merization of the ethereal iron to establish its magnetic moment. This was done by means of the formula $\mu_{\text{eff}} = 2.84\sqrt{\chi_m T}$, and the data are presented in Table III. The distributions examined were 5.60 WF. in aqueous hydrochloric acid.

Acknowledgment.—The authors of this paper thank Ernest H. Swift for his continuous advice and counsel during the experimental work, and for his helpfulness during the preparation of these papers for publication.

Summary

The visible and ultraviolet absorption spectrum of the isopropyl ether layers has been examined. The ultraviolet spectrum of anhydrous ferric chloride in isopropyl ether has also been measured. For the purpose of comparison the ultraviolet spectra of hydrochloric acid solutions of ferric iron were measured, and a great similarity was found between the spectrum of a concentrated hydrochloric acid solution and that of the iron complex in isopropyl ether. Some suggestions regarding the constitution of hydrochloric acid solutions of ferric chloride are made.

The isopiestic measurements indicate the polymerization of the extracted iron, while the magnetic susceptibility study gives a value of 5.95 Bohr magnetons for the magnetic moment of the ethereal iron.

PASADENA 4, CALIF. RECEIVED AUGUST 8, 1949

Effect of Electrolytes Upon the Solubilization of Hydrocarbons and Polar Compounds

BY H. B. KLEVENS[1]

The presence of at least two loci of solubilization has been established by the difference in changes in long X-ray spacings upon the addition of hydrocarbons and of polar compounds.[2,3,4] The existence of these two loci has also been indicated by comparison of solubilization data.[5] In the solubilization of non-polar compounds, the rate of increase in solubilization increases with soap concentration; for polar compounds, this rate shows no change or decreases. These results indicate that the solubilized hydrocarbon occupies a volume in the central hydrocarbon portion of the micelle resulting in a swollen micelle and that the polar compounds, such as long-chain alcohols take a position which is essentially similar to the soap molecules which make up the micelle.

Further evidence for the presence of these two loci and their apparent independence of each other has recently been obtained.[6] This is based on the fact that there is an enhancement of solubilizing power of a soap for a hydrocarbon when polar compounds in the form of long chain alcohols and amines are used as additives and further that the presence of added hydrocarbon increases the solubilization of a long chain alcohol by a soap. The effect of these additives has essentially been to result in the formation of an alcohol–soap micelle with a greatly enhanced solubilization power.

The addition of the long chain alcohols and amines probably results in a change in the curvature of the micelle surface due to a penetration of the alkyl chain of these additives into the palisade of soap hydrocarbon tails as well as to an increase in micellar size. This concept can be readily understood if one accepts a sphere or an oblate spheroid as the shape of the initial micelle. This penetration results in a considerable expansion of the volume available for hydrocarbon solubilization as is evidenced by a marked increase in amount of *n*-heptane solubilized by these alcohol–soap micelles.[6] In those cases where long chain alcohols are the additives, there is no expansion along the minor axis of the oblate spheroid micelle (distance = 2 × length of the soap molecule) as can be seen from the fact that there is no increase in X-ray spacing.[3,4] The increase in volume can probably be considered to be due to an increase in the major axis of this spheroid micelle.

Other additives, which result in such changes in curvature of the micelle surface and in corresponding changes in volume available for solubilization, should show similar solubilization changes. The addition of electrolytes will result in an effective decrease in the energy of repulsion of the like charged soap heads, will thus result in a decrease in curvature of the surface, and will increase the equilibrium size of the micelle. Debye has shown that there was a linear increase in molecular weight of the dodecylamine hydrochloride micelle with equivalents of added chloride ion concentration.[7] Thus, for solubilization of hydrocarbons, those which enter the micelle center and show increases in long X-ray spacings, it is to be expected that there will be an enhancement of solubility upon the addition of electrolytes. Further, since there is this decrease in energy of repulsion upon addition of electrolytes, it would follow that there would be a corresponding decrease in the effective volume available for solubilization in the soap palisade layers. Thus one would expect a marked

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(1) Agricultural Biochemistry, University of Minnesota, Minneapolis, Minn.

