of gyration of this collection of rods to be less than 1% smaller than the radius of gyration of the box if it were uniformly filled. Even if we let the diameter of the central rods go to zero as their density became infinite the difference is still less than 1%. Also changing the 12 Å. center to center separation of the chains over the range from 10 to 15 Å. has little effect on the results. While the assumed intramolecular structure is an obvious oversimplification, the calculation does indicate that in the region of the Guinier approximation density fluctuations due to the polypeptide chains in the protein molecule will not affect the scattering. An interpretation of this part of the scattering curve in terms of models with uniform density should give valid results for the over-all dimensions of the molecule. A closer study would be necessary to determine at what angles the intramolecular structure becomes important in the interpretation of the scattering data.

Acknowledgment.—We wish to thank Professor John Edsall of Harvard University for generously giving us the human mercaptalbumin monomer and dimer preparations.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

A Re-evaluation of the Spectral Change Method of Determining Critical Micelle Concentration[1]

BY PASUPATI MUKERJEE[2] AND KAROL J. MYSELS

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The critical micelle concentration (CMC) is most frequently determined these days by spectral change methods involving color changes of dyes, particularly of pinacyanol, as the detergent concentration changes. A critical examination of this method as applied especially to sodium lauryl sulfate (NaLS) is presented. It is shown that the color change involves the formation of a dye–detergent salt which is highly insoluble but forms a coarse and quite stable suspension in the presence of somewhat more than stoichiometric amounts of detergent. For pinacyanol this salt is red. The presence of the insoluble salt induces the formation of mixed blue micelles at concentrations substantially below the CMC of NaLS itself. The complete solubilization of the dye–detergent salt and therefore the apparent CMC determined by this method depends on a number of factors such as the concentration of dye, the absolute value of the CMC and the temperature. As a result large errors in both absolute and relative values of CMC's are being introduced by the use of this method. The composition of induced mixed micelles and their transition to normal micelles are briefly discussed.

At concentrations generally used (10^{-5} to 10^{-4} *M*) the dye pinacyanol gives a violet solution in water. In the presence of low concentration of many detergents (*e.g.*, 0.03–0.16% sodium lauryl sulfate) it gives a red color. At only slightly higher concentrations (0.22% and up NaLS) a blue solution is produced. The color change between red and blue occurs not very far from the critical micelle concentration (CMC) of the detergent. The same type of behavior is shown by a number of other dyes. The concentration at which the color change occurs is easy to determine experimentally and ever since Harkins and co-workers[3–6] proposed this "spectral change method" of determining the CMC it has become by far the most popular one. The articles describing its use are too numerous to be all quoted and so only a few are cited.[3–11]

In addition to the determination of a large number of CMC's on a variety of systems several structural interpretations are based on the observed color changes and the effects of various factors on the CMC. We shall discuss some of these later.

There have been indications that the method may not be completely reliable: Klevens noted that the values thus found for the CMC tend to be lower than by other methods.[12] Nor was the agreement between different investigators satisfactory[6,9] nor between visual and colorimetric methods of the same investigator.[13] The principal uncertainty of the method arose probably from the insufficient understanding of the reasons for the observed color changes.

The CMC can be defined unambiguously[14] and determined accurately by three independent methods as shown in Fig. 6 and discussed further below. The pinacyanol method, however, gives a discordant result. This led to the present investigation of the color changes of pinacyanol and to the conclusion that, in practice, the method gives only a rough approximation of the CMC.

Experimental

Materials.—The NaLS used has been described.[14] The pinacyanol chloride was obtained from Eastman Kodak Co. Its microanalyses, either as obtained or after recrystallization, failed to give reproducible results in two laboratories. This seems to be due to incomplete combustion of the chloride salt. The lack of change of absorption coefficient upon recrystallization and the microanalysis of the other salts reported below convince us that the purity of the material was quite satisfactory for our purpose.

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[1] Presented in part before the Division of Colloid Chemistry at the New York Meeting of the American Chemical Society, September, 1954.

[2] Colgate–Palmolive–Peet Pre-Doctoral Fellow.

[3] M. L. Corrin, H. B. Klevens and W. D. Harkins, *J. Chem. Phys.*, **14**, 216 (1946).

[4] M. L. Corrin, H. B. Klevens and W. D. Harkins, *ibid.*, **14**, 481 (1946).

[5] M. L. Corrin and W. D. Harkins, THIS JOURNAL, **69**, 679 (1947).

[6] M. L. Corrin and W. D. Harkins, *ibid.*, **69**, 683 (1947).

[7] H. B. Klevens, *J. Phys. Colloid Chem.*, **54**, 1012 (1950).

[8] (a) S. H. Herzfeld, M. L. Corrin and W. D. Harkins, *ibid.*, **54**, 217 (1950); (b) discussion of reference 21.

[9] E. D. Goddard, O. Harva and T. G. Jones, *Trans. Faraday Soc.*, **49**, 980 (1953).

[10] A. L. M. Lelong, H. V. Tartar, E. C. Lingafelter, J. K. O'Loane and R. D. Cadle, THIS JOURNAL, **73**, 5411 (1951).

