Solubilization in Alcohol–Soap Micelles[1]

BY H. B. KLEVENS[2]

There have been a number of indications that there are at least two loci of solubilization in soap micelles.[3] Definite evidence, based on extensive X-ray studies of soap solution–hydrocarbon systems, that the hydrocarbon center of the micelle is one of these loci has been summarized by McBain.[4] The very recent work on similar X-ray studies on soap solution–polar compounds by McBain and McHan[5] on systems containing soap solutions and added dimethyl phthalate and on long-chain alcohol–soap solutions[6] in which no increase (at times a decrease) in long spacing is noted can only be explained by postulating a second loci of solubilization. In these systems, the long-chain alcohols must take a position like that of the soap molecules with their polar groups oriented toward the water layer and their hydrocarbon tails toward the micelle center. This has previously been noted from the extensive X-ray studies of Mattoon[7] on soap mixtures in which it was found that the long X-ray spacing varies linearly with mole ratio of the two soaps in the mixture. This would indicate mutual orientation of each soap in the mixed micelle for in soap mixtures the more soluble soap can be expected to act as a solubilizer for the less soluble one.[3]

If the above hypothesis, as the two types of solubilization, or to be more exact, two loci of solubilization in the micelle, is correct, it should be possible to prepare swollen micelles with enhanced solubilization characteristics. Two methods of preparation are possible by essentially saturating soap solutions with (1) a polar compound such as a long-chain alcohol and with (2) a hydrocarbon. Data, indicating as much as a tenfold increase in amount of hydrocarbon solubilized by alcohol–soap micelles, have been obtained.

Experimental Methods

Saturation of micelles with additive, either hydrocarbon or polar compound, was determined by the turbidimetric method described previously.[8] This method is based on the fact that as the saturation point is exceeded, emulsification, rather than solubilization, begins and the solutions become increasingly turbid with increment addition of hydrocarbon or polar compound. This method is valid when the refractive indices of soap solution and solubilized material are different.

To determine solubilities in swollen micelles the following procedure was adopted. To weighed amounts of soap solutions in ampules, a weighed amount of a long-chain alcohol or other polar material was added, ampules were sealed off and shaken for twenty-four hours. Increasing amounts of *n*-heptane were then added and the vials were placed in a shaker for another forty-eight hours or more until constant optical density values (D) were obtained. Optical densities were obtained and when plotted against moles of added hydrocarbon (if the systems below saturation were clear) yielded two straight lines, the intercept of which was the solubility. One line had a constant or slightly decreasing D with added hydrocarbon below saturation in which D was essentially equal to that of the original soap solution; the other increased markedly at saturation and D increased linearly with further addition of hydrocarbon.

If the amount of *n*-heptanol added initially exceeds its normal solubility in KC_{14} solutions, and if to these solutions are added various amounts of *n*-heptane, curves similar to that seen in Fig. 1 are obtained. The initial opacity is due to the presence of *n*-heptanol emulsion droplets in equilibrium with mixed KC_{14}–*n*-heptanol micelles. Addition of *n*-heptane, which enters the hydrocarbon-like center of the soap–alcohol micelle, causes the micelle to swell. This then allows more alcohol molecules to enter the micelle as is indicated by a marked decrease in D. The solution then becomes clear upon addition of further *n*-heptane indicating that all the excess alcohol molecules as well as added hydrocarbon have been solubilized. Addition of further *n*-heptane yields the typical two straight lines mentioned above in which the intercept is the limit of solubility. The limit of solubility is then this second transition point. The presence and independence of the two loci of solubilization is definitely indicated by the results of this type of experiment. There appears to be little or no mutual mixing of these polar and nonpolar compounds being solubilized. It is also possible to obtain these end-points (limits of solubility) by reversing the order of the addition of compounds to be solubilized.

