of micelles is determined: (1) by a sharp change in color, or (2) by a sharp reduction of fluorescence. Certain dyes exhibit both of these changes.

The critical concentration is not changed appreciably by any of the dyes used, since they are employed at too high a dilution to produce such a change.

CHICAGO, ILLINOIS RECEIVED JULY 22, 1946

[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

The Effect of Salts on the Critical Concentration for the Formation of Micelles in Colloidal Electrolytes[1]

BY M. L. CORRIN AND WILLIAM D. HARKINS

Introduction

The effect of the addition of salts to aqueous solutions of colloidal electrolytes shows that the behavior of the micellar aggregates present is not governed by the principle of ionic strength or the Debye–Hückel relationships; this fact has not been clearly recognized previously. In this work it was found that the extent of lowering of the critical concentration for the formation of micelles by a salt exhibits independence of the number of charges on the ion of the salt which has the same sign of charge as the ion aggregate of the micelle. This behavior, entirely different from that exhibited by ionic solutions in which there are no ionic aggregates, might have been predicted by theory, but it does not seem that such a theory has been developed.

Unfortunately, at the present time, both the size and shape of a soap micelle are unknown, but something has been revealed of its structure by X-ray[1a] and other measurements, and from what is known of molecular orientation at interfaces.[2,3,4]

Whether the micelle consists of a single or several double layers of soap ions or has a form not very far from spherical is too complicated a question for discussion in this paper. However, it seems certain that the hydrocarbon chains of the double layers or spheres are oriented toward each other, whereas the ionic-polar groups, such as —COO^-, are oriented toward the water, where they form an interface, plane or highly curved, according to the form of the micelle. The X-ray diffraction patterns indicate that the soap ions are packed in such a way as to exhibit for close packing an area of about 27 sq. Å., while the micelles exhibit a long spacing which increases with increasing dilution of the soap solution. For example, with potassium laurate, the long spacing varies from 57.0 Å. at 9.1% soap to 42.9 Å. at 35.0% soap. A somewhat shorter spacing, the thickness of the micelle, is twice the length of the soap molecule.

The relationships with respect to ionization at the interface between the soap ions and water are somewhat similar to those at the interface between an emulsion droplet of a paraffin oil in a soap solution. For example, such a droplet 1μ in diameter in a 0.1 molar solution of sodium oleate was found to adsorb 15 million soap molecules in a monolayer of soap at its interface with water. Its velocity in an electric field was found to be equal to that which, according to Stokes' law, would be exhibited by this droplet, provided it were not covered by a layer of soap but were to carry a charge of 2500 electrons.

While the mechanism of conduction associated with the monolayer of soap is very different from that of such a simply charged particle, this seems to indicate that of the 15 million positive sodium ions held by the same number of negative oleate ions almost all are at any one instant held very close to the surface of the droplet, while only relatively few form a diffuse positive ionic layer.

Now, if 0.1 molal sodium ion is added in the form of its salt to a soap solution, this increases the number of positive ions by unity for each cube of 25 Å. edge in the solution, thus increasing considerably the concentration of the "gegenion" in the solution. It is to be expected that this should have the effect of lowering the critical concentration for the formation of micelles.

The effect of salts upon the critical concentration for micelle formation in detergent solutions has been investigated by Howell and Robinson[5] who gave no data, Hartley,[6] Tartar and Cadle[7] and Wright, Abbott, Sivertz and Tartar.[8] These workers employed either conductometric or solubility techniques which were so tedious that extremely few results were obtained. A rapid titrimetric technic for the determination of critical concentrations has recently been developed by the writers.[9]

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[1] The work reported in this paper was done in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

[1a] For references see W. D. Harkins, R. W. Mattoon and M. L. Corrin, THIS JOURNAL, **66**, 220 (1946); *J. Colloid Sci.*, **1**, 105 (1946).

[2] W. D. Harkins, F. E. Brown and E. C. H. Davies, THIS JOURNAL, **39**, 354 (1917).

[3] W. D. Harkins, E. C. H. Davies and G. L. Clark, *ibid.*, 541 (1917).

[4] I. Langmuir, *ibid.*, 1848 (1917).