(2) H. Kiessig and W. Philippoff, *Naturwissen.*, **27**, 593 (1939).

(3) J. W. McBain and O. R. Hoffman, *J. Phys. Colloid Chem.*, **53**, 39 (1949).

(4) W. D. Harkins and R. Mittelmann, *J. Colloid Sci.*, **4**, 367 (1949).

(5) H. B. Klevens, *J. Am. Oil Chem. Soc.*, **26**, 456 (1949).

(6) H. B. Klevens, *J. Chem. Phys.*, **17**, 1004 (1949); THIS JOURNAL, **72**, 3581 (1950).

(7) P. Debye, *Ann. N. Y. Acad. Sci.*, **51**, 575 (1949).

decrease in the amount of solubilized long chain alcohols in the presence of added salts. The experimental data which follow substantiate these hypotheses.

Experimental Methods

The solubility of the hydrocarbons and the long chain alcohols were determined by a turbidimetric method[8] which was a modification of the one used by Engler and Dieckhoff.[9] This depends on the fact that, below solubilization, the opacity of an initially clear soap solution remains practically unchanged and that, above solubilization, the system becomes increasingly turbid with added hydrocarbon or alcohol. Two straight lines can usually be drawn through the data of optical density *vs.* concentration of added hydrocarbon and the intercept of these lines is the limit of solubilization.

To weighed samples of soap solutions plus added electrolyte were added different concentrations of hydrocarbon or alcohol. Vials were shaken at 25 ± 2° for about forty-eight hours to ensure equilibrium, for it has been indicated that equilibrium was often reached only after some twenty-four to forty-eight hours.[8]

The soap was prepared from a carefully fractionated methyl ester of tetradecanoic acid followed by saponification with hot alcoholic potassium hydroxide. Solutions were prepared so that there was always an excess of about 5% potassium hydroxide to prevent formation of acid soap. The long chain alcohols were obtained from Humphrey–Wilkinson Co. (formerly Chemical Division of Connecticut Hard Rubber Co.) and were purified by fractional distillation. The *n*-heptane obtained from Westvaco Chlorine Co. was used without further purification.

Effect of Potassium Chloride on Solubilization of *n*-Heptane and *n*-Octanol.—The solubility of *n*-heptane and *n*-octanol in 0.32 *M* potassium tetradecanoate (KC_{14}) solutions containing increasing amounts of potassium chloride is shown in Table I. The marked increase in the amount of *n*-heptane solubilized in the presence of added electrolyte is in accordance with previously reported findings[10,11] in the case of other electrolytes, and this enhancement in solubilization follows the predictions of the above hypothesis. The even more striking decrease in the amount of solubilized *n*-octanol is in marked contrast to the increase in the case of the hydrocarbon, *n*-heptane, but again these results are those expected from the above discussion.

When the concentration of the KC_{14} is decreased to 0.05 *M*, a similar increase in the amount of *n*-heptane solubilized with added potassium chloride is observed. However, there is seen to be an initial increase in the amount of *n*-octanol solubilized with added potassium chloride followed by a decrease when the concentration of potassium chloride is further increased. The results in the case of the hydrocarbon are similar to those at higher soap concentrations and are as expected. It is known that the full colloidal properties of a soap solution do not begin at the point of micelle formation, the critical micelle concentration (CMC). Thus McBain has indicated that the full colloidal properties of sodium dodecanoate are not evident until the concentration reaches 0.15 *M*.[12] The initial increase in solubility of the polar compound thus must be due to the fact that, at 0.05 *M* KC_{14} concentration, the micelles which are present have not reached their full solubilizing capacity. The addition of about 0.5 *M* potassium chloride to this soap concentration probably results in the formation of micelles with maximum solubilizing power for long-chain alcohols. These micelles can be considered to be equivalent to those which are found at higher soap concentrations, such as 0.32 *M* KC_{14}, in the absence of added potassium chloride.