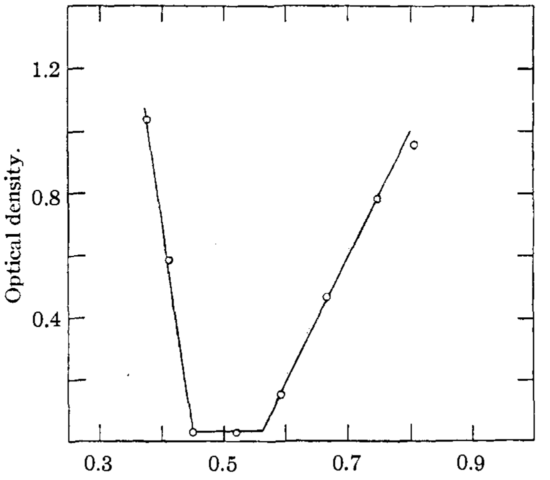

Fig. 1.—Effect of added *n*-heptane upon the turbidity of a soap–alcohol system in which initial alcohol concentration is greater than its solubility.

Potassium tetradecanoate was prepared by saponification of the corresponding methyl ester, which had been

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[1] Presented at 116th American Chemical Society Meeting, Atlantic City, New Jersey, September 18–23, 1949.

[2] Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minn.

[3] H. B. Klevens, *J. Am. Oil Chem. Soc.*, **26**, 456 (1949); W. D. Harkins and H. Oppenheimer, THIS JOURNAL, **71**, 808 (1949).

[4] J. W. McBain, "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

[5] J. W. McBain and H. McHan, THIS JOURNAL, **70**, 3838 (1948); J. W. McBain and O. A. Hoffman, *J. Phys. Colloid Chem.*, **53**, 39 (1949).

[6] W. D. Harkins, R. W. Mattoon and R. Mittelmann, *J. Chem. Phys.*, **15**, 763 (1947).

[7] W. D. Harkins, R. W. Mattoon and M. L. Corrin, THIS JOURNAL, **68**, 220 (1946).

[8] W. Heller and H. B. Klevens, *J. Chem. Phys.*, **14**, 567 (1946).

fractionally distilled at low pressures. Three recrystallizations from ethanol and from ethanol–acetone mixtures were made. To prevent hydrolysis, the soap solutions were so prepared that they contained initially an excess of about 5% potassium hydroxide.

The long-chain alcohols and mercaptan were obtained from Humphrey–Wilkinson Co. (formerly Chemical Division of Connecticut Hard Rubber Co.) and from Eastman Kodak Co. The long-chain amine was supplied by the Armour Laboratories. These were purified by fractional distillation. The *n*-heptane was obtained from Westvaco Chlorine Co. and since it had been shown to have only negligible amounts of unsaturated or branch-chain impurities by spectroscopic measurements,[9] it was used as obtained.

All solubilization experiments were run at 25 ± 2°.

Effect of Added *n*-Heptanol on Solubility of *n*-Heptane in Potassium Tetradecanoate Solutions.—The effect of polar groups on solubilization is seen in Fig. 2 where the solubility of *n*-heptane and *n*-heptanol in potassium tetradecanoate solutions (KC_{14}) are compared. These results are essentially in agreement with those reported recently.[3] At concentrations above 0.38–0.40 *M* KC_{14}, gel formation occurs upon addition of *n*-heptanol to KC_{14} solutions which interferes somewhat with completing mixing. These gels can be liquefied upon slight heating or upon the addition of a hydrocarbon such as *n*-heptane.