[11] K. Shinoda, *J. Phys. Chem.*, **58**, 541 (1954).

[12] H. B. Klevens, *ibid.*, **51**, 1143 (1947).

[13] S. H. Herzfeld, *ibid.*, **56**, 953 (1952).

[14] R. J. Williams, J. N. Phillips and K. J. Mysels, *Trans. Faraday Soc.*, in press.

The cetyltrimethylammonium bromide was obtained from Eastman Kodak Co. and purified by extraction with ether and recrystallization from methyl alcohol, repeated twice. Microanalysis and theory: C, 62.35 (62.61); H, 11.63 (11.62); N, 4.05 (3.84); Br, 21.63 (21.93).

Lauric acid obtained from the same source was recrystallized twice from acetone. It was dissolved in a slight excess of sodium hydroxide. Methylene blue was a U.S.P. sample (minimum purity 98.5% on a moisture-free basis), and brom phenol blue was from the Coleman and Bell Co. Both were used as received.

Method.—Standard solutions of dye and of detergent were prepared on a weight to weight basis. In experiments where no additional electrolyte was used, a stock solution of the detergent above the CMC was made up in a dye solution and this was added to the same dye solution in water to get various concentrations of the detergent. Thus the dye concentration was constant throughout. Where electrolytes were used, two stock solutions, one below and the other above the CMC were prepared, both containing the same concentration of dye and salt. Finally, mixtures of these two stock solutions were used for measurements. Dilutions by weight and ordinary distilled water were employed except for conductivity measurements when distilled water equilibrated with laboratory atmosphere was used.

A Beckman UV spectrophotometer and 1 or 0.5 cm. cells were used for optical determinations and a Jones–Dyke[15] bridge for conductivimetry. We used a 25 mm. "spinning top" air-driven ultracentrifuge[16] with two rotors, one of the Ford–Williams–McBain type,[17] the other a hollow bowl of 8-cc. capacity with a groove for holding a strip of filter paper on its inner periphery. The former gives convection-free sedimentation; the other involves considerable convection but small precipitates are effectively immobilized by the filter paper. An angle SS-1 Servel centrifuge was also used.

Solutions of pinacyanol in water and in the presence of detergents show some fading, particularly in light. In NaLS the effect is slight and becomes negligible in the dark (<1% per hour).

The color of solutions in the transition zone changes somewhat soon after preparation and depends in the early stages on the order of mixing of solutions above and below the CMC. After about 2 hours at room temperature in the dark these changes and differences become undetectable. All our measurements were therefore made on samples kept in the dark for 180 ± 10 minutes from the time of adding the more concentrated solution to the more dilute one.

The spectra which we obtained are basically identical with those reported[3,4] for similar systems. It may be noted, however, that our band maxima for any dye concentration remained constant within 30 Å. in all solutions. The extinction values were measured at the band maxima.

Over periods of months, the reproducibility for colorimetric measurements was of the order of 10% in extinction coefficient, of 1% in concentration, and for conductivimetric measurements of the order of 0.05%.

Preparation of Salts.—Approximately 0.1–0.5% solutions were used, a slight excess of the dye being added to the detergent. The precipitate was filtered, washed thoroughly with water, dissolved in methyl alcohol, filtered and the alcohol evaporated. The orange-red mono-salt of bromo phenol blue with cetyltrimethylammonium had to be precipitated in and washed with about $M/40$ H_2SO_4, while for the blue di-salt about $N/100$ NaOH had to be used.

The Red Color below the CMC

The color change observed with many dyes upon addition of a very small amount of detergent has been variously attributed to a novel effect which makes dilute detergents differ from other electrolytes[9]; to the formation of ion pairs[18]; of micelles[19]; of an insoluble complex salt[20] $(S_mD_n)_x$ with $m >> n$ but m not large enough to form micelles[12]; the presence of dye dimers and higher aggregates with one or more soap molecules.[20] The solution has been reported optically clear.[18]

In fact, however, the color, which is red for pinacyanol, and characterized by an absorption band (the γ-band) at 483 mμ, is due to the presence of a highly insoluble simple salt of the detergent anion with the dye cation. When stoichiometric amounts or excess dye is present, a fine precipitate settles out slowly. Excess detergent reduces flocculation so that a stable suspension is formed. Centrifugation (a few minutes at 150,000 × g, or less effectively, half an hour at 20,000 × g) causes, however, complete sedimentation. Extended standing also causes growth of the particles followed by flocculation and sedimentation. In the presence of salt the suspension is much less stable and tends to flocculate in a short time.

The detergent–dye salt can be recrystallized from alcohol to form large monoclinic needles, blue-violet in color. Microanalysis gave the following results.

Anal. Calcd. for $(C_{25}H_{25}N_2SO_4(CH_2)_{11}CH_3)$: C, 71.81; H, 8.14; N, 4.53; S, 5.19. Found: C, 72.00; H, 8.03; N, 4.78; S, 5.02.

Another proof that the red color is associated with large insoluble particles is the complete lack of diffusion of the red color in several days through a cellophane membrane into another detergent solution of same concentration.

