

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

Determination of the Critical Concentration for Micelle Formation in Solutions of Colloidal Electrolytes by the Spectral Change of a Dye¹

BY M. L. CORRIN AND WILLIAM D. HARKINS

I. Introduction

A new and extremely simple method for the determination of the critical concentration for micelle formation by the spectral change in a dye has been developed by the writers. Earlier work on related spectral changes, as described below, has in no case been applied to the determination of critical concentrations.

In 1934 Hartley^{1a} reported that the color of sulfonphthalein indicators in buffered solution is altered by the addition of detergents; an effect is noted only when the charge on the detergent aggregate is opposite to that on the indicator ion. This phenomenon was utilized in the determination of the total concentration of anionic or cationic detergents in solution by titration with a known solution of detergent of opposite sign in the presence of brom phenol blue.² However this method is inapplicable to the fatty acid soaps. *No attempt was made to determine the critical concentrations of detergent solutions by use of these dyes.* In 1945 Sheppard and Geddes³ reported that the absorption spectrum of pinacyanol chloride in aqueous solutions is altered by the addition of a cationic detergent, cetylpyridinium chloride. No attempt was made to use the pinacyanol for the measurement of critical concentrations; in fact, as shown below, *the spectral change observed with pinacyanol chloride and cationic detergents is so slight as to make this dye useless for the determination of the critical concentrations of cationic detergents.* Pinacyanol chloride may be employed for the determination of the critical concentrations of only anionic detergents by the spectral method.

In 1938 Hartley⁴ introduced what might be termed the "solubilization method" for the determination of critical concentrations. This method makes use of the fact that the solubility of water insoluble organic materials in soap solutions⁵ becomes marked only in the presence of micelles, *i.e.*, at concentrations exceeding the critical concentration. Hartley employed a colored organic material and determined the amount of substance solubilized by a colorimetric method. The same general procedure may be employed with colorless substances and the concentrations

suitably determined. The solubilization of dyes in detergent solutions has been investigated by McBain and his co-workers⁶ without explicit application to the determination of critical concentrations. Critical concentrations have been measured by the "solubilization method" with both colored and colorless organic materials by R. S. Stearns and W. D. Harkins.⁷

The spectral method for the determination of critical concentrations described below differs in principle from the "solubilization method" in that what is observed is not the amount of colored material solubilized as a function of the detergent concentration but the spectral behavior of a dye at constant concentration in solutions of varying detergent concentration. It is not, therefore, necessary in employing the spectral method to determine the solubility of the dye in a number of solutions of different soap concentration to determine the critical concentration. A detergent solution of known concentration (above the critical concentration) and containing the proper dye is merely titrated with an aqueous solution of the dye to the characteristic color change; the detergent concentration at this point is the critical concentration. This method, is very much more rapid than the "solubilization method" since only one detergent solution is required and only a few minutes are required to attain equilibrium.

The use of pinacyanol chloride for the determination of the critical concentrations of anionic detergents has been reported in a previous paper.⁸ The present paper deals with the use of this and other dyes for the determination of the critical concentrations of both anionic and cationic detergents.

II. Results and Discussion

It was found that the absorption spectrum of pinacyanol chloride in aqueous solutions of anionic soaps changes abruptly at the critical concentration for the formation of micelles.⁸ The long wave length α and β bands at about 6150 and 5700 Å., respectively, increase rapidly in intensity when the soap concentration is increased beyond the critical concentration while the γ band at about 4800 Å. disappears.⁹ The α and β bands are

(6) J. W. McBain and Sr.-A. A. Green, *ibid.*, **68**, 1731 (1946), and earlier papers.

(7) R. S. Stearns and W. D. Harkins, unpublished work.

(8) M. L. Corrin, H. B. Klevens and W. D. Harkins, *J. Chem. Phys.*, **14**, 480 (1946).

(9) The γ band appearing only in very dilute solutions of anionic detergents is not equivalent to the γ band discussed by Sheppard.¹⁰ We have followed Sheppard's notation in that the absorption bands in each specific case are designated by α , β and γ in order of decreasing wave length. In dilute soap solutions the γ band appears at about 4800 Å.; the γ band described by Sheppard in aqueous solutions of the dye is about 5300 Å.

(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) G. S. Hartley, *Trans. Faraday Soc.*, **30**, 444 (1934).

(2) G. S. Hartley and D. F. Runnicles, *Proc. Roy. Soc. (London)*, **A168**, 420 (1938); C. S. Samis and G. S. Hartley, *Trans. Faraday Soc.*, **34**, 1288 (1938).