TABLE I

SOLUBILIZATION OF *n*-HEPTANE AND *n*-OCTANOL IN POTASSIUM TETRADECANOATE SOLUTIONS WITH ADDED POTASSIUM CHLORIDE

Moles KCl/ 1000 g. soln.	Sol. (S) moles n-C_7H_{16}/ 1000 g. soln.	S n-C_7H_{16} (added KCl) / S n-C_7H_{16} (no KCl)	S Moles n-C_8OH/ 1000 g. soln.	S n-C_8OH (added KCl) / S n-C_8OH (no KCl)
	0.32 *M* KC_{14}			
0	0.105	1	0.165	1
0.10	.133	1.27	.148	0.90
.20	.154	1.47	...	..
.25	....	..	.129	.79
.35	.175	1.67	...	..
.50	.190	1.81	.097	.59
.75	.201	1.91	...	..
1.00	.210	2.00	.057	.35
1.30	....	..	.045	.27
	0.05 *M* KC_{14}			
0	0.0087	1	0.024	1
0.10	....	..	.028	1.16
.20	.016	1.84	...	..
.25	....	..	.032	1.33
.35	.019	2.18	...	..
.50	.023	2.65	.036	1.50
.75	....	..	.029	1.20
1.00	.030	3.45	.020	0.83
	0.007 *M* KC_{14}			
0 (0)[a]	0.0006	1	0.005	1
0.01 (0.0022)	.0008	1.33	.014	2.80
.025 (.0038)	.0012	2.00	.021	4.20
.05 (.0047)	.0014	2.3	.024	4.80
.10 (.0054)	.0016	2.7	.028	5.60
.30 (.0060)	.0018	3.0	.030	6.00

[a] Concentration micellar soap.

In those cases where solubilization is attempted at concentrations which are normally in the region of the CMC (0.0066 *M* for KC_{14} as determined by refraction[13] and 0.0070 *M* from dye solubilization[14]), upon the addition of potassium chloride results similar to those observed in Table I are obtained. It can be seen that there is an enhancement in solubilization of both the hydrocarbon,

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

(9) C. Engler and E. Dieckhoff, *Arch. Pharm.*, **230**, 561 (1892).

(10) P. H. Richards and J. W. McBain, THIS JOURNAL, **70**, 1338 (1948).

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

(12) J. W. McBain, "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

(13) H. B. Klevens, *J. Phys. Colloid Chem.*, **52**, 130 (1948).

(14) I. M. Kolthoff and W. Stricks, *ibid.*, **52**, 915 (1948).

n-heptane, and the polar compound, *n*-octanol. The addition of electrolytes brings about a decrease in the CMC and a direct relationship can be shown between the amount of micellar soap present due to this decrease in CMC and the amount of solubilized oil. Additional points obtained by increasing the concentration of micellar soap not by added electrolytes but by increase in KC_{14} concentration are found to result in the same solubilization values for equal micellar soap concentrations. The increase in solubilization of both hydrocarbon and polar compound upon addition of potassium chloride to this initial soap concentration of 0.007 *M* KC_{14} is not incompatible with the above hypotheses since this soap concentration is considerably below that at which the addition of electrolyte begins to affect the shape and size of micelles. The maximum observed in the case of *n*-octanol solubility in 0.05 *M* KC_{14} is more clearly understood when these data at 0.007 *M* KC_{14} are compared with those at 0.05 *M* KC_{14}.

When the concentration of added electrolyte is kept constant and that of the KC_{14} is varied, solubilization data of the type observed in Fig. 1 are obtained. The increased solubilization in the case of the *n*-heptane when potassium chloride is added to the KC_{14} solutions follows the interpretation outlined above. When the long chain alcohol is being solubilized, the initial increase at lower soap concentrations, followed by a decrease at about 0.10 *M* KC_{14} is in accord with previous data. This would indicate that at about 0.1 *M* KC_{14} in the presence of 0.25 *M* KCl, the influence of added salt in increasing the solubilization of *n*-octanol is just balanced by its influence in decreasing the solubilization of the alcohol. At concentrations above 0.1 *M* KC_{14}, there is a constant decrease per unit added soap concentration between the salt free and salt containing systems.