That this suspension appears clear is not surprising in view of its fineness and extreme dilution (10^{-4} to 10^{-5} M).

This formation of a very insoluble salt between ionic dyes and oppositely charged detergents is a very general phenomenon. Hiskey and Downey[21] found it independently for methyl orange and octadecyltrimethylammonium chloride. A report on a considerable number of detergents and dyes will be submitted shortly, but it may be mentioned that we have prepared and analyzed three insoluble compounds:

Anal. Calcd. for methylene blue–lauryl sulfate $(C_{16}H_{18}N_3S\text{–}SO_4C_{12}H_{25})$: C, 61.20; H, 7.85; N, 7.64; S, 11.63. Found: C, 61.00; H, 8.09; N, 7.36; S, 11.30. Calcd. for cetyltrimethylammonium–brom phenol blue $(C_{16}H_{33}(CH_3)_3N\text{–}Br_4O_6C_{19}H_{11})$: C, 48.58; H, 5.69; Br, 34.02. Found: C, 48.43; H, 5.70; Br, 34.09. Calcd. for dicetyltrimethylammonium–brom phenol blue $(C_{16}H_{33}(CH_3)_3N)_2\text{–}Br_4O_6C_{19}H_{10}$: C, 55.97; H, 7.75; Br, 26.14. Found: C, 55.54; H, 8.09; Br, 26.30.

Since the formation of a salt obviously requires the presence of opposite charges on the dye and detergent it explains the previously noted corresponding requirement for the success of the spectral change method[5] and Hartley's[22] "sign rule" for the indicator effect.

The Blue Color above the CMC

Above the CMC the color is blue for pinacyanol and is characterized by two absorption bands, α at

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[15] P. H. Dyke, *Rev. Sci. Instr.*, **2**, 379 (1931).

[16] Manufactured by Joseph Grebmeier of Mountain View, California.

[17] J. W. McBain, "Colloid Science," Reinhold Publ. Corp., New York, N. Y., 1950, p. 228.

[18] E. L. Colichman, THIS JOURNAL, **72**, 1834 (1950).

[19] E. L. Colichman, *ibid.*, **73**, 1795 (1951).

[20] H. B. Klevens, *Chem. Revs.*, **47**, 1 (1950).

[21] C. F. Hiskey and T. A. Downey, *J. Phys. Chem.*, **58**, 835 (1954).

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

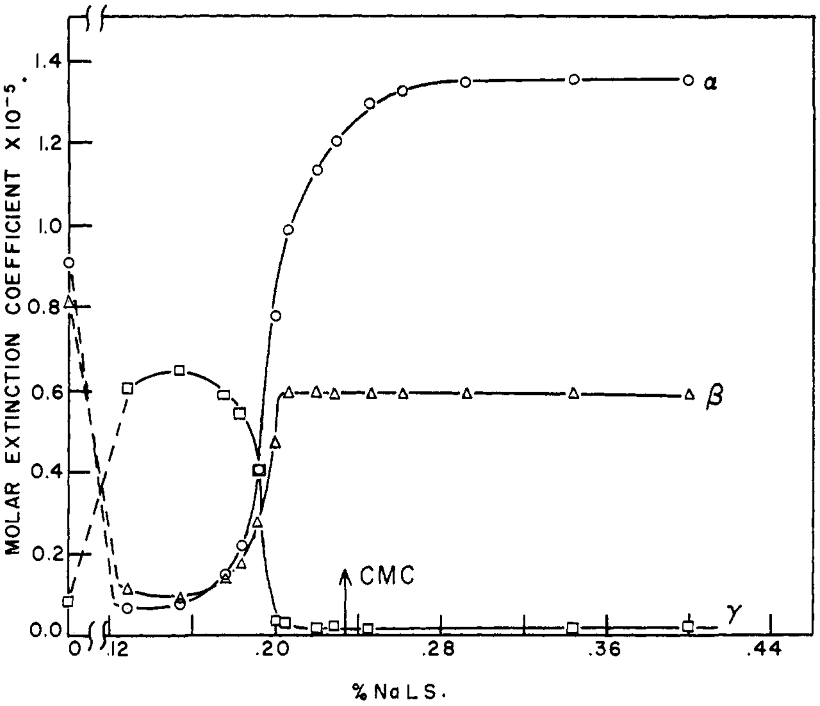

Fig. 1.—The extinction coefficients at the band maxima of pinacyanol in water and in the presence of NaLS; dye concn. 1 × 10^{-5} *M*; band maxima: in water α 600 mμ, β 550 mμ; in NaLS solution, α 610 mμ, β 562 mμ, γ 485 mμ.

610 mμ and β at 565 mμ. The spectrum here is very similar to the one in organic solvents and indicates a monomeric state of the dye.[23] It is not very different from the spectrum of the dye in water, the latter being due to a monomer–dimer equilibrium according to Sheppard, *et al.*[24] The blue color is unaffected by centrifugation which completely removes the red color. This shows a much finer degree of dispersion. In fact, it is possible to separate by centrifugation a solution in the transition zone into a blue supernatant and a red precipitate.