[5] O. R. Howell and H. G. B. Robinson, *Proc. Roy. Soc.* (London), **A155**, 386 (1936).

[6] G. S. Hartley, *J. Chem. Soc.*, 1968 (1938).

[7] H. V. Tartar and R. D. Cadle, *J. Phys. Chem.*, **43**, 1173 (1939).

[8] K. A. Wright, A. D. Abbott, V. Sivertz and H. V. Tartar, THIS JOURNAL, **61**, 553 (1939).

[9] M. L. Corrin and W. D. Harkins, *ibid.*, **69**, 679 (1947).

Consequently a systematic investigation of the effects of salts upon the critical concentrations of detergents, using the titrimetric method, has been undertaken.

The addition of salts to soap solutions is known to depress the critical concentration. A decrease of approximately 25% in this value for sodium dodecyl sulfonate upon the addition of an equimolar quantity of sodium chloride was reported in one case.[8] Larger depressions were reported by Hartley.[6]

Experimental

The data for the effect of potassium chloride, potassium sulfate, and sodium pyrophosphate upon the critical concentration of potassium laurate are presented in Table I and Fig. 1. The value of the critical concentration is reduced almost sevenfold with respect to that of the pure soap when sufficient potassium chloride is added to make the solution 0.59 *M*.

The investigation of the salt effects was extended to systems of sodium decyl sulfonate and sodium dodecyl sulfate in order to avoid any complications due to hydrolysis.

Table I

The Critical Concentration of Potassium Laurate in the Presence of Added Salts

Molarity of salt	Crit. concn.	Decrease of crit. concn., %	Crit. concn. pure soap / Crit. concn. with salt
	Potassium chloride		
0	2.30 $\times 10^{-2}$ *M*		
8.380 $\times 10^{-3}$	1.97	14	1.17
1.321 $\times 10^{-2}$	1.76	23	1.31
1.680	1.69	27[a]	1.36
3.872	1.29	44	1.78
4.217	1.25	46	1.84
4.263	1.23	47	1.87
5.471	1.12	51	2.05
6.466	1.07	53	2.15
6.631	1.01	56	2.28
7.466	0.992	57	2.32
1.038 $\times 10^{-1}$	.844	63	2.72
1.062	.830	64	2.77
1.199	.796	65	2.89
1.485	.748	67	3.07
1.739	.577	75	3.99
2.411	.547	76	4.21
2.617	.527	77	4.36
3.142	.458	80	5.02
3.335	.464	80	4.96
4.338	.353	85	6.52
5.927	.348	87	6.61
	Potassium sulfate		
7.650 $\times 10^{-3}$	1.74 $\times 10^{-2}$	24	1.32
1.756 $\times 10^{-2}$	1.33	42	1.73
2.915	1.10	52	2.09
4.664	0.912	60	2.52
6.565	.770	67	2.99
1.045 $\times 10^{-1}$	.594	71	3.87
1.418	.484	79	4.75
1.869	.425	82	5.41
	Sodium pyrophosphate		
5.178 $\times 10^{-3}$	1.65 $\times 10^{-2}$	28	1.39
1.388 $\times 10^{-2}$	1.10	52	2.09
2.151	0.856	63	2.69
3.053	.747	68	3.08

[a] This value may be compared to 26% lowering in equimolar sodium dodecyl sulfonate and sodium chloride at 40°.[8]

Table II

The Critical Concentration of Sodium Decyl Sulfonate in the Presence of Added Salts

Molarity of salt	Crit. concn.	Decrease of crit. concn., %	Crit. concn. of pure soap / Crit. concn. with salt
	Sodium Chloride		
0	4.00 $\times 10^{-2}$		
4.918 $\times 10^{-3}$	3.82	4.5	1.04
1.350 $\times 10^{-2}$	3.50	13.0	1.14
2.855	3.17	21.0	1.26
5.272	2.93	27.0	1.37
	Sodium Sulfate		
4.210 $\times 10^{-3}$	3.72	7.0	1.08
7.970	3.52	12.0	1.14
1.978 $\times 10^{-2}$	3.12	22.0	1.28
3.461	2.73	32.0	1.47