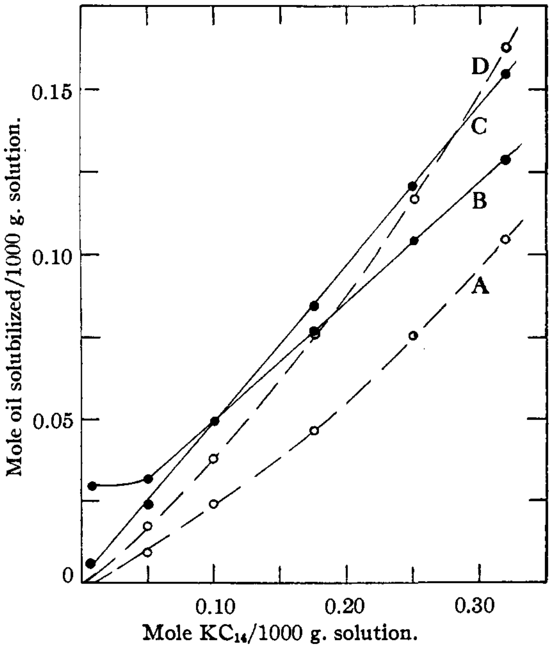

Fig. 1.—Effect of added KCl upon the solubilization of *n*-heptane and *n*-octanol in potassium tetradecanoate solutions (25°): (A), *n*-heptane in KC_{14}; (B), *n*-octanol in 0.25 *M* KCl + KC_{14}; (C), *n*-octanol in KC_{14}; (D), *n*-heptane in 0.25 *M* KCl + KC_{14}.

Effect of Different Salts on Solubilization.—The CMC of various soaps and detergents decrease in a regular fashion with equivalent concentration of added electrolyte[13,15] and depend only on the concentration of that ion which is opposite in charge to that on the colloidal electrolyte. It was of some interest to determine whether similar effects would be observed in solubilization of polar and non-polar compounds. The data in Fig. 2 indicate that these similarities observed in the formation of micelles do not carry over to solubilization. However, it is seen that for equivalent concentrations of added electrolyte to 0.32 *M* KC_{14}, $KCl > K_2SO_4 > K_4Fe(CN)_6 \cdot 3H_2O$ in the solubilization of *n*-heptane whereas the reverse order holds when *n*-octanol is solubilized. The ratios of oil solubilized in the three salts are about the inverse of each other when the hydrocarbon and polar compound solubilities are com-