It is therefore apparent that the blue color is due to solubilization of the dye detergent salt, *i.e.*, to its incorporation into micelles. This is in agreement with the assumptions of all previous workers and we shall provide definite proof for it.

The Transition Region.—Figure 1 shows the typical changes in absorption maxima for the 3 characteristic bands. The γ-band of the red solution decreases at an accelerated rate until it disappears. This corresponds to the solution and disappearance of the precipitate. The β-band of the blue solution increases simultaneously and flattens out at the same point at which the γ-band disappears. This corresponds to the incorporation of the dye into micelles. The α-band begins by increasing just like the β-band, but does not flatten until much beyond this point. We shall return to the α-band later.

The correctness of this interpretation may be proved by comparing colorimetric and conductivimetric measurements on the same system containing both dye and detergent. Figure 2 shows our results for NaLS in the presence of 4 × 10^{-5} *M* pinacyanol chloride. It may be seen that equivalent conductivity[25] shows first deviations from linearity when the γ-band begins to decrease and the α- and β-bands begin to increase. The equivalent conductivity then decreases showing the formation of micelles, with a definite kink at the point where the γ-band disappears and the β-band flattens.

Thus micelles are indeed formed in the color transition region. We shall show that these are micelles induced by the presence of the dye and that they bear little relation to the CMC of the detergent alone.

Induced Micellization.—Full circles in Fig. 3 show the equivalent conductivity of NaLS alone. Open circles show the effect of the presence of 4 × 10^{-5} *M* pinacyanol (the line of Fig. 2), and open squares, the effect of 10^{-4} dye. It is clearly apparent that the drop in equivalent conductivity and hence micellization occurs at markedly lower concentrations in the presence of dye and that throughout the transition region the amount of micellized detergent is greatly increased by the presence of dye.

In other words, conductivity shows the existence of micelles induced by the presence of dye at concentrations at which the detergent when alone does not micellize or micellizes only to a lesser extent.

Solubilization of pinacyanol need therefore not represent the new type of solubilization advocated by Harkins.[26] This is not the new case of soluble hydrophilic dye adsorbed on the surface of the micelle. It is the solubilization of a water insoluble, but highly polar, dye–detergent salt by formation of mixed micelles more stable than those of the detergent alone.

An estimate of the composition of these mixed micelles may be obtained from the conductivity curve. At the kink, *i.e.*, when all the dye–detergent salt has just been solubilized, the equivalent conductivity in the 4 × 10^{-5} dye solution is 1.1% lower than a straight line extrapolation. Since the concentration at this point is 7.3 × 10^{-3} *M*, this means that at least 8.1 × 10^{-5} *M* of NaLS, *i.e.*, about 2 moles of NaLS per mole of dye have been micellized. Since 1 LS^- ion from the dye–detergent salt did not contribute to the original conduc-

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

(24) S. E. Sheppard, *et al.*, *Rev. Mod. Phys.*, **14**, 303 (1942).

(25) Since this system contains a fixed concentration of pinacyanol chloride and a variable one of NaLS, we have computed Λ as $(K - K_0)/C$ where *K* is the measured conductivity, *C* the concentration of NaLS, and K_0 the solvent correction plus the excess conductivity due to the replacement of some LS^- by Cl^- ions, when the dye–detergent salt is formed. The latter quantity was estimated from the difference in conductivity produced by addition of dye to a 0.140% NaLS solution.

(26) W. D. Harkins, R. Mittlemann and M. L. Corrin, *J. Phys. Colloid Chem.*, **53**, 1350 (1949).