Table III

The Critical Concentration of Sodium Dodecyl Sulfate in the Presence of Added Salts

Molarity of salt	Crit. concn., *M*	Decrease of crit. concn., %	Crit. concn. pure soap / Crit. concn. with salt
	Sodium Chloride		
0	6.02 $\times 10^{-3}$		
2.047 $\times 10^{-3}$	5.11	15.0	1.18
4.877	4.47	25	1.35
9.363	4.19	30	1.44
1.852 $\times 10^{-2}$	3.40	44	1.77
3.105	2.75	54	2.19
4.601	2.11	65	2.85
7.527	1.73	71	3.48
1.467 $\times 10^{-1}$	1.35	78	4.46
2.426	1.11	82	5.42
2.687	1.10	82	5.47
3.163	0.973	84	6.19
3.540	0.866	86	6.95
	Sodium Sulfate		
3.481 $\times 10^{-3}$	4.54 $\times 10^{-3}$	25	1.33
6.865	3.58	41	1.68
1.184 $\times 10^{-2}$	3.12	48	1.93
1.806	2.40	60	2.51
3.029	1.97	67	3.06
3.999	1.74	71	3.46
8.363	1.36	77	4.43
1.436 $\times 10^{-1}$	0.998	83	6.03
	Sodium Pyrophosphate		
1.551 $\times 10^{-3}$	4.55 $\times 10^{-3}$	24	1.32
5.546	3.32	45	1.81
1.866 $\times 10^{-2}$	1.86	69	3.24
4.134	1.24	79	4.85
6.018	1.06	82	5.68