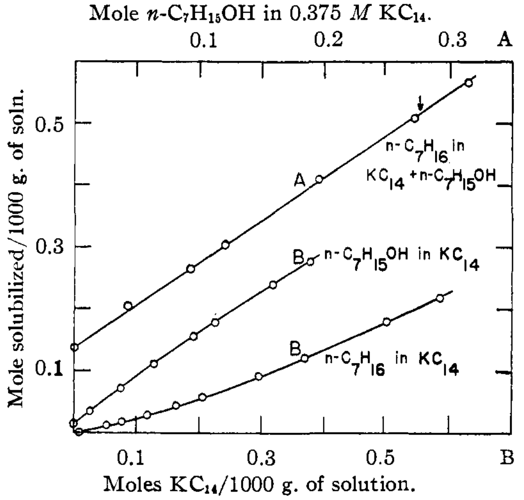

Fig. 2.—Solubilization of *n*-heptane and *n*-heptanol in potassium tetradecanoate (KC_{14}) solutions (B): enhancement of *n*-heptane solubility in 0.375 *M* KC_{14} by addition of *n*-heptanol (A). Arrow indicates limit of solubility of *n*-heptanol in 0.375 *M* KC_{14} solutions.

A marked enhancement of solubility of *n*-heptane is obtained upon addition of *n*-heptanol to KC_{14} solutions. This is clearly evident as indicated in Fig. 2 in the case where varying amounts of *n*-heptanol are added to 0.375 *M* KC_{14} solutions before solubilization of *n*-heptane is attempted. A linear increase in solubilization of *n*-heptane with increase in *n*-heptanol is noted. The slope of this curve is much steeper than the solubility of *n*-heptane in pure KC_{14} solutions indicating an enhancement in solubilizing power of the shorter-chain non-charged alcohol or compared with the KC_{14} molecule.

Effect of Alcohol Chain Length on Enhancement of Solubilization of *n*-Heptane.—The data indicating the effect of added long-chain alcohols, *n*-heptanol through *n*-dodecanol, on the increased solubilizing power of 0.35 *M* KC_{14} solutions for *n*-heptane are collected in Table I. It is evident from these data that, with increase in chain length of the alcohol, there is an ever increased solubilization of *n*-heptane. This increase is more pronounced than the addition of equivalent amounts of KC_{14}. This enhanced effect is well illustrated in Fig. 3 in which the effect of the addition of these alcohols as well as additional KC_{14} on the solubilizing power of 0.35 *M* KC_{14} can be seen. The solubilization of *n*-heptane is plotted against total moles of solubilizer (0.35 *M* KC_{14} + *n* moles KC_{14} or some long-chain alcohol).

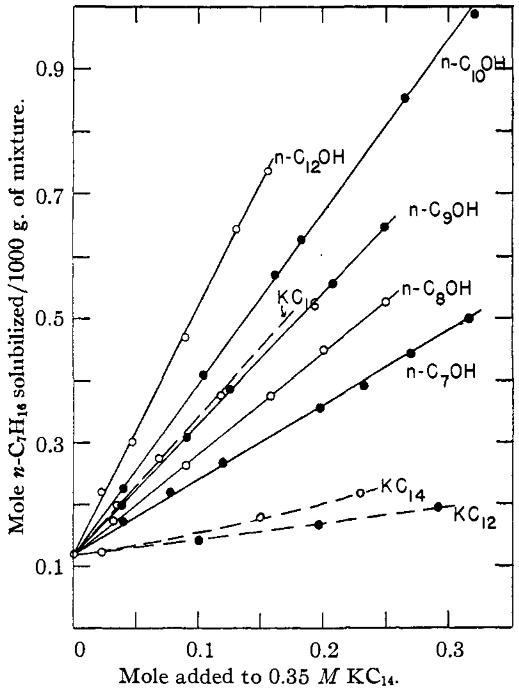

Fig. 3.—Enhancement of solubilization of *n*-heptane in 0.35 *M* potassium tetradecanoate solutions by the addition of long-chain alcohols. Dotted curves indicate the corresponding effect when other fatty acid soaps are the additives.

For comparison with the effect of long chain alcohols as additives, data obtained with the addition of other fatty acid soaps[10] are included in Fig. 3. The addition of potassium dodecanoate (KC_{12}) and shorter chain soaps results in a decrease in solubilization below that of equivalent amounts of KC_{14} whereas the addition of potassium hexadecanoate (KC_{16}) shows a marked increase in solubilization. The increase upon the

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[9] H. B. Klevens and J. R. Platt, This Journal, 69, 3055 (1947).