(3) S. E. Sheppard and A. L. Geddes, *J. Chem. Phys.*, **13**, 63 (1945).

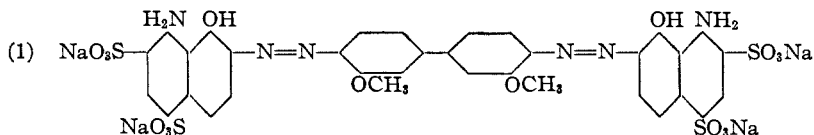
(4) G. S. Hartley, *J. Chem. Soc.*, 1968 (1938).

(5) J. W. McBain and M. E. L. McBain, *THIS JOURNAL*, **58**, 2610 (1936)

characteristics of solutions of the dye in organic solvents and are attributed to the monomeric form of the dye (only a shoulder of the 5300 Å. band appears in ethanol). In water a band at about 5500 Å. appears in relatively concentrated solutions of the dye¹⁰; this band which may be due to a shift of the 5700 Å. β -band is apparently dependent upon polymer formation. The γ band is observed only in dilute solutions of anionic soaps. The spectral change of pinacyanol chloride at the critical concentration is of much greater magnitude with anionic soaps than with cationic materials.^{3,11} This difference is due primarily to the appearance of the γ band in the case of anionic soaps which leads to a far greater wave length shift when the critical concentration is reached than the shift from the 5500 Å. water band to the organic type spectrum.

The phenomena described above have been attributed to solubilization of the monomeric form of the dye within the interior of soap micelles.¹² The question, however, arises: is the spectral shift due to preferential solubilization of the monomeric form of the dye within the micelles or to the fact that within the micelles the dye is in an essentially hydrocarbon-like environment? No evidence upon the basis of which a choice between these two alternatives can be made is given by pinacyanol chloride, since with this dye a non-polar environment invariably leads to only the monomeric form. However, the problem may be attacked by the use of other dyes.

The absorption spectrum of phenol blue is known to vary with the polarity of the solvent.¹³ The wave length of the band maximum in water is 6680 Å., in methyl alcohol 6120 Å., in acetone 5820 Å., and in cyclohexane 5520 Å. However, its spectrum in micellar solutions of either potassium laurate or dodecylammonium chloride possesses a broad absorption band in the neighborhood of 6500 Å.¹⁴ The shift observed is much smaller than would correspond to solution of the dye in a hydrocarbon solvent. It should be noted that phenol blue is almost quantitatively extracted from aqueous solution by toluene. It thus



appears that solution of the dye within the micelle to yield spectra characteristic of the dye solutions in non-polar solvents cannot be the sole criterion for the suitability of a dye for the determination of critical concentrations. In order to further test this conclusion, recourse was had to the following dyes whose spectra in alcohol are visually distinguishable from those in water: Orange G (S189), Azophloxin 2G (S40), Bordeaux B (S123), Congo Brown G (S680), New Methylene Blue (S1043) and Ponceau G (S37). The information in parentheses refers to the Schultz number. With both anionic and cationic soaps no change was produced in the spectra of these dyes.

It is thus necessary to consider the alternative explanation, *i.e.*, that one of the several forms of the dye which exist in equilibrium in aqueous solution is preferentially solubilized in the soap micelle. The equilibrium in the case of pinacyanol chloride is between monomer and dimer (the possibility of larger dye aggregates in soap solutions below the critical concentration is indicated below). It should, however, be possible to employ other systems in which the equilibrium is of different nature. Such systems which employ acid-base equilibria are considered later.

Pinacyanol chloride is effective only with anionic soaps. Its spectral change with cationic soaps is too small to permit a ready determination of the critical concentrations of detergents of this type. This is believed due to the fact that the dye ion of pinacyanol chloride is cationic. The existence of aggregated dyes in which the dye ion is anionic is well-known.¹⁵ One such dye is Sky Blue

FF (1).¹⁶ Evidence for its aggregation has been obtained by conductivity measurements.¹⁷ Sky Blue FF forms blue solutions both in water and in solutions of cationic soaps above the critical concentrations for micelle formation. Below the critical concentration, however, the solutions exhibit a definite reddish color. The color change is sharp and sufficiently marked to permit visual determination of the end-point when a soap solution containing the dye is titrated against a solution of the dye in water. This change occurs at a concentration of 1.27×10^{-2} molar for dodecylammonium chloride and 6.43×10^{-2} molar for decyltrimethylammonium bromide. The critical concentrations obtained by others by the use of different methods is for the former 1.30×10^{-2} molar¹⁸ and for the latter 6.5×10^{-2} molar.¹⁹

(15) H. A. Standing, *Trans. Faraday Soc.*, **41**, 410 (1945).

