ing point of an authentic sample of octahydropyrrocoline picrate.[9] The infrared absorption spectra of the two samples were identical. Fraction F, b.p. 95° (0.1 mm.), yield 2.7 g. (47%), which became semi-solid on standing at room temperature, exhibited a strong infrared absorption band in the hydroxyl region (3345 cm.$^{-1}$). The picrate of fraction F was formed in ether and recrystallized from ethyl acetate-cyclohexane as small, yellow needles, m.p. 176–176.5°.

Anal. Calcd. for $C_{14}H_{20}N_4O_8$: C, 45.16; H, 5.41; N, 15.05. Found: C, 45.24; H, 5.64; N, 14.88.

While the analytical results were indicative of a monocyclic aminoalcohol, the melting point of the picrate was close to that of the picrate of the bicyclic aminoalcohol, 8-hydroxyoctahydropyrrocoline (see above). A mixture of the picrate of fraction F with the picrate of 8-hydroxyoctahydropyrrocoline melted at 152–158°, and the two picrates were therefore not identical. Although only small differences were detectable in the infrared spectra of the two picrates, the spectra of the corresponding free bases had well-defined differences.

N-Methylation.—Fraction F (5-hydroxyazacyclononane) was N-methylated by means of formaldehyde–formic acid as described above. The product was converted directly to the picrate, yellow rods from ethanol, decomposition point 285–289° after initial darkening at 258°, with an analysis consistent with that required for 1-methyl-5-hydroxyazacyclononane picrate.

Anal. Calcd. for $C_{15}H_{22}N_4O_8$: C, 46.63; H, 5.74; N, 14.50. Found: C, 46.89; H, 5.89; N, 14.63.

Concentration Effect in the Electrolytic Reductions.—As observed in pairs of runs, the following results indicate an apparent effect of concentration on the proportion of monocyclic and bicyclic products formed following initial C_α–N bond cleavage:

	1-Keto-quinolizidine		8-Ketoöcta-hydropyrrocoline	
Concn. (per 100 ml. of 30% H_2SO_4), g.	5.35	12.6	1.93	4.33
Yield bicyclic amine, %	4.5	38	None detected	21
Yield monocyclic amino-alcohol, %	59	41	73	47

1-Ketoöctahydropyrrocoline (11.4 g. per 100 ml.) gave no bicyclic amine.

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[CONTRIBUTION FROM THE LABORATOIRE DE CHIMIE PHYSIQUE, INSTITUT PASTEUR, PARIS, FRANCE]

Solubilization in Alcohol–Soap Micelles. II. Electrolytes as Additives[1]

BY H. B. KLEVENS[2]

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The addition of electrolytes to alcohol–soap systems results in an initial marked increase in hydrocarbon solubility followed by a decrease when the concentration of electrolyte is further increased. The effect of KCl > K_2SO_4 > $K_4Fe(CN)_6\cdot 3H_2O$ for systems in which the concentrations of both alcohol and soap are low but the change in added electrolyte is minimized at higher soap and/or alcohol concentration. The apparent maxima in hydrocarbon solubility observed are probably due to the presence of micelles of a maximum solubilizing power and do not involve changes from solutions in which the hydrocarbon is dissolved to one in which water is solubilized.

Since it has been reported that the addition of electrolytes to soap solutions results in an increase in hydrocarbon solubility[3-5] and to a decrease in the amount of polar compound dissolved[3,4] and that the addition of long chain polar additives to soap solutions markedly enhances the solubility of hydrocarbons,[6] it was of some interest to determine what would be the competitive effect of these two apparently opposing additives (electrolyte and long chain alcohol). The addition of electrolyte decreases the long range coulomb repulsion forces and the polar additives tend to increase the van der Waals attraction forces with probably no effect on the forces of repulsion. These effects would tend to initially increase the micelle size and possibly the disorder in the micelle (for the micelle would be made up of C_{14} soap molecules and much shorter, C_8, alcohol molecules. This disorder will result in a marked increase in solubilizing power.[7] At higher salt and alcohol concentrations, the competitive effects should predominate.

Experimental Methods

The solubility of hydrocarbons was determined by a turbidometric method described previously.[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 decrease the amount of hydrolysis. The long chain alcohols were obtained from the Humphrey-Wilkinson Company and were purified by fractional distillation. The *n*-heptane obtained from Westvaco Chlorine Company was used without further purification since spectroscopic studies have shown it to be quite free of unsaturates and branch chain isomers.[9]

The Effect of Added Electrolyte on Solubility of *n*-Heptane in Soap–Alcohol Micelles.—The data in Fig. 1 show the effect of added electrolyte upon the solubility of *n*-heptane in potassium tetradecanoate (KC$_{14}$)–octanol-1 solutions. For those systems with high alcohol–soap ratios, there appears to be an optimum value of hydrocarbon solubility. These apparent maxima occur at decreasing values of KCl with increasing alcohol–soap ratios, and have approximately the same solubility values for *n*-heptane of about 0.55 mole per 1000 g. of soap–alcohol solution. At higher electrolyte concentrations than those reported here, for solutions with alcohol–soap mole ratios of 1.2, 0.88, 0.635 and 0.38, the systems were initially turbid since the concentrations of added KCl were sufficient to decrease the octanol-1 solubility.