[10] H. B. Klevens, unpublished data.

TABLE I

EFFECT OF ADDED LONG CHAIN ALCOHOLS ON SOLUBILIZATION OF *n*-HEPTANE IN 0.35 *M* POTASSIUM TETRADECANOATE SOLUTIONS

Moles added alcohol/1000 g. KC_{14} soln.	Moles n-C_7H_{16} solubilized/1000 g. alcohol–KC_{14} soln.	$\frac{\text{Sol. in } KC_{14}\text{–alcohol}}{\text{Sol. in } KC_{14}}$	$\frac{\text{Moles } KC_{14}}{\text{Moles (alcohol} + KC_{14})}$	$\frac{\text{Moles } n\text{-}C_7H_{16}}{\text{Moles (alcohol} + KC_{14})}$	Molecules n-C_7H_{16}/micelle	No. KC_{14} + alcohol molecules/micelle	Molecules KC_{14}/micelle
			n-Heptanol				
0	0.116	1.0	1.0	0.331	22	66	66
0.0411	.174	1.49	0.895	.445	30	80	71
.0812	.222	1.91	.810	.515	34	88	71
.120	.268	2.31	.745	.570	38	94	71
.195	.356	3.07	.642	.652	44	105	70
.230	.395	3.40	.603	.695	46	108	65
.270	.442	3.82	.563	.714	48	111	63
.318	.500	4.32	.524	.747	50	114	61
						Av.	67
			n-Octanol				
0.0380	0.183	1.58	0.902	0.472	31	82	73
.0902	.262	2.26	.796	.595	40	98	78
.158	.375	2.78	.690	.739	49	112	77
.201	.451	3.90	.636	.820	55	120	77
.249	.528	4.55	.583	.880	59	126	74
						Av.	76
			n-Nonanol				
0.0381	0.198	1.71	0.902	0.510	34	87	79
.0901	.307	2.65	.796	.698	47	109	86
.126	.386	3.33	.734	.811	54	118	87
.208	.558	4.81	.627	1.01	67	138	86
.248	.647	5.58	.585	1.08	72	144	84
						Av.	84
			n-Decanol				
0.0390	0.227	1.96	0.900	0.583	39	96	87
.107	.410	3.53	.765	.895	60	128	98
.162	.570	4.91	.683	1.11	74	147	101
.184	.629	5.41	.655	1.18	78	153	100
.264	.855	7.37	.570	1.39	92	170	97
.322	.989	8.53	.521	1.47	98	179	94
						Av.	96
			n-Dodecanol				
0.0221	0.220	1.89	0.942	0.597	40	98	92
.0442	.301	2.60	.888	.765	51	115	102
.0901	.472	4.07	.795	1.07	72	139	109
.131	.645	5.57	.727	1.34	90	168	122
.156	.737	6.35	.692	1.46	97	177	122
						Av.	109

addition of KC_{16} is much more than could be expected if only the increase in chain length by two carbon atoms over KC_{14} is important. The insolubility of the KC_{16} at the temperature at which these experiments have been run and the equivalent insolubility of the long-chain alcohols may also be factors in addition to chain length which influence this enhancement in solubilization. The effect of increased temperature on these solubilization experiments will throw more light on this point.