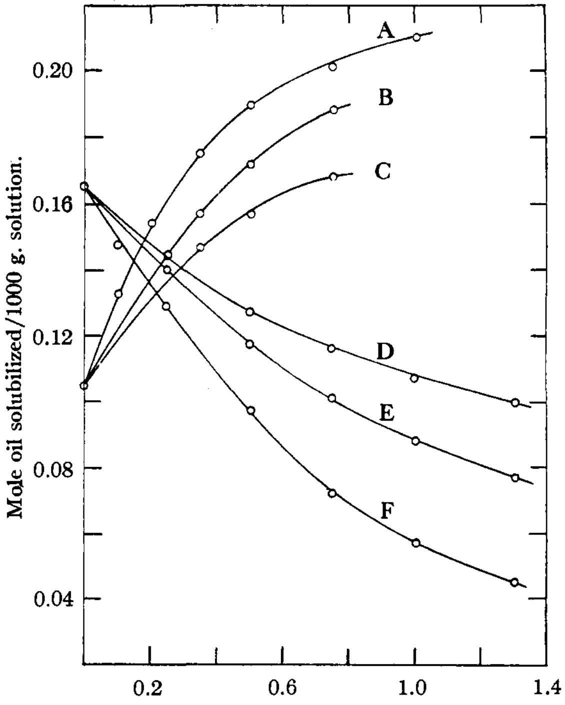

Fig. 2.—Effect of addition of various electrolytes on solubilization of *n*-heptane in 0.32 *M* KC_{14} plus: (A) KCl, (B) K_2SO_4, (C) $K_4Fe(CN)_6 \cdot 3H_2O$; and of *n*-octanol in 0.32 *M* KC_{14}: plus (D) $K_4Fe(CN)_6 \cdot 3H_2O$, (E) K_2SO_4, (F) KCl.

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(15) K. A. Wright, A. D. Abbott, V. Sivertz and H. V. Tartar, This Journal, 61, 553 (1939).

pared. These data lend further support to the presence of two loci of solubilization in the micelle. For each factor in the form of electrolyte additive which enhances solubilization of *n*-heptane, there is a corresponding one which decreases the solubilization of the long chain alcohol.

Transition Phenomena

If the enhancement of solubilization of *n*-heptane in alcohol–soap micelles is due to the penetration of the alcohol molecules into the palisade layer and thus to a reduction in the curvature of the micelle surface as well as to an increase in the micelle size,[6] it is to be expected that as the chain length of the solubilized alcohol is increased there should be some penetration beyond the ends of the hydrocarbon tails of the soap molecules into the region where added hydrocarbons are usually considered to be solubilized. If this were to occur, there should be some increase in the double layer thickness of the oblate spheroid micelle. It has been shown that with added *n*-decanol as well as with shorter chain alcohols there is no increase in this spacing.[4] The portion of the alcohol tail which extends beyond the end of the palisade layer of soap molecules probably penetrates into the adjacent soap layer of the micelle. This would explain, in part, the increase in enhancement of solubilization of *n*-heptane by alcohol–soap micelles as the chain length of the alcohol is increased.[6] It also would account for the decrease in X-ray spacing, for the solubilization data indicate that the penetration of the long chain alcohols into the micelle is greater than that of the soap molecules themselves.

Certain anomalies in the effect of salts on solubilization of alcohols are then to be expected as the length of the alcohol molecule is increased. The data in Fig. 3 include the C_7, C_8, C_{10} and C_{12} alcohols and show some of the unusual solubility effects encountered in these systems. The factors involved in the variation in solubilization of *n*-heptane and *n*-octanol discussed previously can as readily be applied to *n*-heptanol. The solubilization data of the C_{10} and C_{12} alcohols in the presence of added electrolyte indicate that a gradual transition must be considered to occur in going from the shorter chain alcohols to longer chain alcohols to the hydrocarbons. The decrease in the effectiveness of added electrolyte in reducing the amount of solubilized alcohol as the alcohol chain length is increased can be noted by comparing the data between 0 and 0.5 *M* potassium chloride. These differences are 0.085 *M* for *n*-C_7OH, 0.068 *M* for *n*-C_8OH, 0.014 *M* for *n*-$C_{10}OH$ and -0.005 *M* for *n*-$C_{12}OH$, and it can be seen that these values decrease roughly linearly with increase in chain length.

Viscosity Characteristics

It was noticed during the course of these experiments that many of the systems exhibited very high viscosities, often becoming rigid. Relative viscosities (R.V.) were measured by the simple procedure of measuring the time necessary for a small ball to drop through a given length of soap solution containing various additives. The times were divided into ten divisions, R.V. 1–10, with the most viscous being 1, the least 10. A comparison of a few systems are seen in Table II. It is evident that the onset of turbidity and the maximum viscosity are not found in the same systems. The addition of electrolyte causes some initial increase in viscosity probably due, in part, to the increase in size of the micelles in accordance with the results on light scattering.[7] It has been observed that, instead of the usual broad, diffuse M-band found at higher soap concentrations, the appearance of this band changes to a broad, distinct band as gelation occurs, however with no change in spacing.[4] No X-ray evidence is available on the concordant results of salts and long chain alcohols as additives. However, the formation of the most viscous systems below saturation indicates the presence of another transition point in these systems which may be correlated with a maximum micellar size. Further independent evidence will be necessary before these transitions can be fully understood.