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[1] Experimental work done in part at the Division of Agricultural Biochemistry, University of Minnesota, St. Paul, Minnesota.

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It is seen from the data in Table I that even in more dilute solutions (0.1 *N* KC_{14}) this same factor of solubilizing power (mole hydrocarbon per mole soap) is operative. The maximum solubilizing power for this series is about 2.0 as compared with 2.2 for the 0.25 *M* KC_{14} series.

TABLE I

EFFECT OF ADDED ELECTROLYTE ON SOLUBILIZING POWER OF POTASSIUM TETRADECANOATE–OCTANOL-1 MICELLES (*n*-HEPTANE, 25°)

KCl (moles/1000 g.)	0	0.1	0.3	0.5	0.74	1.0	1.5	2.0
$C_8H_{17}OH$ (moles/1000 g.)	Solubilizing power (moles hydrocarbon per mole soap)							
	0.1 *N* Potassium tetradecanoate							
0	0.252	0.451		0.748	0.871	1.02	1.15	
0.0318	.467	.642		1.12	1.33	1.57	1.89	
.0635	.586	.959		1.49	1.71	1.92	1.81	
.0953	.882	1.19		1.77	1.93	1.83		
	0.25 *N* Potassium tetradecanoate							
0	0.302	0.410	0.561	0.642		0.721		0.778
0.0318	.422	.558	.763	0.881		1.21		1.69
.0635	.525	.688	.916	1.10		1.50		2.05
.0953	.643	.835	1.12	1.30		1.61		2.02
.159	.866	1.12	1.46	1.70		2.16		
.222	1.08	1.36	1.56	2.01		2.20		
.301	1.36	1.62	1.98	2.15				

The decrease in the critical micelle concentration (CMC) depends only on the concentration of that ion which is opposite in charge to that on the colloidal electrolyte.[10,11] Data on the solubility of *n*-heptane and octanol-1 in soap solutions indicate that for equivalent concentrations of added electrolyte KCl > K_2SO_4 > $K_4Fe(CN)_6 \cdot 3H_2O$ in the solubilization of a hydrocarbon whereas the reverse order holds when a long chain alcohol is being dissolved.[4] The effect of the addition of both electrolyte and alcohol on CMC decrease has been shown to be approximately additive.[12] The data in Table II for 0.1 and 0.5 equivalent of added electrolyte indicate that KCl > K_2SO_4 > $K_4Fe(CN)_6 \cdot 3H_2O$ for the lower concentration of electrolyte additive but that for the 0.5 *N* series these differences are much smaller or are non-existent. It is also seen that the percentage decrease in the 0.1 *N* electrolyte series is smaller in the higher alcohol concentration series. These data do not show the increase in solubility of hydrocarbon nor the decrease of polar compound dissolved as was found previously upon electrolyte addition.[4] The maximum solubility is approached more rapidly at higher soap and at higher alcohol concentrations, and is affected more at lower soap and alcohol concentrations by the character of the gegen ion atmosphere.

The Effect of Change in the Polar Group on Solubility.—Previous data on the solubility of *n*-heptane in soap solutions have shown that there is a much greater enhancement when the polar additive is a long chain amine in place of an alcohol of corresponding length.[6] This can be attributed to a greater penetration of the amine into the palisade layer of the micelle. Further the addition of shorter chain amines results in a more marked decrease in CMC than when alcohols of corresponding length are added to soap and detergent solutions.[13] A comparison of the data in Table III shows that the addition of equivalent amounts of a long chain amine to a soap–salt system will result in a much higher solubility of *n*-heptane than is found when a corresponding alcohol is the additive. However, the increase appears to approach a limiting value at lower concentrations of amine than of alcohol additive.

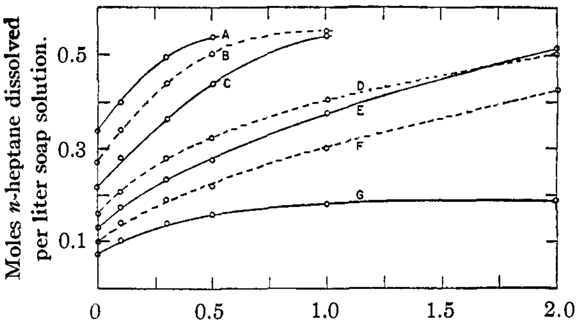

Fig. 1.—Effect of added KCl on solubility of *n*-heptane in swollen micelles: 0.25 *M* K tetradecanoate plus (A) 0.301, (B) 0.222, (C) 0.159, (D) 0.095, (E) 0.064, (F) 0.032 and (G) 0 moles octanol-1 per liter.