(16) The use of this dye was suggested to the authors by J. L. Molliet.

(17) F. H. Holmes and H. A. Standing, *Trans. Faraday Soc.*, **41**, 568 (1945).

(18) A. W. Ralston and C. W. Hoerr, *THIS JOURNAL*, **64**, 772 (1942).

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

(10) S. E. Sheppard, *Rev. Mod. Phys.*, **14**, 303 (1942).

(11) The use of cationic detergents by Sheppard and Geddes was designed to avoid "the possibility of an electrochemical combination of the dye and the charged gelatin (detergent)." It is precisely because a combination of some sort occurs in the system pinacyanol chloride-anionic detergent that this dye is suitable for the spectral determination of the critical concentrations of such detergents.

(12) It is problematical whether the spectral shifts observed may be explained simply by the dimerization hypothesis. It is established, however, by other than spectral means that an aggregated form of the dye exists in aqueous solutions at a sufficiently high dye concentration.¹⁰ Whether such polymer formation is responsible for the appearance of new absorption bands or whether these bands are present at all times and merely become more pronounced on aggregation is a question beyond the scope of this paper. In any event, the observed spectral shift, regardless of its mechanism, is observed simultaneously with aggregation of the dye.

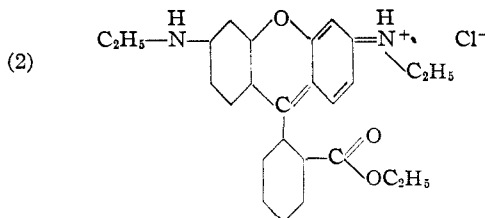
(13) L. G. S. Brooker, *THIS JOURNAL*, **63**, 3214 (1941).

(14) The phenol blue was kindly supplied by Dr. L. G. S. Brooker.

The extent of aggregation of Sky Blue FF in the absence of salts is unknown.¹⁷ Valko, however, assigns an aggregation number of 3.7 to dye solutions ranging in concentration from 0.002 to 0.02% in the presence of from 0.02 to 0.05 molar sodium chloride.²⁰ The striking feature, however, concerning Sky Blue FF is that the spectra in the micellar soap solution and in water are essentially identical. The dye is suitable as a critical concentration indicator only because a markedly different spectrum appears in cationic soap solutions below the critical concentration. It has been shown that the aggregation number of Sky Blue FF is increased thousand-fold by the addition of a cationic detergent (presumably below the critical concentration).²¹ Furthermore, according to Valko, non-ionic detergents have a smaller effect while anionic soaps have essentially no influence on the degree of aggregation. The change in spectrum of the dye below the critical concentration with cationic soaps may thus be explained on the basis of formation of large dye aggregates. The formation of such aggregates is known to produce spectral changes.^{10,22} It is also quite probable that the γ band appearing in solutions of anionic soaps below the critical concentration is also due to such an effect since the cyanines are known to form highly aggregated systems under the proper conditions.²³

Other dyes suitable for the titrimetric determination of the critical concentrations of cationic soaps are eosin, which changes from a highly fluorescent orange color in micellar solutions to a red with pronounced quenching of fluorescence in solutions below the critical concentration, and fluorescein, in which the fluorescence observed in micellar solutions is strongly quenched below the critical concentration. These dyes are anionic and evidence is available to support the view that polymerization equilibrium exists in their aqueous solutions.²⁴ The critical concentrations as determined by eosin are 6.35×10^{-2} for decyltrimethylammonium bromide and 1.36×10^{-2} molar for dodecylammonium chloride, and by fluorescein, 6.10×10^{-2} molar for decyltrimethylammonium bromide and 1.30×10^{-2} molar for dodecylammonium chloride.