If points are taken at a definite solubilizer concentration, say 0.45 *M* (0.35 *M* KC_{14} + 0.10 *M* additive) for each of the additives and if these are plotted as functions of alcohol chain length or number of carbon atoms in the chain, curves similar to those in Fig. 4 are obtained. The increase in slope of these curves is indicative of the effect of chain length in a homologous series on additive properties. It should be noted that, for any particular concentration, there is no linear relationship between solubilization and chain length. If these curves are extended, using the equivalent decrease in slope found at longer chain lengths, they will be found to intercept the equivalent KC_{14} concentrations (indicated by bars in Fig. 4) at points which would indicate that KC_{14} would correspond to an alcohol of chain length of about five carbon atoms. Actually, the addition of *n*-pentanol to KC_{14} solutions has resulted in in-

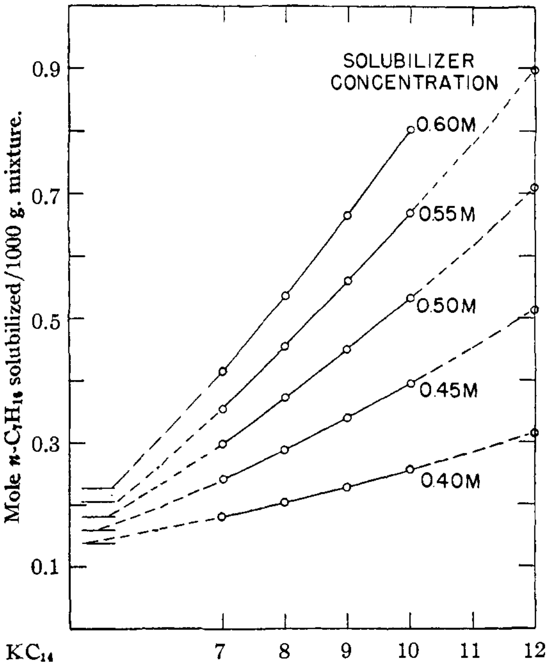

Fig. 4.—Effect of chain-length of alcohol additive for constant solubilizer concentration (0.35 M KC_{14} + n moles additive) upon solubilization of n-heptane. Bars indicate effect of KC_{14} as additive.

creases in solubilization above this extrapolated value due possibly to the solubility of n-heptane in the C_6 alcohol.

The ratio indicating the increased solubilization of n-heptane in alcohol–soap micelles is indicated in column 3 of Table I. No attempts have been made to extend this enhancement further. The solubilities of the longer-chain alcohols are extremely low and their effect as additives has not been determined. The addition of further amounts of long chain alcohols beyond equivalent concentrations of alcohol and soap has not been attempted so no answer as to the minimum number of soap molecules necessary for micelle formation in the presence of relatively large amounts of long-chain alcohol molecules can be advanced. However, when these data are obtained, much more information can be surmised as to the role of both the charged hydrophilic head and the hydrophobic long-chain tail on orientation of soap molecules in solution and on their aggregation as micelles.

From the mole ratio of hydrocarbon to solubilizer (soap + alcohol), it is possible to calculate the number of n-heptane molecules per soap micelle if a value of 66 soap molecules per micelle is used. This is about an average of the values for a soap of this chain length.[11] A value of about 150 molecules per hydrocarbon swollen micelle[12] might also be used but since the effect of addition of long-chain alcohols on micellar size is not definitely known, the smaller value is used in these calculations. A constant factor can be used to correct these figures if a more definite value is obtained. By use of a value of 66 molecules per micelle, it is seen (column 6, Table I) that, with increasing alcohol concentration, the number of n-heptane molecules solubilized per micelle increases more than fourfold. Over the same concentration range, from 0.35 to 0.60 M, the number of n-heptane molecules (M) solubilized per micelle when KC_{14} is the additive only changes from 22 to 25, whereas, with n-decanol as additive, the increase is from 22 to 90.

By assuming that the density of n-heptane in all these swollen micelles is the same, it is possible to calculate directly, using the value of 22 n-heptane molecules per micelle, the number of alcohol and soap molecules in a micelle necessary to accommodate this increased amount of hydrocarbon. The values of N, the total number of molecules, alcohol plus soap, in this micelle are collected in column 7 of Table I. With increase in added alcohol, N is seen to approach a constant value.