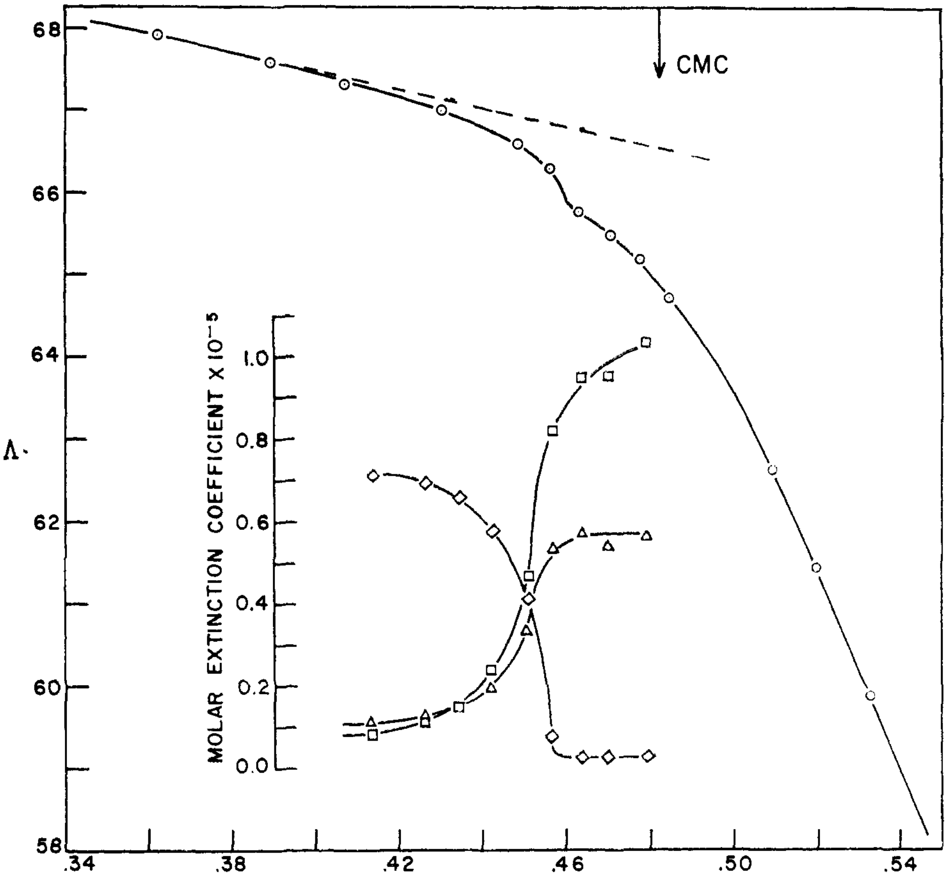

Fig. 2.—Spectral and conductivity changes in the transition region of NaLS-pinacyanol system; dye concn. 4 × 10^{-5} *M*; equivalent conductances corrected for NaCl present.[25]

tivity, this gives at least 3 LS^- ions per one dye ion in the micelle.

A better estimate takes into account the equivalent conductivity of the NaLS in the mixed micelles. If this is of the order of the equivalent conductivity of the simple NaLS micelles, *i.e.*, about 30,[27] the drop in equivalent conductivity corresponds to 2.1% so that 15 × 10^{-5} *M* of NaLS is micellized and the mixed micelle contains probably about 4.7 LS^- ions per dye cation.

A similar calculation for the 10^{-4} dye concentration yields at least 3.6 and probably about 5.7 LS^- ions per dye cation. While neither estimate is very precise, it is obvious that the mixed induced micelles, when they form at first, must contain several, but not many, LS^- ions per dye ion. If the degree of aggregation of this mixed micelle is of the same order as that of other well established micelles (35–100),[28] it is obvious that each induced micelle contains a number (6–40) of dye molecules.

It is perhaps worth noting that 4 × 10^{-5} *M* dye represents only 0.5 mole % of the CMC of the detergent. Yet the formation of micelles is induced at a concentration over 15% lower (Fig. 3). This shows how very sensitive association may be to small amounts of impurities.

Redistribution of the Dye. The α-Band.—The solution does not reach a steady state after all the dye–detergent salt has been solubilized and the induced mixed micelles formed. As shown in Fig. 1, the α-band continues to increase markedly as the NaLS concentration increases by about 30% and as shown in Fig. 3, the conductivity continues to approach that of the dye-free soap over the same interval.

We attribute these changes to the gradual transition from dye-rich induced micelles to the more normal type containing no more than one dye ion per micelle. This behavior could be expected since normal micelles will form in large amounts as the CMC is exceeded and the dye may be expected to distribute itself more or less uniformly among the micelles present. As most of the NaLS above the γ-band disappearance point should be micellized, by the time the α-band flattens out there are some 240 micellized LS^- ions per dye, *i.e.*, about 3 ordinary micelles available to each pinacyanol in the 10^{-5} *M* dye solution. In 4 × 10^{-5} *M* dye (Fig. 3) there are at least 80 LS^- ions, or about one micelle, per dye when the conductivity becomes close to that of detergent alone.

That the dye changes its environment in this interval is shown by the change of the α/β absorption ratio (Fig. 1), and that the micelles become very similar to the normal ones in both kind and number is shown by the merging of the conductivity lines (Fig. 3). It also may be noted that the final value of α/β absorption ratio is in our case 2.28 which is within 1% of what Sheppard[23] finds for organic media.

The Time of Redistribution of the Dye.—It is known that the rate of establishment of equilibrium between the monomers and the micelles is rapid compared to the time necessary for the ordinary physico-chemical measurements.[29] The redistribution of the dye from dye-rich micelles to others should be of the same order as the time of attainment of equilibrium in micellar systems. An approximate upper limit of the time of redistribution of dye-rich micelles to less rich ones was ob-

[27] D. Stigter, *Rec. trav. chim.*, **73**, 611 (1954).

[28] P. Debye, *J. Phys. Colloid Chem.*, **53**, 1 (1949); J. N. Phillips and K. J. Mysels, *ibid.*, **59**, 325 (1955).

[29] G. S. Hartley, *Trans. Faraday Soc.*, **31**, 199 (1935).