This mechanism is further verified by the behavior of Rhodamine 6G (2), a dye studied by Lewschin.²⁵ The spectral behavior is analogous to that of pinacyanol, since in water the spectra vary greatly with dye concentration; as the dye



concentration increases a new band appears. *The change in spectra is accompanied by variations in fluorescence; with the formation of a polymeric form of the dye the fluorescence is quenched.* Rhodamine 6G also resembles pinacyanol chloride in that the dye ion is cationic. On the basis of the discussion above it should be effective in determining the critical concentrations of anionic soaps only. That is actually the case. Rhodamine 6G is ineffective with cationic soaps, while with anionic detergents its solutions above the critical concentration are orange in color and highly fluorescent. As these solutions are diluted at constant dye concentration, the color changes abruptly to red, and the fluorescence almost completely disappears. Both color and fluorescence changes occurred at concentrations of 2.34×10^{-2} molar for potassium laurate, 3.87×10^{-2} for sodium decyl sulfonate, and 6.12×10^{-3} molar for sodium dodecyl sulfate. These values agree well with those determined by other means.²⁶

The effect of charge on the interaction of dyes and soaps is discussed by Hartley.^{1a} It was found that the addition of soaps to buffered solutions of hydrogen ion indicators produced color changes which, in several instances, amounted to 1.5 pH units. Such changes were produced, however, when the charge on the dye ion was opposite to that on the soap micelles. Hartley made no measurements over a wide range of soap concentration, although a critical concentration for sodium dodecyl sulfonate on the order of 1×10^{-4} molar at 50° has been deduced by us from his data as valid in the presence of acetic acid-acetate buffer. The value of the critical concentration of this detergent as determined by solubility measurements is 1.05×10^{-3} molar.²⁷ The presence of salts, however, has been shown to produce a marked lowering of the critical concentration.

Work in this Laboratory on the effect of soaps on the color of hydrogen ion indicators tends generally to confirm Hartley's results. In general, the color of an indicator opposite in ion charge to that on the soap micelle is displaced toward the color of the dye at the neutral point in the presence of micellar soap. Due, however, to the presence of the acid, base or buffer required to put the dye into a form in which a color change will take place, the critical concentrations obtained are different from those determined in water. Thus, when suf-

(26) K. A. Wright, A. D. Abbott, V. Sivertz and H. V. Tartar, *THIS JOURNAL*, **61**, 549 (1939); A. Lottermoser and F. Püschel, *Kolloid-Z.*, **63**, 175 (1933).

(27) H. V. Tartar and K. A. Wright, *THIS JOURNAL*, **61**, 539 (1939).

(20) E. Valko, *Trans. Faraday Soc.*, **31**, 230 (1935).

(21) E. Valko, *J. Soc. Dyers Colourists*, **55**, 174 (1939).

(22) G. Kortüm, *Z. physik. Chem.*, **B33**, 1 (1936); **B34**, 255 (1936); see also V. Kargin and E. B. Fodiman, *Acta physicochim. U. R. S. S.*, **1**, 220 (1934).

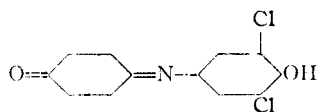
(23) The γ band appearing in pinacyanol solutions containing anionic detergent below its critical concentration is not to be confused with the J bands characteristic of the cyanines in a highly polymerized form.¹⁰

(24) S. E. Sheppard and A. L. Geddes, *THIS JOURNAL*, **66**, 1995 (1944).

(25) W. L. Lewschin, *Acta physicochim. U. R. S. S.*, **1**, 685 (1934).

ficient acid was added to methyl red to produce a sharp color change over a small range of soap concentration, the critical concentration for decyltrimethylammonium bromide was found to be 4.3×10^{-2} molar, while in the absence of acid it is 6.43×10^{-2} molar as determined with Sky Blue FF.

It has been found that the color change in the indophenol dyes is the sharpest, and the error introduced by the presence of acid the least. Thus, if a 1×10^{-4} molar solution of the sodium salt of 2,6-dichlorophenolindophenol (3) is made



3×10^{-4} molar in hydrochloric acid, the color changes from blue to red. On the addition of sufficient cationic soap to produce micelles the color changes back to blue. On dilution with the acidified dye solution the color changes to red at the critical concentration. Values obtained with the use of this dye are 1.24×10^{-2} molar for dodecylammonium chloride and 6.02×10^{-2} molar for decyltrimethylammonium bromide. The color changes observed with the sulfonphthaleins are not nearly as satisfactory. The general results of critical concentration measurements made with the dyes discussed in this paper are tabulated in Table I.