Since the initial amounts of soap and added alcohols are known, it is possible, from this initial mole ratio and from the calculated number of soap and alcohol molecules per micelle, to calculate the number of KC_{14} molecules per micelle. These values are seen in the last column in Table I and are found to be fairly constant for any one added alcohol. The averaged value for any added alcohol is seen to increase with increase in chain length of the alcohol. The entrance of the alcohol into the palisade layer of the soap micelle will bring about a change in the curvature of the micelle surface which will be further enhanced by an increase in the length of the hydrocarbon tail of the long-chain alcohol.

The Effect of Change in the Polar Group on Solubilization.—Data, similar to those obtained showing the enhancement of solubility of n-C_7H_{16} by the addition of long-chain alcohols, have been obtained with added amines and mercaptans as seen in Table II. In contrast to the effect of added n-octanol, substitution in the additive molecule of $-NH_2$ and $-SH$ for the $-OH$ group results in a 1.6- and 1.9-fold increase respectively over that of the added alcohol. The n-octylamine is seen to be about equivalent to n-decanol in the increase of the solubilizing power of KC_{14}, and the n-octylmercaptan falls midway between n-decanol and n-dodecanol, approximately where one would expect the data for n-undecanol to fall. This increase found when $-NH_2$ and $-SH$ are substituted for $-OH$ groups in an alkyl chain of the same length would indicate that more than just the length of the alkyl chain is important in micelle formation and in solubilization. Thus the effect of added $-SH > -NH_2 > -OH$ for equal chain

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[11] P. Debye, *J. Phys. Colloid Chem.*, **53**, 1 (1949).

[12] H. B. Klevens, *ibid.*, in press.

lengths upon the decrease in the critical micelle concentration.[10]

Discussion

The addition of long-chain alcohols, amines and mercaptans to soap solutions has been shown to greatly enhance the solubilization of *n*-heptane. This increase must depend on at least two factors: (1) alkyl chain length as indicated by increase in number of carbon atoms in the *n*-alkyl alcohols and (2) type of polar group for $-SH > -NH_2 - OH > -COO^-$ for equal chain lengths in the effectiveness of these alkyl derivatives as additives.

TABLE II

EFFECT OF CHANGE IN POLAR GROUP OF ADDITIVE UPON SOLUBILIZATION OF *n*-HEPTANE IN 0.35 *M* POTASSIUM TETRADECANOATE SOLUTIONS

Moles additive/ 1000 g. KC_{14} soln.	Moles *n*-heptane solubilized/ 1000 g. KC_{14}-additive soln.	$\frac{\text{Sol. in } KC_{14}\text{-additive}}{\text{Sol. in } KC_{14} \text{ soln.}}$	$\frac{\text{Moles } KC_{14}}{\text{Moles (additive} + KC_{14})}$	Molecules n-C_7H_{16}/ micelle	No. KC_{14} + additive molecules/ micelle	Molecules KC_{14}/ micelle
n-Octanol						
0	0.116	1.0	1.0	22	66	66
0.0380	.183	1.58	0.902	31	82	73
.0902	.262	2.26	.796	40	98	78
.158	.375	2.78	.690	49	112	77
.201	.451	3.90	.636	55	120	77
.249	.528	4.55	.583	59	126	74
					Av.	76
n-Octylamine						
0.0388	0.251	2.16	0.900	43	102	92
.0603	.323	2.78	.853	52	117	99
.1206	.518	4.46	.745	74	147	110
.1650	.660	5.70	.680	86	163	110
.211	.815	7.02	.623	96	175	109
					Av.	104
n-Octylmercaptan						
0.0261	0.226	1.95	0.930	40	98	91
.0522	.327	2.82	.870	54	120	105
.101	.503	4.34	.778	74	147	114
.137	.670	5.78	.718	92	170	122
.197	.906	7.80	.639	110	191	122
					Av.	111

