs. 5a and b. In general the increase from 7 to 8 carbon atoms has by far the largest effect.



Concentration of soap: 0.3 molar.



Figs. 5a and b.—Effects of soaps from 8 to 14 carbon atoms in length upon the solubility of alcohols from 7 to 12 carbon atoms in length. Concentration of soap: 0.3 molar.

The data upon which the figures are based are assembled in Tables I to III.

TABLE II

SOLUBILITY OF ALCOHOLS IN SOLUTIONS OF POTASSIUM DODECANOATE AND TETRADECANOATE

Moles KC_{14} per 1000 g. soap solution	Moles alcohol per 1000 g. soap solution
n-Heptanol in potassium tetradecanoate	
..(water)	0.0103
0.00774	.026
.0397	.044
.132	.108
.200	.163
.275	.210
.386	
n-Decanol in potassium tetradecanoate	
..(water)	0.0003
0.037	.012
.075	.028
.131	.054
.197	.085
.370	.174
.556	.272

Figure 6 gives a few curves which illustrate the relationship between soap concentration and the solubility of non-polar oils,[4] in solutions of potassium tetradecanoate, with a curve for decanol added for comparison. From other experiments it is known that decanol is about twice as soluble as heptanol. With the 10 C atom chain the curva-

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(4) R. S. Stearns, H. Oppenheimer, E. Simon and W. D. Harkins, *J. Chem. Phys.*, **15**, 496-507 (1947)

TABLE III

SOLUBILITY OF *n*-PRIMARY ALCOHOLS, AMINES AND MERCAPTANS IN SOLUTIONS OF DETERGENTS OF 0.3 MOLE PER 1000 G. SOLUTION (SOLUBILITY IN MOLES PER 1000 G. SOAP SOLUTION)

Soap	KC_8	KC_9	KC_{10}	KC_{11}	KC_{12}	KC_{13}	KC_{14}	Na dodecyl sulfate
				Alcohol				
$C_7H_{15}OH$	0.099	0.139	0.188	0.201	0.201	0.212	0.226	0.260
$C_8H_{17}OH$	.023	.095	.127	.148	.146	.156	.158	.171
$C_9H_{19}OH$	.004	.076	.0965	.1165	.126	.132	.140	.144
$C_{10}H_{21}OH$	.003	.063	.0923	.104	.111	.122	.136	.138
$C_{11}H_{23}OH$	.003	.072	.0865	.107	.1075	.116	.114	.125
				Amine				
$C_{10}H_{21}NH_2$	0.004	0.102	0.11	0.113	0.113	0.113	0.119	0.110
				Mercaptan				
$C_7H_{15}SH$	0.0007	0.0014	0.0102	0.0171	0.0393	0.0591	0.090	0.0925

ture is not so different from that in non-polar solubilization as with 7 C atoms.

IV. Discussion. Solubilization of Polar-Nonpolar Long Chain Molecules.—Papers on solubilization alone, such as that presented here and those of others,[5,6] give no evidence whatever to show where in the micelle polar–non-polar molecules are solubilized.

However, earlier work in this Laboratory[1b,2] and extensive X-ray investigations[7] give evidence, on the basis of the effects of long chain alcohols and amines on the X-ray bands and on the critical micelle concentration, which shows that the position and orientation of a polar–non-polar molecule is similar to that of a soap molecule. Thus the long polar–non-polar molecules are found to lie with their chains between those of the soap molecules, and their polar-hydrogen-bonding groups toward the water.

Summary

The solubility relations exhibited by polar–non-polar long chain substances in solutions of long chain electrolytes are found to be different from those with non-polar compounds. The former are in general more soluble than the latter. The curve for *n*-heptanol is concave, that for *n*-heptane convex, toward the concentration axis. Curves which relate polar–non-polar solubility are given for all of the ordinary soaps of from 7 to 14 C atoms for all of the *n*-primary alcohols of from 7 to 11 C atoms.

The effects of long chain polar–non-polar molecules on the X-ray bands and on the critical micelle concentration as presented in other communications from this Laboratory indicate the locus of such molecules in the micelle. Their position is like that of the soap molecules in that their polar groups are oriented toward the water and their hydrocarbon chains lie between those of the soap.

No work on solubilization gives evidence for this point of view. It shows merely that whereas two types of solubility behavior are expected on the above basis, they are also found.

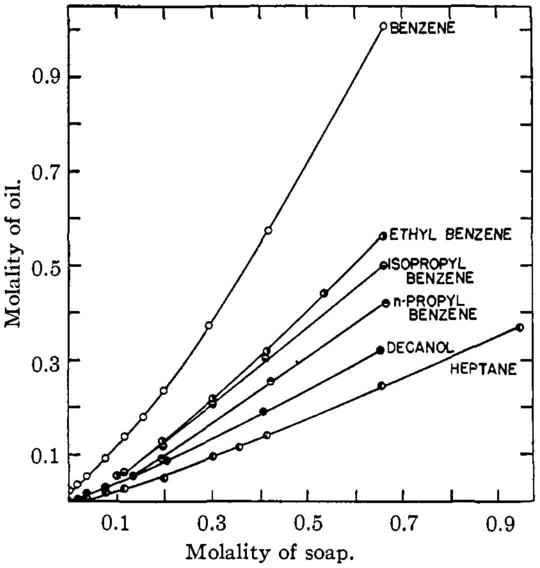

Fig. 6.—Solubility of decanol and of five hydrocarbons in solutions of potassium tetradecanoate.

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FINAL REVISED VERSION RECEIVED JUNE 20, 1948

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(5) A. W. Ralston and D. N. Eggenberger, THIS JOURNAL, **70**, 983 (1948).

(6) P. H. Richards and J. W. McBain, *ibid.*, **78**, 1338 (1948). J. W. McBain and M. McHan, unpublished work, Chicago meeting, A. C. S., Sept. 1947.

(7) W. D. Harkins and R. Mittelmann, presented for publication.