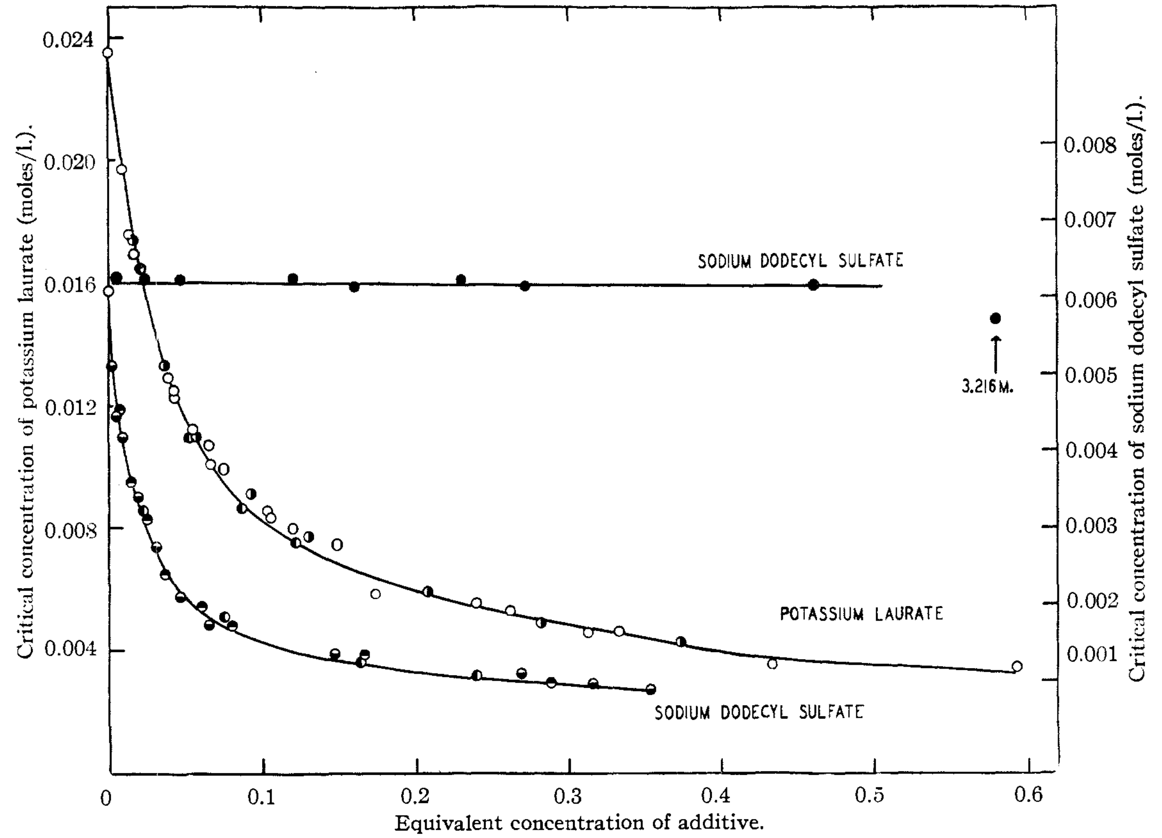

Fig. 1.—The effect of salts upon the critical concentrations of anionic detergents: ○ KCl, ◒ NaCl, ◑ K_2SO_4, ◐ $Na_4P_2O_7$, ◓ Na_2SO_4, ● urea.

These soaps are known to be non-hydrolyzed. The addition of more than approximately 0.05 M sodium chloride to a solution of sodium decyl sulfonate results, however, in precipitation of the detergent in the form of crystals. The range of measurements with this material was therefore limited.

The critical concentrations of potassium and sodium decyl sulfonate are equal within the limits of error of the titrimetric method. This equality with respect to sodium and potassium soaps when the critical concentration is expressed on a molar basis is quite general and explains the identical depression of the critical concentration resulting by the addition of sodium and potassium salts.

The values obtained on the addition of salts to sodium decyl sulfonate are reported in Table II.

Data for sodium dodecyl sulfate are plotted in Fig. 1 and tabulated in Table III. With this detergent the decrease in critical concentration by the addition of 0.354 molar sodium chloride is seven-fold.

The effect of salts upon the critical concentrations of dodecylammonium chloride and decyltrimethylammonium bromide are given in Tables IV and V and plotted in Fig. 2. Excellent agreement was observed when Sky Blue FF and acidified 2,6-dibromophenol indophenol were used as indicators.

The significant feature in all cases investigated is that the critical concentration is affected only by the concentration of that ion opposite in charge to that on the colloidal aggregate. The concentration and charge of the ion bearing the same charge as that on the aggregate seem to have no effect on the critical concentration.

In order to compare salt effects on different detergents it is convenient to plot the logarithm of the critical concentration (crit. concn.) against the logarithm of the gegenion concentration, *i.e.*, the sum of the concentrations of gegenions contributed by the detergent and by the salt. Such plots for potassium laurate and sodium dodecyl sulfate are given in Fig. 2 and those for dodecylammonium chloride and decyltrimethylammonium bromide in Fig. 4. The straight lines have been calculated by least squares and may be expressed as follows:

$$\log \text{(crit. concn.)} = -0.56969 \log m^{+} - 2.6172 \text{ (potassium laurate)}$$

$$\log \text{(crit. concn.)} = -0.45774 \log m^{+} - 3.2485 \text{ (sodium dodecyl sulfate)}$$

$$\log \text{(crit. concn.)} = -0.56232 \log m^{-} - 2.8577 \text{ (dodecylammonium chloride)}$$

$$\log \text{(crit. concn.)} = -0.34287 \log m^{-} - 1.5761 \text{ (decyltrimethylammonium bromide)}$$

It should be noted that an empirically linear log-log plot has but little significance since this treatment tends in general to give apparent linear relationships.

It was also thought advisable to investigate the effect of a typical non-electrolyte, urea, on the critical concentration of sodium dodecyl sulfate. The results are plotted in Fig. 1. No significant change in critical concentration was noted with urea concentrations below 0.5 molar. At the higher concentrations of urea a slight depression of the critical concentration of the detergent was observed. The critical concentration at 3.126 molar urea is 5.72×10^{-3} molar; this is identical with that observed in sodium chloride solutions approximately 1×10^{-3} molar. The effect of urea is thus almost insignificant in comparison with that of an electrolyte.