TABLE II

EFFECT OF CHANGE IN ELECTROLYTE ADDITIVE ON SOLUBILITY OF *n*-HEPTANE IN 0.25 *N* POTASSIUM TETRADECANOATE–OCTANOL-1 (25°)

Electrolyte	0.0318 *N* Octanol-1 series Mole oil 1000 g. soln.	0.0318 *N* Octanol-1 series Solubilizing power	0.0953 *N* Octanol-1 series Mole oil 1000 g. soln.	0.0953 *N* Octanol-1 series Solubilizing power
	0.1 *N* Additive			
KCl	0.140	0.558	0.209	0.835
K_2SO_4	.131	.523	.200	.800
$K_4Fe(CN)_6 \cdot 3H_2O$	.128	.512	.195	.780
	0.5 *N* Additive			
KCl	0.220	0.881	0.325	1.30
K_2SO_4	.224	.895	.320	1.28
$K_4Fe(CN)_6 \cdot 3H_2O$	.222	.888	.317	1.27

TABLE III

SOLUBILITY OF *n*-HEPTANE IN THE SYSTEMS 0.25 *N* KC_{14}–0.1 *N* KCl–OCTANOL-1 AND 0.25 *N* KC_{14}–0.1 *N* KCl–1-AMINO OCTANE

Polar additive (mole/1000 g. soln.)	Mole heptane 1000 g. soln.	Solubilizing power	Mole heptane 1000 g. soln.	Solubilizing power
	Octanol series		Aminoöctane series	
0	0.101	0.403	0.101	0.403
.010	.113	.452	.134	.536
.032	.140	.558	.195	.780
.050	.171	.684	.214	.857

Discussion

The addition of both polar compounds and electrolytes to soap solutions has been shown to result in an initial marked increase in solubility of hydrocarbons over the use of either pure soap, soap–polar compound or soap–electrolyte systems as solubilizers. At higher concentrations of either

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electrolyte or polar additive or both an apparent maximum value of solubilizing power is reached and this maximum is followed by a decrease in solubility. These data are to be contrasted with the fact that the presence of both alcohol and electrolyte results in approximately additive decreases in CMC values.[12] However, it is to be noted that there may be discontinuities in various properties in soap solutions which may explain these observed differences, one in the region of the CMC and the other at much higher concentrations. The maxima in solubilizing power observed may be dependent on the presence of micelles of a maximum degree of disorder and an optimum size for solubilization. Further addition of electrolyte and/or polar additive would then result in a decrease in the disorder in the micelle and a corresponding decrease in solubility for hydrocarbons.

Careful diffusion measurements of Hartley and Runnicles[14] indicate that no changes in micelle size occur upon the addition of electrolytes. However, light scattering measurements by Debye[15] and diffusion measurements of Graydon[16] on the effect of added electrolytes on micellar size can be interpreted as indicating an increase in micellar weight. These apparent differences have been shown[7,17] to be due to the type of soap or detergent used (for example, whether potassium dodecanoate or dodecylammonium chloride) and to the concentration of both soap and electrolyte. At dodecylammonium chloride concentrations below 0.05–0.10 *M*, there is a linear increase in micellar weight[15] and solubility of hydrocarbons[17] up to 0.05 *N* added electrolyte; above this electrolyte concentration, there is a marked increase in micellar weight coupled with a sharp decrease in the ratio of hydrocarbon solubilized to soap concentration. For potassium dodecanoate, at concentrations up to 0.15–0.20 *N*, there is no change in micellar weight with addition of as much as 1.0 *N* electrolyte; at higher electrolyte concentrations, there is a marked increase in micellar weight.[16,18] For solutions of potassium dodecanoate above 0.2 *N*, less electrolyte is needed to bring about this marked increase in micellar weight. The solubilization of hydrocarbons increases only slightly with addition of electrolyte to these latter soap solutions.

The addition of polar additives results in a marked increase in micellar weight as well as in asymmetry of the micelle.[13] No data are as yet available on micellar size in the presence of both alcohol and electrolyte additive except for one approximate value of 300,000 reported for the system 0.15 *M* KC_{12}–0.015 *M* octanol-1–1.0 *M* KCl.[16] This is to be compared with an apparent micellar weight of about 30,000–35,000 for the corresponding soap–salt system as determined by diffusion[16] and one of about 75,000–100,000 which has been calculated from hydrocarbon solubility data in alcohol–soap micelles. These values can further be compared with one of about 700,000 reported for the *n*-hexadecyltrimethylammonium bromide-KBr system[19] in which it is assumed that the micelle is rod shaped (prolate spheroid). The viscosity measurements of Philippoff[20] indicate little or no temperature and electrolyte effects in the region of the CMC but marked changes are observed at higher soap concentrations. Evidence now being obtained from light scattering and dissymmetry measurements in the region of the CMC and at higher concentrations will throw more light on the existence of micelles of a maximum solubilizing power. The aggregation, which is indicated by marked increases in micellar weight, results in the formation of micelles with decreased solubilizing power.

The data presented in this report, in which a maximum value of solubility of hydrocarbons is obtained at definite soap–salt–alcohol ratios, indicate that this solubility is limited by competition between the action of the electrolyte (decrease in the repulsion energy with little or no increase in the energy of attraction) and that of the polar additive (little or no change in the repulsion forces coupled with a marked increase in attraction forces).

PARIS XV, FRANCE

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