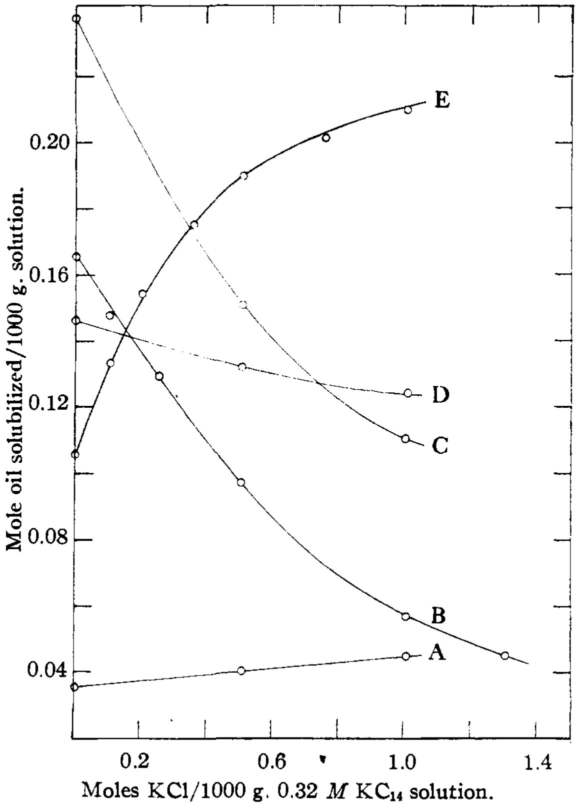

Fig. 3.—Effect of chain length of alcohol on solubilization in 0.32 *M* KC_{14} solution plus added KCl: (A), *n*-dodecanol; (B), *n*-octanol; (C), *n*-heptanol; (D), *n*-decanol; (E), *n*-heptane.

It is known that the addition of electrolytes results in a decrease or a very small increase in the intermicellar spacing (D_I) of anionic and cationic detergents.[3,16,17,18] The marked increase in viscosity coupled with the increase in micellar weight must be explained by an increase in the size of the micelle in a direction perpendicular to the plane of the oriented soap molecules in the micelle and to the formation of some non-specified network which leads to gelation. The attractive forces involved in this association cannot be clearly elucidated at the present time but they must be similar in nature to those which are encountered in the association of hydrophilic particles in which both polar groups and hydration layer (or bound water) play some part. Upon the addition of an apolar compound, solubilized in the hydrocarbon region of the two layer micelle, there is an increase in D_I as well as in the micellar X-ray band, D_M, an increase in micellar weight, and a marked decrease in viscosity. The swelling occurs parallel to the plane of the soap molecules in the micelle and probably results in a more spherical shaped micelle. There must also be some decrease in the long axis of the two layer micelle as is evidenced by the decrease in the association forces and the marked decrease in viscosity.

TABLE II

RELATIVE VISCOSITIES OF 0.32 N POTASSIUM TETRADECANOATE–KCl SOLUTIONS WITH ADDED n-OCTANOL

Moles n-C_8OH/ 1000 g. soln.	Appearance	Relative viscosity 1 N KCl[a]
0.0318	C[b]	3
.0477	C	1
.0635	C	9
.0794	T[c]	10
.0954	T	10
		0.25 N KCl
0.0635	C	7
.0794	C	4
.0953	C	1
.1112	C	8
.1270	C	10
.1429	T	10
.1588	T	10
		0.10 N KCl
0.0794	C	1
.0953	C	3
.1112	C	7
.1270	C	10
.1429	T	10
.1588	T	10

[a] Initially viscous before addition of alcohol, R. V. = 4. [b] Clear. [c] Turbid.