TABLE I

THE TITRIMETRIC DETERMINATION OF CRITICAL CONCENTRATIONS WITH VARIOUS DYES

Dye	Potassium laurate	Sodium dodecyl sulfate	Sodium decyl sulfonate	Decyl-trimethyl ammonium bromide	Dodecyl ammonium chloride
Pinacyanol chloride	0.0235	0.00602	0.0400		
Rhodamine 6G	.0234	.00612	.0387		
Sky Blue FF				0.0643	0.0127
Eosin				.0635	.0136
Fluorescein				.0610	.0130
2,6-Dichlorophenolindophenol				.0602	.0124

NOTE ADDED IN PROOF.—The spectral effects noted at the critical concentration may be due either to adsorption of the dye upon the surface of the micelle or to its incorporation within the micelle. It is possible that the solubilization process involves both mechanisms. Each of the following additional dyes may be used for the determination of the critical concentrations of that class of detergents for which it is suitable. The list gives a few examples of the detergents which have been measured by the particular dye. With potassium laurate and sodium dodecyl sulfate: Acridine Orange (f), Acridine Yellow (f), Acriflavine (f) and Quinaldine Red (c). With potassium laurate: Neutral Blue (c), Nile Blue A in dilute base (c) and Phenosafranin (c). With sodium dodecyl sulfate: Neutral Red (c). With dodecylammonium chloride: Primuline (c), Dichlorofluorescein (f, c) and Brom Cresol Purple (c). A color change is designated by (c) and a change in fluorescence by (f).

Experimental

Detergent solutions were prepared by weight by adding to a known quantity of thoroughly dried material the proper quantity of dye solution. Aliquot portions of this solution were then titrated with an aqueous solution of the dye (same concentration as in sample) using the original detergent solution as a blank. The end-point was taken as the first visible change of color or fluorescence in the titrated sample with reference to the blank. The temperature in all instances was $26 \pm 2^\circ$ for the visual determinations.²⁸ It was found practicable to carry out the titrations in small volumetric flasks since the colors may be compared through approximately equal thicknesses of solution in the necks of the flasks. All spectrophotometric measurements were made on the spectrophotometer described by Hogness, Zscheile and Sidwell.²⁹

Materials.—Potassium laurate was prepared by the saponification of carefully fractionated methyl laurate with potassium hydroxide in ethanol. The soap was twice recrystallized from alcohol and washed with acetone. Sodium decyl sulfonate was prepared by the method of Reed and Tartar.³⁰ Sodium dodecyl sulfate was supplied by Procter and Gamble. Dodecylammonium chloride was prepared by the method of Ralston and Hoerr.³¹ Decyltrimethylammonium bromide was made from a carefully fractionated sample of decyl bromide by the method of Scott and Tartar.¹⁹ The dyes employed were of commercial grade, since it was felt that at the low dye concentrations used the effect of electrolytic impurities is insignificant.³²

Summary

The suitability of a dye as an indicator in the determination of the critical concentration for the formation of micelles in soap solutions is related to the existence of an equilibrium mixture of the dye in aqueous solution from which one form is preferentially solubilized by the soap micelle. In addition, the charge on the dye ion must be opposite to that of the micelle. In general, the variation of the spectrum of a dye with change in environment is not a sufficient condition for the suitability of the dye as a critical concentration indicator.

Pinacyanol chloride and Rhodamine 6G are shown to be suitable for the determination of the critical concentrations of anionic soaps, while Sky Blue FF, eosin, fluorescein, and acidified 2,6-dichlorophenolindophenol may be used with cationic detergents.

Dye systems involving acid-base equilibria may be employed for the determination of critical concentrations. With cationic soaps acidified solutions of the indophenols are satisfactory. The necessary presence of acids, bases or buffering salts renders the use of acid-base dyes less satisfactory than dyes in which a polymerization equilibrium exists.

Methods are described by means of which the critical concentration may be determined in a few minutes by a titration in which the disappearance

(28) The change in critical concentration with temperature is very slight.^{28a}

(29) T. R. Hogness, F. P. Zscheile, Jr., and A. E. Sidwell, *J. Phys. Chem.*, **41**, 379 (1937).

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

(31) A. W. Ralston and C. W. Hoerr, *ibid.*, **68**, 851 (1946).

(32) Dodecylammonium chloride and decyltrimethylammonium bromide were prepared by Miss A. Roginsky of this Laboratory.

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 ap-

preciably by any of the dyes used, since they are employed at too high a dilution to produce such a change.

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The Effect of Salts on the Critical Concentration for the Formation of Micelles in Colloidal Electrolytes¹

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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 $-\text{COO}^-$, 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 1 μ 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 Robinson⁵ who gave no data, Hartley,⁶ Tartar and Cadle⁷ 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

(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)*, **A165**, 386 (1936).

(6) C. 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).