Procedure.—Solutions of known concentration in detergent and salt were prepared by the volume dilution of stock solutions; these solutions were adjusted to the proper dye concentration. Aliquot portions were then titrated

Table IV

The Critical Concentration of Dodecylammonium Chloride in the Presence of Added Salts

Molarity of salt	Crit. concn., *M*	Decrease of crit. concn., %	Crit. concn. pure soap / Crit. concn. with salt
	Sodium Chloride		
0	1.31×10^{-2a}		
0	1.31^{b}		
8.016×10^{-3}	1.16^{a}	11	1.13
1.711×10^{-2}	9.88×10^{-3b}	26	1.33
2.747	7.93^{a}	39	1.65
4.959	7.16^{b}	45	1.83
9.230	5.13^{b}	.61	2.55
	Barium Chloride		
7.670×10^{-3}	1.05×10^{-2a}	20	1.25
1.268×10^{-2}	8.66×10^{-3}	34	1.51
1.758	8.01^{b}	39	1.64
2.188	7.48^{a}	43	1.75
3.159	6.21^{a}	53	2.11
3.446	5.89^{b}	55	2.22
4.067	5.56^{a}	58	2.36
	Lanthanum Chloride		
7.103×10^{-3}	1.15×10^{-2a}	12	1.14
1.267×10^{-2}	8.12×10^{-3a}	38	1.61
1.719	6.95^{a}	47	1.88

[a] Sky Blue FF. [b] Acidified 2,6-dibromophenolindophenol.

Table V

The Critical Concentration of Decyltrimethylammonium Bromide in the Presence of Added Salts

Molarity of salt	Crit. concn., *M*	Decrease of crit. concn., %	Crit. concn. of pure soap / Crit. concn. with salt
	Sodium Chloride		
0	6.36×10^{-2}		
4.959×10^{-2}	5.69	11	1.12
1.320×10^{-1}	5.05	21	1.26
2.186	4.38	31	1.45
3.224	3.70	42	1.72
5.650	3.15	50	2.02
	Barium Chloride		
2.150×10^{-2}	5.84	8	1.09
5.640	5.11	20	1.24
1.002×10^{-1}	4.54	29	1.40
1.429	3.88	39	1.64
2.424	3.29	48	1.93

against an aqueous solution of the dye of the same concentration as that in the samples. The original solutions were used as blanks and the end-point was taken as the point at which a visual color difference appeared between the sample and blank. All measurements were made at least in duplicate. The following dye concentrations were employed. For anionic detergents the pinacyanol chloride was 1×10^{-5} molar; for cationic detergents the Sky Blue FF was 1×10^{-4} molar and the 2,6-dibromophenolindophenol 1×10^{-4} molar in dye and 3×10^{-4} molar in hydrochloric acid. All measurements were made at 26 ± 2°. The variation of critical concentration over this temperature range is insignificant.[8] Critical concentrations determined in this way are not accurate to the number of significant figures reported; the relative values for a given detergent are, however, of this precision.

Materials.—Potassium laurate was prepared by the saponification of carefully fractionated methyl laurate; the soap was recrystallized twice from ethanol and washed several times with acetone. Sodium decyl sulfonate was prepared by the method of Reed and Tartar from frac-