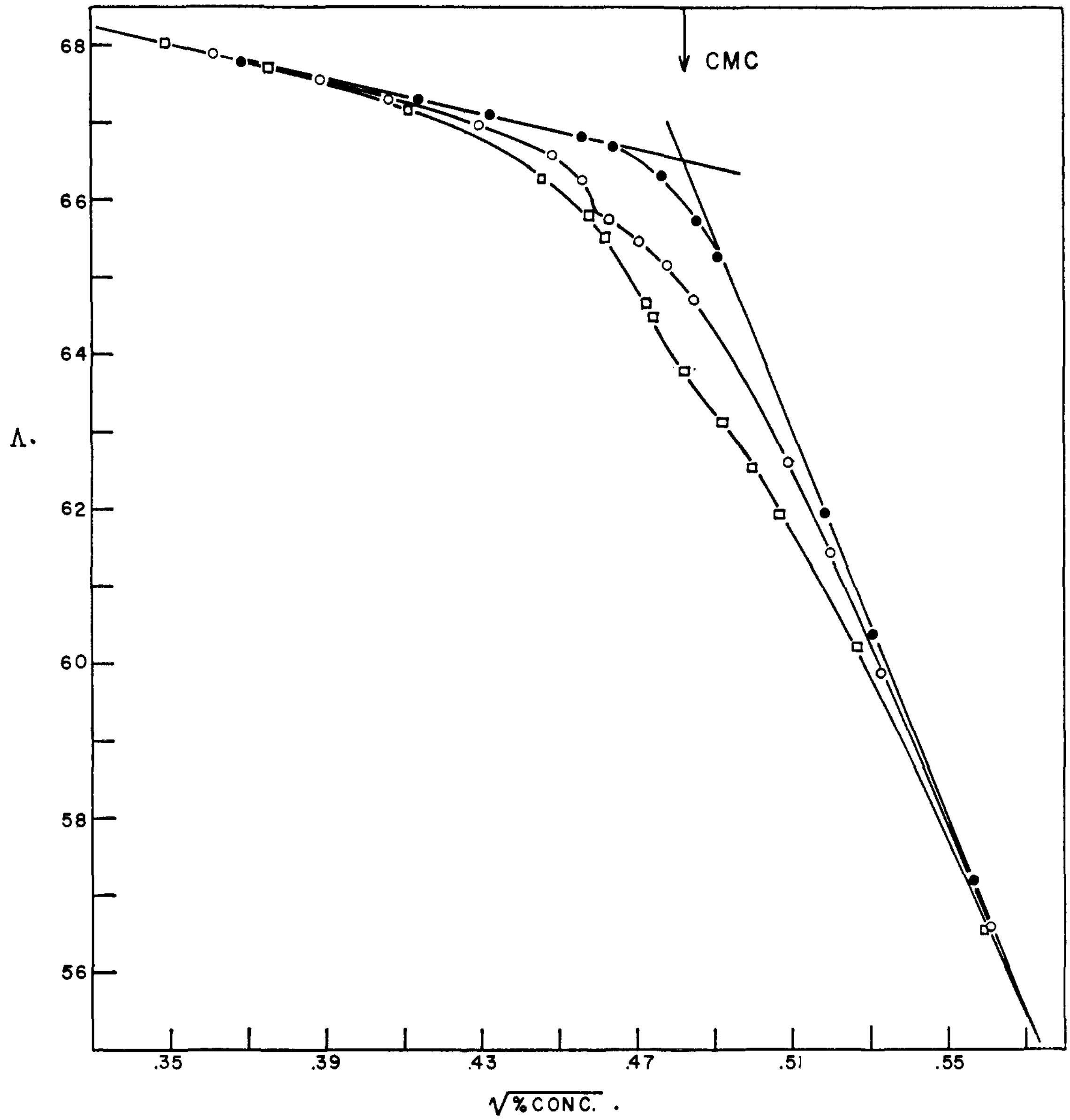

Fig. 3.—Conductivity of sodium lauryl sulfate: in water ●, in 4 × 10^{-5} M pinacyanol O, and in 1 × 10^{-4} M pinacyanol □, corrected for NaCl present.[25]

tained from the following experiments. Two solutions of NaLS in 1 × 10^{-5} M pinacyanol having concentrations of 0.2055 and 0.2190%, respectively, were used. These concentrations are in the region where the α-band is increasing in intensity with concentration of NaLS while the β-band has flattened out (Fig. 1). To each solution a small amount of solid NaLS was added. The solutions were then shaken thoroughly and their α-band intensities redetermined. The operations took less than 25 seconds. During this time the extinction coefficients at the maximum of the α-band increased from 0.507 and 0.578 (×10^5) to 0.648 and 0.662 (×10^5), respectively. These new values did not change further over an interval of several minutes. Therefore the total time necessary for the redistribution of the dye is less than 25 seconds and the micellar equilibrium should be completed in the same interval.

Effect of Temperature.—The solubility of the pinacyanol–lauryl sulfate in water at room temperature is less than 10^{-7} M as judged by the fact that it gives no visible color in the supernatant. At higher temperature, however, it dissolves to give a *blue* solution in which presumably the two ions exist in monomeric form. Thus above 60° a blue solution, which is supposed to indicate the CMC, may be observed below 10^{-4} M detergent concentration. In the presence of excess (but below the CMC) of detergent, the solubility is of course reduced and the blue solution is not formed until higher temperatures.

If a solution slightly above the CMC and blue at room temperature is heated, it becomes red around 50–60° and then turns blue when heated further. This is due to the simultaneous increase of the CMC[30] and of the solubility of the salt with tempera-

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(30) B. D. Flockhart and A. R. Ubbelohde, *J. Coll. Soc.*, **8**, 428 (1953).

ture. At first the former predominates and as the solubilizing micelles disintegrate upon heating, the red salt precipitates. Upon further heating, however, the salt dissolves to give a simple monomeric solution.