Discussion

According to the theory of micelle formation, the addition of an electrolyte will reduce the energy of repulsion of the like charged colloidal electrolyte heads and will increase the size of the micelle. It might also be considered that the characteristic thickness of the ionic atmosphere around each colloidal electrolyte ion in the micelle will be reduced as the concentration of added electrolyte is increased. Thus the curvature of the micelle will have to change and a correspondingly larger micelle will result. In the region of the CMC, it has been indicated that there is a linear increase in molecular weight of dodecylamine hydrochloride with equivalents of added Cl^- up to 0.05 N.[7] No data have been reported for higher additive concentrations although much larger micelles and/or aggregates must be expected at higher salt concentrations. Debye has reported the presence of blue Tyndall colors in soap solutions at high salt concentrations.[19] This would correspond to a micelle or aggregate of about 1000–2000 soap molecules. There is no indication that the linearity of increase in micellar size continues beyond the reported limits. The data in Table I in the region of the CMC indicate a fairly linear increase in the solubilization of n-heptane up to a concentration of 0.05 M added potassium chloride beyond which concentration there is a much smaller increase.

At higher soap concentrations, calculations from X-ray measurements indicate an increase in micellar size with soap concentration.[7] The presence of ionic charges around one micelle might be expected to have an influence on those of its neighboring micelles and as the concentration of soap is increased this effect would be enhanced. Thus the addition of more soap to a soap solution would tend to result not only in an increase in the number of micelles but also in an increase in the size. This can in part explain the fact that the rate of increase in solubilization for hydrocarbon increases and for polar compounds decreases with soap concentration. These factors also comply with the hypothesis as to the loci of solubilization in soap micelles. From extrapolation of solubilization data on n-heptane and n-heptanol to higher soap concentrations, one would obtain a crossover of these two sets of data above 1.5 M KC_{14},[6] which is as expected from the above discussion. The addition of electrolyte would also result in increased micellar sizes even at these high soap concentrations as is indicated by the solubilization changes discussed above.

The continued increase in hydrophobic properties as the chain length of the alcohols is increased is quite evident from their solubilization data. It is evident that a marked change occurs between the C_8 and the C_{10} alcohol in the experiments where KC_{14} is the solubilizer. This would indicate that little or none of the C_8 hydrocarbon tail extends into the hydrocarbon center of the micelle and that a portion of the C_{10} and more of the C_{12} alcohol penetrates into the micelle center and possibly into the adjacent palisade layer. Preliminary results from this Laboratory with

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[16] H. Kiessig and W. Philippoff, *Naturwiss.*, **27**, 593 (1939).

[17] K. Hess, H. Kiessig and W. Philippoff, *Fette u. Seifen*, **48**, 377 (1941).

[18] W. D. Harkins, R. W. Mattoon and M. L. Corrin, *J. Coll. Sci.*, **1**, 105 (1946).

[19] P. Debye, private communication.

potassium dodecanoate indicate that the transition occurs with the C_8 alcohol, but additional evidence, now being obtained, will be necessary before more definite ideas as to the extent of penetration of these long chain alcohols into the soap micelle can be advanced.