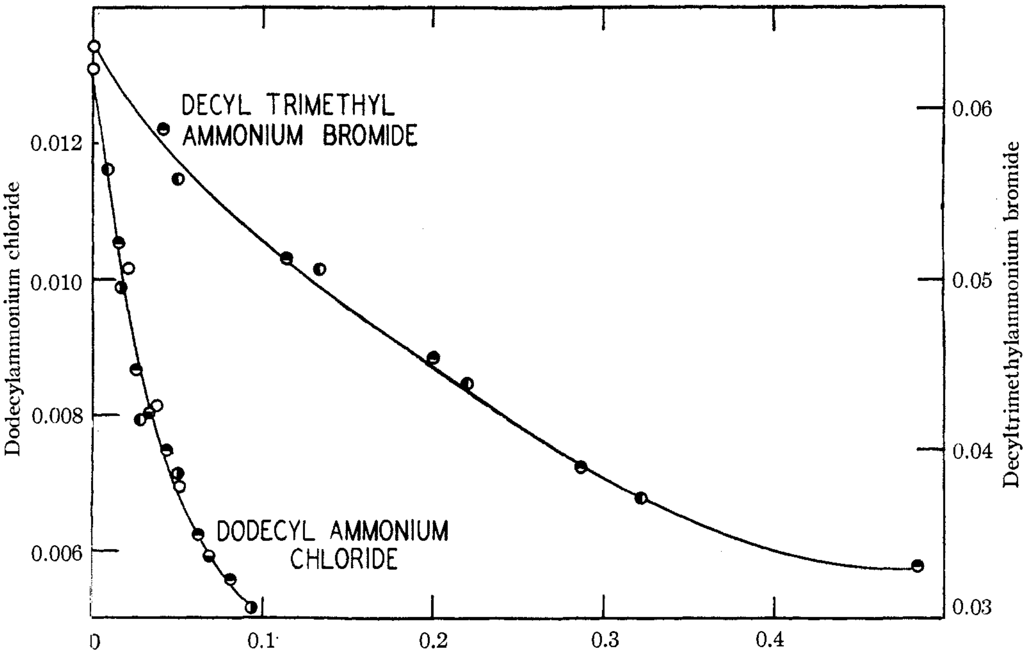

Fig. 2.—The effect of salts upon the critical concentrations of cationic detergents: ◑ NaCl (indophenol), ◐ NaCl (sky blue), ◒ $BaCl_2$ (indophenol), ◓ $BaCl_2$ (sky blue), ○ $LaCl_3$.

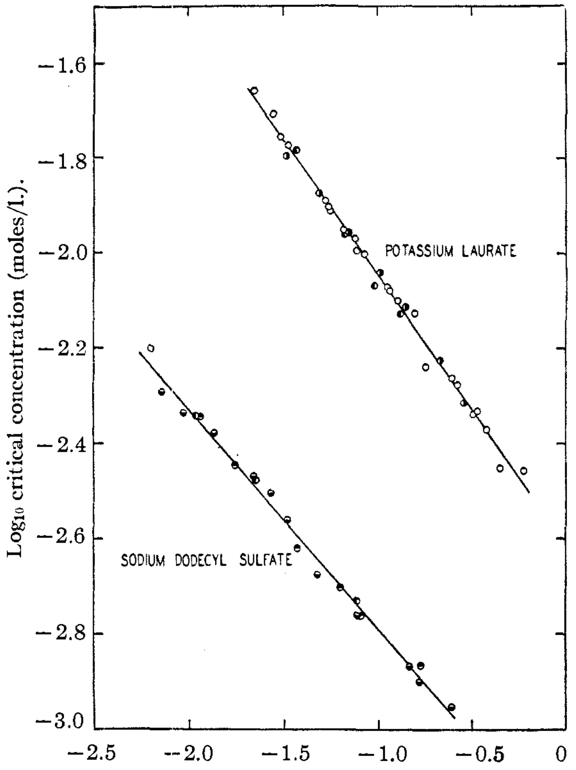

Fig. 3.—Log-log plot of the salt effect with anionic detergents: ○ KCl, ◒ NaCl, ◑ K_2SO_4, ◓ Na_2SO_4, ◐ $Na_4P_2O_7$.

tionated decyl bromide.[10] Sodium dodecyl sulfate was a pure material supplied by Proctor and Gamble. Dodecylammonium chloride was prepared by the method of Ralston and Hoerr[11] from carefully purified dodecylamine. Decyltrimethylammonium bromide was prepared by the method of Scott and Tartar[12] from fractionated decyl bromide.[13] The criterion of detergent purity employed in this work was the agreement of the observed critical concentrations with those reported in the literature.

The salts employed were of reagent grade and were used without further purification. The dyes were commercial products.

Discussion

The sharp change in the properties of solutions of colloidal electrolytes observed at the critical concentration for micelle formation is ordinarily explained by recourse to the following process (for anionic detergents)

$$n\mathrm{M}^+ + m\mathrm{A}^- \rightleftharpoons \mathrm{M}_n\mathrm{A}_m{}^{-(m-n)} \qquad (1)$$

where M^+ represents an alkali metal ion, A^- a long chain paraffin anion, and where m is greater than n. Such a formulation leads to the prediction of the observed experimental facts.[14] A similar picture can be drawn for cationic detergents.