Relation to the CMC

The definition of the CMC is always somewhat arbitrary. Most workers have defined it as the point of intersection of two lines extrapolating some measured property from above and from below the region where a sudden change occurs. This corresponds to the concentration where micelles would just begin to form if they formed at the same rate at low as at high concentrations.[14] This point can be determined within 1% or better by independent methods so that there is little doubt about its value—0.234% for NaLS in water (Fig. 6). Micelles may exist below this value, but their amount decreases rapidly as the concentration is lowered and becomes less than 0.2% of the total NaLS at −0.22%.[14] Figure 3 shows the lines defining the CMC for NaLS based on conductivity measurements. The corresponding concentration is also indicated in the other figures.

In the spectral change method the definition of the CMC is quite arbitrary. Visually there is no sharp transition and the first color change noted on dilution seems to be due to the decrease of the α-band before the β- or γ-bands register any variation. Experienced workers have found visually CMC's higher than indicated by colorimeters.[13] We have not been successful in pinpointing any concentration visually and, as Fig. 1 shows clearly, the spectrophotometer indicates no abrupt change in this region. Yet it seems that the titration end-point is generally taken in this region. The gradual rise of α- and β-bands and decrease of the γ-band at low concentrations certainly do not define precisely any concentration either. On the other hand, two definite concentrations are given, one by the disappearance of the γ-band and simultaneous flattening of the β-band the other by the intersection and maximum slope of the three bands at the half point of the transition region.

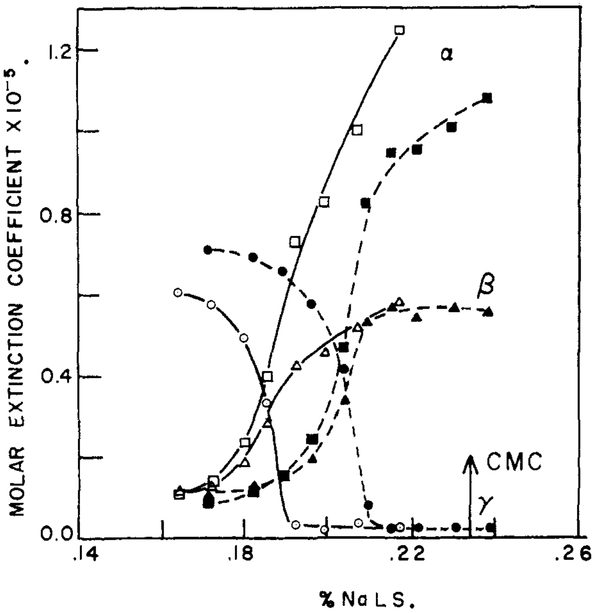

Fig. 4.—Effect of concentration of pinacyanol upon the spectral change; solid lines and open symbols for 2×10^{-6} *M* dye; dashed lines and full symbols for 4×10^{-5} *M* dye.

Whichever definition is chosen, however, the result depends on the concentration of the dye. Figure 4 shows colorimetric values obtained at two dye concentrations. A 10% shift is clearly apparent. The result could be expected from our interpretation. The disappearance of the γ-band corresponds to complete solubilization of all dye–detergent salt. Obviously less detergent will have to be micellized to dissolve completely a lesser amount of the salt and the result will be attained at a lower over-all concentration of detergent. In fact, solubilization of the lesser amount of dye will be completed before induced micellization is half way completed with the larger amount.

Figure 5 shows the increase of the CMC determined with pinacyanol upon increasing the dye concentration. The graph suggests that at about 2×10^{-4} *M* dye the true value might be reached. Optical densities are too high to make such a determination convenient.

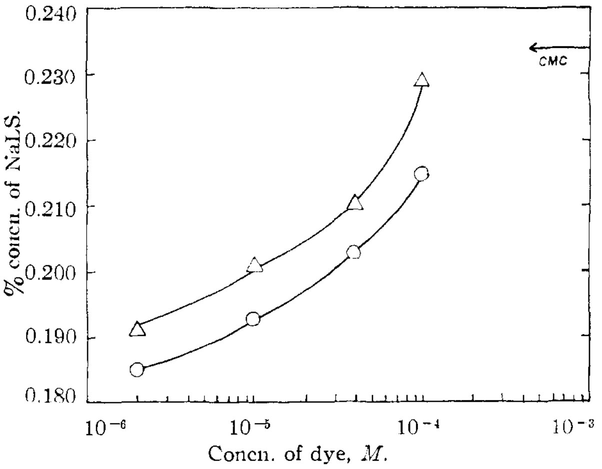

Fig. 5.—Effect of concentration of pinacyanol upon the apparent CMC measured by the maximum slope of spectral change (○) and by the levelling of the γ-band (△).