For any one polar group, say –OH, the increase in solubilizing power with chain length can best be explained by taking into account the fact that solubilization is related to the type of micelle present and to the critical concentration (CMC). The addition of long-chain alcohols decreases this CMC, as is indicated by a decrease in the value from 0.0066 *M* in KC_{14} to one of 0.0040 *M* in KC_{14} plus 0.005 *M* *n*-heptanol.[10] The addition of the alcohol results in an increase in the total van der Waals attraction due to the presence of the added hydrocarbon tail without a corresponding increase in the coulombic repulsion forces usually associated with the like-charged polar groups of the soap or detergent. Thus the average contribution per added carbon atom to the total attraction energy is much larger in the case where the additive is a long chain alcohol than where it is the same or another soap. Further, as the chain length of the alcohol is increased, there is a corresponding increase in the total attraction. This would result in some increase in micelle size, and coupled with this, an increase in solubilizing power. This is consistent with the results on the increase in solubilization of *n*-heptane with increase in chain length of added alcohol and with the observation that increase in chain length of the soap will increase the size of the micelle[11] and will increase the solubilization of a hydrocarbon.[8]

Coupled with this decrease in CMC upon addition of long-chain alcohols is the fact that there is an increase in the size of the micelle. Thus, based on a modified long spacing X-ray band, Mattoon has calculated that, in a 0.57 *M* KC_{14} solution, there are about 75 soap molecules per micelle and in this solution saturated with *n*-dodecanol the number increased to 180.[6] This is about 2.4 times the original value compared to an increase of 1.8–1.9 times as is indicated by the solubilization data in Table I in which a value of 66 soap molecules per micelle is taken as a unit.

The series $-COO^- < -OH < -NH_2 < -SH$ for equal alkyl chain lengths with regard to solubilization of *n*-heptane can be explained by the fact that the average contribution per carbon atom to the total attraction energy (and thus to increase in micelle size) must follow this same regularity. The penetration of the alkyl chain into the palisade layer of the micelle must increase with decrease in the energy of adhesion between the polar compound and water. Orientation theory predicts an increase in adhesional energy of a polar compound over that of a hydrocarbon since it postulates that the polar groups are oriented toward the water with a resultant dipole–dipole action coupled with the possibility of some hydrogen bonding. The –OH, $-NH_2$, $-COO^-$ groups are known to be capable of hydrogen bond formation and there is some evidence which indicates that this occurs with the –SH group although much weaker than the others.[13] Thus the simplest explanation of the changes in solubilizing power with different polar groups is one based on the approach of the polar group to the surface water layer of the micelle. The added molecule containing the fatty acid ion would lie, on the average, in the plane of the initial fatty acid ions of the micelle. Those with the –OH group would not penetrate as far into this layer as the $-COO^-$ additives and thus the contribution per carbon atom of the former to the total attraction would be greater. The penetration of the $-NH_2$ group would be less and the smallest would be that of the –SH compounds, and, correspondingly, there would be a further increase in attraction per carbon atom with decrease in penetration. The

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(13) M. L. Huggins, *J. Phys. Chem.*, **40**, 723 (1936); *J. Org. Chem.*, **1**, 407 (1936).

values of the energy of adhesion between additive and water and total energy of adhesion are 41 ergs/sq. cm. and 93 with *n*-heptane and 92 and 165 with *n*-heptanol, respectively.[6] The high dipole moment of the water does not give a very strong induced dipole in the hydrocarbon and thus there is probably no solubilized hydrocarbon molecules passing from the interior of the micelle into the palisade layer of the soap micelle. As this attraction increases through $-SH$, $-NH_2$, $-OH$ and $-COO^-$, this high dipole moment of the water results in more penetration of these molecules into the polar end of the palisade in about the above order.