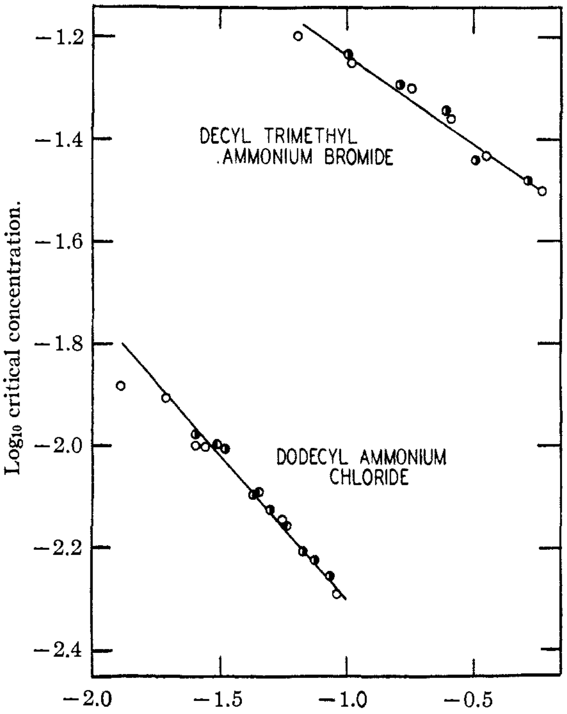

Fig. 4.—Log-log plot of the salt effect with cationic detergents: ○ NaCl, ◑ $BaCl_2$, ◐ $LaCl_3$.

The activity product relation for (1) then takes the form

$$(a_{\mathrm{M}^+})^n(a_{\mathrm{A}^-})^m/(a_{\mathrm{M}_n\mathrm{A}_m}) = K \qquad (2)$$

It is obvious from the experimental behavior reported that if this formulation is correct the activity coefficient of the aggregate cannot be a function of the ionic strength of the solution, since the behavior of neutral long chain electrolytes at concentrations lower than the critical concentration is similar to that of strong electrolytes.[12]

In aqueous solutions of ordinary electrolytes the charge on any ion is always insufficient to produce enough repulsion between the ions of like charge to keep them apart at very large distances. At the interionic distances exhibited in dilute solutions (mean thickness of the ionic atmosphere about 30 Å. for a uni-univalent electrolyte at an ionic strength of 0.01) the repulsion between ions of like charge is increased as the charge per ion increases in such a way as to give the relations expressed by the principle of ionic strength and the related Debye–Hückel theory.

In the case of a colloidal electrolyte the relations are different. The charge on the surface of the aggregated colloid ion is relatively large and may be considered as distributed in a sheet, with distances between charges in the sheet on the order of 4.5 Å. for an ordinary soap. The repulsion between the ions in this sheet and the adjacent salt ions of like charge is here sufficiently great to produce a greater separation than that considered above for simple salt ions of like charge. The re-

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[10] R. M. Reed and H. V. Tartar, THIS JOURNAL, **57**, 570 (1935).

[11] A. W. Ralston and C. W. Hoerr, *ibid.*, **68**, 851 (1946).

[12] A. B. Scott and H. V. Tartar, *ibid.*, **65**, 692 (1943).

[13] The cationic detergents were prepared by Miss A. L. Roginsky of this Laboratory.

[14] J. Grindley and C. R. Bury, *J. Chem. Soc.*, 679 (1929); see also G. S. Hartley "Aqueous Solutions of Paraffin Chain Salts," Hermann et Cie., Paris, 1936.

sult of this increased interionic distance is that the magnitude of the charge on each ion becomes much less significant and the effect is determined by the total charge. As a result those principles which indicate a large variation with the charges of individual ions now become invalid. It is essential that a quantitative theory of these relations be developed.

In a qualitative sense the amount of lowering of the critical concentration of a detergent depends upon the tendency of that detergent to form aggregates. In Table VI are plotted the critical concentrations of several detergents together with the ratio of this concentration to the critical concentration in the presence of 0.05 molar sodium chloride.