Summary

Additional evidence as to the presence of two loci of solubilization in soap micelles is obtained from solubilization data of hydrocarbon and polar compounds in soap solutions containing added electrolyte. The addition of potassium chloride to a 0.32 *N* potassium tetradecanoate (KC_{14}) solution results in an enhancement of solubility of *n*-heptane and a decrease of *n*-octanol. With 0.05 *N* KC_{14}–KCl solutions, the solubilities of both polar and non-polar compounds increase. However, after the initial increase up to about 0.50 *N* potassium chloride, the solubility of the alcohol again decreases. Even though the critical micelle concentration of a soap depends only on the equivalent concentration of the ion opposite in charge to that of the colloidal electrolyte, the nature of both anion and cation affect solubilization. Thus in the solubilization of *n*-heptane for equivalent concentrations of additive, $KCl > K_2SO_4 > K_4Fe(CN)_6 \cdot 3H_2O$ whereas the reverse order holds when *n*-octanol is solubilized. However, these latter data present additional proof as to the two loci of solubilization, one in the hydrocarbon center of the micelle, the other in the palisade layer in the region occupied by the soap molecules. As the chain length of the solubilized alcohol is increased, there is a gradual transition from polar type to non-polar type solubilization most strikingly indicated when comparing C_8 and C_{10} alcohols. Qualitative measurements of viscosity indicate that the addition of very small amounts of long chain alcohols to soap–salt systems result in the formation of very viscous, almost gel-like, systems. The maximum viscosities always occur at concentrations of alcohol below the limit of solubilization (as indicated by turbidity).

ST. PAUL, MINN. RECEIVED NOVEMBER 11, 1949

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. XII. The Metalation of Olefins and Dienes and their Use in Alfin Polymerization of Butadiene[1]

BY AVERY A. MORTON, FRANK D. MARSH, ROBERT D. COOMBS, ANNE L. LYONS, SIEGFRIED E. PENNER, HUGH E. RAMSDEN, VERNON B. BAKER, ERNEST L. LITTLE AND ROBERT L. LETSINGER

Since early in the study of polymerization in this Laboratory, the metalation of olefins[2] and dienes[3] has been prominent because some products help induce catalytic polymerization and most undergo double bond shifts such as might occur in the polymer. This paper describes the metalation of ethylene, several straight chain and branched olefins, diallyl and some conjugated dienes. Many products can serve as organometallic intermediates in reactions. Vinylsodium and most of the branched chain alkylsodium compounds are free from or unaffected by allylic shifts, hence each gives one monosubstituted product. Others give mixtures. New β,γ-unsaturated carboxylic acids have been isolated. Isobutene disodium has interesting possibilities in Wurtz reactions. All metalated compounds, except for diallyl and 2-methyl-1,3-pentadiene, are relatively ineffective as catalysts with butadiene.

Metalation of Olefins.—Amylsodium converted ethylene to vinylsodium in good yield provided sodium isopropoxide was present. Vinylsodium, in turn, metalated benzene, hexene-1, toluene and fluorene with progressive ease (see Table I). Like phenylsodium, it did not add to 1,1-diphenylethylene. In eighteen hours there was no addition where amylsodium reacted[4] completely in four to six hours.

TABLE I

METALATION OF HYDROCARBONS BY VINYLSODIUM–SODIUM ISOPROPOXIDE

Hydrocarbons		Reaction time, days	Acrylic acid recovered, %	Carboxylic acid from metalation, %
Compound	Moles[a] Hy/VS			
Benzene	2.0	12	56	11
Hexene-1	2.0	12	19	42
Toluene	1.5	8	10	53
Fluorene	1.2	7	0	88

[a] Hy/VS. is hydrocarbon to vinylsodium.

The same reagent with possibly a trace of pentoxide metalated 1-alkenes (Table II), mostly by replacement of an allylic hydrogen so that on carbonation the ratio of straight chain and branched chain acids was 2:3. However, the proportions of allylic isomers varied with the reagent since the reaction of methyl iodide with octenylsodium gave about 2:1 straight to branched chain products. Some metalation at C-1 without allylic shift occurred but this fell

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(1) This work was in large part carried out under the auspices of the Office of Rubber Reserve, Reconstruction Finance Corporation, and in small part, with the aid of a grant from The Research Corporation, New York.

(2) Morton, *Chem. Reviews*, **35**, 16 (1944); Morton, Brown, Holden, Letsinger and Magat, THIS JOURNAL, **67**, 2224 (1945).

(3) Morton and Brown, *ibid.*, **69**, 160 (1947).

(4) Morton and Wohlers, *ibid.*, **69**, 167 (1947).