Summary

The use of long chain alcohols, *n*-heptanol through *n*-dodecanol, as additives has been found to markedly increase the solubilization of *n*-heptane in potassium *n*-tetradecanoate solutions. Use of long-chain alcohols as additives have a much greater enhancement of solubilizing power than equivalent amounts of added soaps of the same chain length. When the polar group on the additive is changed, it is found that for equal chain lengths $-COO^- < -OH < -NH_2 < -SH$ in the enhancement of solubilization. This is explained by a greater penetration into the palisade layer of the soap micelle of these various polar compounds in the same order noted in the increase in solubilizing power. This is in agreement with the attraction of these polar groups for the water layer due to the high dipole moment of the latter.

ST. PAUL, MINN. RECEIVED OCTOBER 24, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF ROCHESTER]

Hydrogenolysis of Certain Substituted Aromatic Acids and Carbonyl Compounds by Lithium Aluminum Hydride

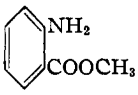
BY LLOYD H. CONOVER[1] AND D. S. TARBELL

The observation[2] that the 5-carbethoxy group, in certain 2-amino-5-carbethoxythiazole derivatives, is reduced to a methyl group by lithium aluminum hydride led us to study the behavior toward this reagent of some analogously substituted benzene derivatives. The results indicate that an aromatic acid, carbonyl compound or carbinol, which contains an amino group ortho or para to the oxygen function, undergoes hydrogenolysis to a methyl or methylene group, when it is treated with excess lithium aluminum hydride.[2a] Although this point is not established beyond doubt, the hydrogenolysis reaction appears to require the presence of a strongly electron-donating group in the ortho or para position. In support of this, it was found that *m*-aminobenzoic acid is reduced only to *m*-aminobenzyl alcohol, and ethyl benzoate to benzyl alcohol, under conditions which reduce *o*- or *p*-aminobenzoic acids to the corresponding toluidines. A possible explanation for the lack of reactivity of compounds containing active hydrogens lies in the immediate formation of an insoluble precipitate by reaction between the compound and lithium aluminum hydride. Such precipitation is marked both in the case of *m*- and *p*-aminobenzoic acid; thus here it does not seem to be the determining factor.

The hydroxyl group might be expected to promote the hydrogenolysis, just as the amino group does, but the hydroxy compounds examined—*p*-hydroxybenzoic acid, ethyl *p*-hydroxybenzoate, methyl salicylate and 2,4-dihydroxybenzaldehyde—showed no detectable amount of the expected cresol derivatives. Since mixing of the reactants in these cases resulted in virtual solidification of the reaction mixtures, the failure of these reactions may well be traceable to the precipitation phenomenon. This possibility is supported by the fact that the only methoxy compound studied, 4,4′-dimethoxybenzophenone, gave a considerable amount of 4,4′-dimethoxydiphenylmethane.

The 2-amino-5-carbethoxythiazoles were reduced to 2-amino-5-methyl compounds merely by standing in ether solution at room temperature with excess reducing agent.[2] The benzene derivatives did not give very good yields of hydrogenolysis products under these conditions; the yields were much greater, however, when the reduction was carried out in ether–dibutyl ether mixtures (sometimes containing benzene) at about 80° for several days. Temperatures above 100° were unsatisfactory, probably due to the instability of lithium aluminum hydride at these temperatures.[3]

The reduction apparently proceeds with the rapid formation of the benzyl alcohol, which undergoes hydrogenolysis to yield the oxygen-free compound. These relationships were demonstrated with methyl anthranilate I, which, treated with excess lithium aluminum hydride at 65° for



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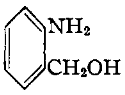

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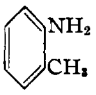

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[1] Abbott Laboratories Fellow, 1948–1950.

[2] Conover and Tarbell, THIS JOURNAL, **72**, in press (1950).

[2a] Witkop, *ibid.*, **72**, 614 (1950), has reported the hydrogenolysis of an *o*-aminoketone (spiro-(cyclopentane-1,2′-pseudoindoxyl)) by an excess of lithium aluminum hydride.

[3] Finholt, Bond and Schlesinger, *ibid.*, **69**, 1199 (1947).