TABLE VI

CRITICAL CONCENTRATIONS FOR MICELLE FORMATION IN 0.05 MOLAR SODIUM CHLORIDE

Detergent	Crit. concn. pure detergent	$\frac{\text{Crit. concn. pure detergent}}{\text{Crit. concn. in 0.05 } M \text{ NaCl}}$
Decyltrimethylammonium bromide	6.36×10^{-2}	1.13
Dodecylammonium chloride	1.31×10^{-2}	1.91
Sodium decyl sulfonate	4.00×10^{-2}	1.33
Potassium laurate	2.33×10^{-2}	2.01
Sodium dodecyl sulfate	6.11×10^{-3}	2.87

It is apparent, in the cases considered, that the lower the critical concentration, *i.e.*, the greater the tendency toward aggregation, the greater is the lowering of the critical concentration by equal amounts of salt. As might be expected, this correlation is true only within each class of detergents.

Summary

It is shown that the behavior of the colloidal aggregates of long chain electrolytes cannot be described in terms of the principle of ionic strength or the related Debye–Hückel relationships. The depression of the critical concentration of such electrolytes, as measured by the spectral change of a dye, is related only to the concentration of that ion of an added salt which bears a charge opposite to that on the colloidal aggregate. The nature of the other ion is without effect.

The logarithm of the critical concentration of a colloidal electrolyte is a linear function of the logarithm of the total concentration of the ion opposite in charge to that on the aggregate. Urea, a non-electrolyte, is found to have a negligible effect in lowering the critical concentration.

Within each class of detergents, *i.e.*, anionic or cationic, the depression of the critical concentration brought about by equal amounts of salt is, in the cases investigated, greater the lower the critical concentration of the detergent.

The above relationships, and the fact that the form of the mass law usually applied to colloidal electrolytes is found to be invalid, indicate that they form *a new type of electrolyte in which salt ions of the same charge as the colloidal aggregate are repelled to such a distance as to give independence of the magnitude of the charge per ion*, with dependence upon only the sum of the charges on all such ions, in the formation of the aggregate. With ions of ordinary salts these ions are sufficiently close together to give the well-known high dependence on the charge per ion.

CHICAGO, ILLINOIS RECEIVED JUNE 26, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. XXII. The Reaction of the Sodium Derivatives of Allyl or Propenylbenzene with Proton Donors[1]

BY TOD W. CAMPBELL[2] AND WILLIAM G. YOUNG

The recent synthesis of the sodium derivative of allylbenzene $[C_6H_5CH{=}CH{-}CH_2]^-Na^+$ by Levy and Cope[3] suggests an interesting extension of our work on allylic organo-metallic compounds. Since this compound should be more ionic in nature than the corresponding Grignard reagent, it might be expected to give a greater opportunity for determining the reaction products to be expected from a resonating carbanion than with the corresponding Grignard reagent, which may be largely covalent in nature. In spite of the fact that the sodium derivatives might be expected to behave differently than the Grignard reagent, Levy and Cope found that the allylic sodium compound reacted at the secondary position in coupling reactions with allylic halides, just as has been reported from the reaction of cinnamylmagnesium chloride with carbon dioxide, phenyl isocyanate, ethyl chlorocarbonate[4] and acetaldehyde.[5]

On the other hand, we have found that proton donating agents give entirely different mixtures of products from cinnamylmagnesium chloride[6] and the sodium derivatives of allyl- and propenylbenzene. Preliminary work with carbon dioxide, ketones and α-haloacetic acids has also revealed differences in the products of the reactions

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(1) Presented before the Organic Division at the Chicago Meeting of the American Chemical Society, September 10, 1946.

(2) Abbott Laboratories Research Fellow 1944–1945.

(3) Levy and Cope, THIS JOURNAL, **66**, 1684 (1944).

(4) Gilman and Harris, THIS JOURNAL, **49**, 1825 (1927); **53**, 3541 (1931).

(5) Ou Kuin-Houo, *Ann. chim.*, **13**, 175 (1940).

(6) Young, Ballou and Nozaki, THIS JOURNAL, **61**, 12 (1939).