Thus in water the pinacyanol method gives lower results for NaLS. This is not always the case, however. In particular when the CMC is low, for example, in the presence of large amounts of salt, the pinacyanol results may be high. Figure 6 shows this effect. The solid line summarizes the previously mentioned results of conductivity, light scattering and dye solubilization for the effect of Na^+ ion concentration on the CMC of NaLS.[14] The dashed lines show results of other investigators using pinacyanol and also our results with this dye. In all cases the slope determined with pinacyanol is lower and the lines actually cross. The error which may thus be introduced into any calculation based on the slope needs no emphasis.

Qualitatively at least, this behavior is also understandable in terms of the preceding. The disappearance of the γ-band corresponds to complete

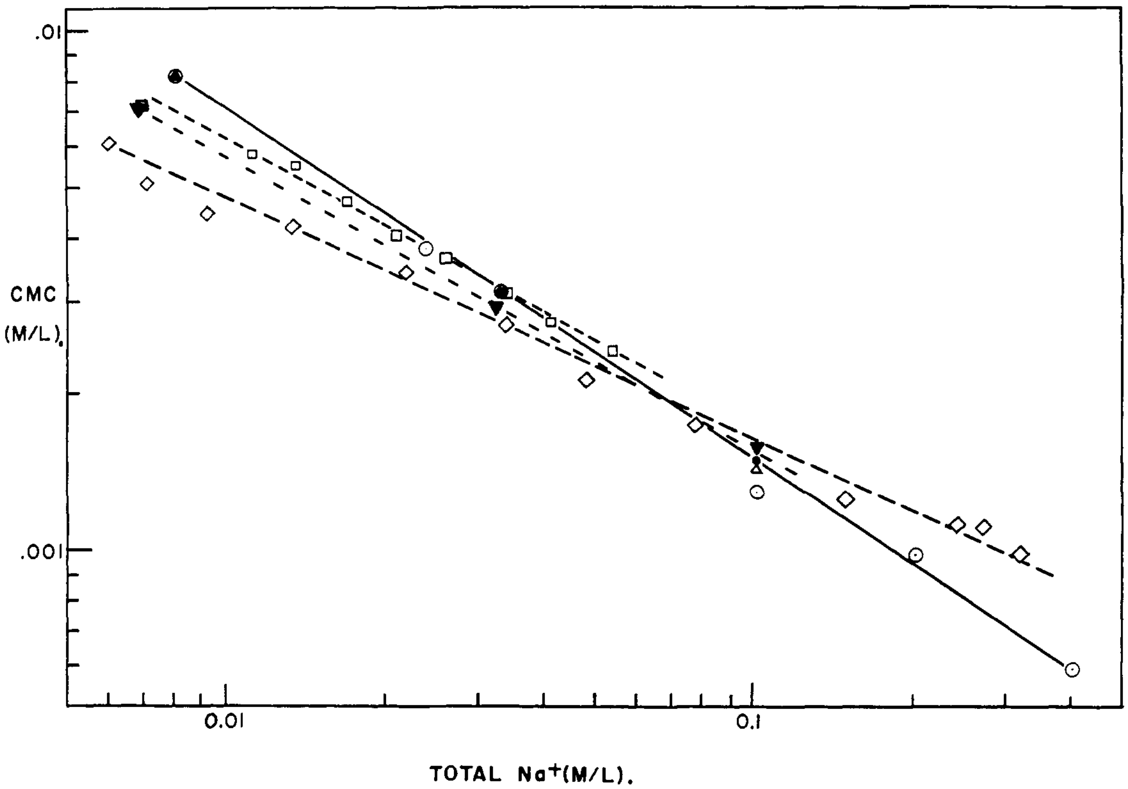

Fig. 6.—Variation of CMC of NaLS with total gegenion concentration at the CMC. Solid line shows results[14] of conductivity ●, solubilization △, light scattering ○. Dashed lines show results by the pinacyanol method: our work (γ-band levelling) ▼; Corrin and Harkins,[6] ◇; Goddard, Harva and Jones,[9] Na_2SO_4 □.

solubilization of all the dye–detergent salt. This in turn requires that a certain amount of detergent be micellized. When the CMC is low, this amount becomes a larger proportion of all the detergent present and the process may not be completed till above the CMC of the detergent. The CMC determined may therefore become quite high, especially with the visual titration technique. Quantitatively the effect is more pronounced than predicted by this simple picture. It seems that induced micellization begins closer to the CMC and is more effective at low CMC's than at higher ones.

The pinacyanol method has been used to determine the effect upon the CMC of agents, such as alcohol, which change greatly the structure of the micelle. While we have not investigated this point, it seems that here the ratio of real CMC to the one determined will be particularly altered.

Thus the pinacyanol method may be used to determine a vague range[7]—from the beginning to the end of spectral change—which will include the true CMC. Such a range is, however, of little use in most interpretations. For absolute determination of the CMC the method is unreliable since different observers are likely to use as the end point different features of the broad range of color changes and since concentration of the dye affects any of these. The method is also inaccurate since no feature corresponds in a definite or fixed way to the CMC of the dye-free detergent. Its only advantage is its great simplicity. On the other hand, the system involved can give a valuable insight into the processes of micellization and solubilization.

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LOS ANGELES, CAL.