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The Determination of Critical Concentrations for the Formation of Soap Micelles by the Spectral Behavior of Pinacyanol Chloride*

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The absorption spectrum of pinacyanol chloride in aqueous solutions of anionic soaps changes sharply to that characteristic of its solutions in organic solvents over a short range of soap concentration. This effect is attributed to the formation of micelles, in whose hydrocarbon-like layers or cores the dye is solubilized. The concentration of soap at which this spectral change occurs is taken as "the critical concentration for the formation of micelles." In water the dye exhibits an absorption band at 5500A which disappears rapidly as the concentration of molecular soap increases. Thus, even 0.00006 molar potassium laurate gives a large effect. At about 0.0126 M the γ -band at about 4800A reaches a high intensity, which falls, with further increase of concentration, very rapidly close to the critical concentration. At 2.3 to 2.4×10^{-2} for potassium laurate and 6×10^{-3} for the myristate the α -band (ca. 6150A) and the β -band (ca. 5700A) begin to increase rapidly in intensity and these are considered as the critical concentrations, since these are the prominent bands in the solution of the

dye in an oil. Alkali oleate and dilinoleate soaps exhibit an additional band (ω -band) at about 5200A. Some other critical concentrations determined by this method are $3.6-5.2\times10^{-4}$ molar for sodium cetyl sulfate, $2.5-3.2\times10^{-2}$ molar for potassium dehydroabietate, 7-12×10-4 molar for potassium oleate, and 2.5×10⁻⁴ molar for potassium dilinoleate. The values for the last two soaps are uncertain, since their behavior differs considerably from that displayed by the salts of saturated acids. All measurements were made at 25.8°C with the exception of the sodium cetyl sulfate which was investigated at 35.8°C. An absorption band at approximately 4800A appears in all the soap solutions measured below the critical concentration with the exception of potassium dilinoleate. This band is absent when salts or bases are added to the dye solution. A titrametric method has been developed for the determination of critical concentrations of soaps in the presence of added salts and hydrocarbons.

A QUEOUS solutions of most soaps exhibit a more or less abrupt change in physical properties over a relatively short concentration range; this phenomenon has been attributed to the formation of oriented soap aggregates, and the concentration at which it occurs has been termed "the critical concentration for the formation of micelles." The nature of the transition taking place at the critical concentration is as yet unknown, and a controversy still exists concerning the possible existence of aggregates at lower concentrations. The structure of soap aggregates in the neighborhood of the critical concentration is also a matter of dispute.

The work in this field has been extensive, and no effort is made to cite all authors or publications. Thus, conductivity studies indicate a sharp change in slope when the equivalent conductance is plotted against the square root of the soap concentration; the effect has been reported for alkali salts of the aliphatic fatty acids, long

Reconstruction Finance Corporation.

¹ (a) J. W. McBain, M. E. Laing, and A. F. Titley, J. Chem. Soc. 115, 1279 (1919). (b) P. Ekwall, Kolloid Zeits. 101, 135 (1942).

chain amine salts,² sulfonates,³ and sulfates.⁴ The concentration at which this change occurs is dependent upon the chain length of the detergent of a given type and, to a far less extent upon the temperature. Similar effects have been noted in studies of freezing point depression,⁵ density,⁶ surface tension-time effects,⁷ viscosity,⁸ and transference number.⁹ For a given detergent at a given temperature the change in all such physical properties occurs at approximately the same concentration.

² A. W. Ralston and C. W. Hoerr, J. Am. Chem. Soc. **64**, 772 (1942).

⁸ K. A. Wright, A. D. Abbott, V. Sivertz, and H. V. Tartar, J. Am. Chem. Soc. **61**, 549 (1939).

⁴A. Lottermoser and F. Puschel, Kolloid Zeits. **63**, 175 (1933).

⁸ S. A. Johnston and J. W. McBain, Proc. Roy. Soc. 181, 119 (1943).

6 (a) C. R. Bury and G. J. Parry, J. Chem. Soc. 626 (1935). (b) K. A. Wright and H. V. Tartar, J. Am. Chem. Soc. 61, 544 (1939).

⁷(a) N. K. Adam and H. L. Shute, Trans. Faraday Soc. **34**, 758 (1938). (b) G. C. Nutting, F. A. Long, and W. D. Harkins, J. Am. Chem. Soc. **62**, 1496 (1940). (c) H. V. Tartar, V. Sivertz, and R. E. Reitmeier, J. Am. Chem. Soc. **62**, 2375 (1940).

⁸ K. A. Wright and H. V. Tartar, J. Am. Chem. Soc. **61**, 545 (1939).

⁹ C. W. Hoerr and A. W. Ralston, J. Am. Chem. Soc. 65, 976 (1943).

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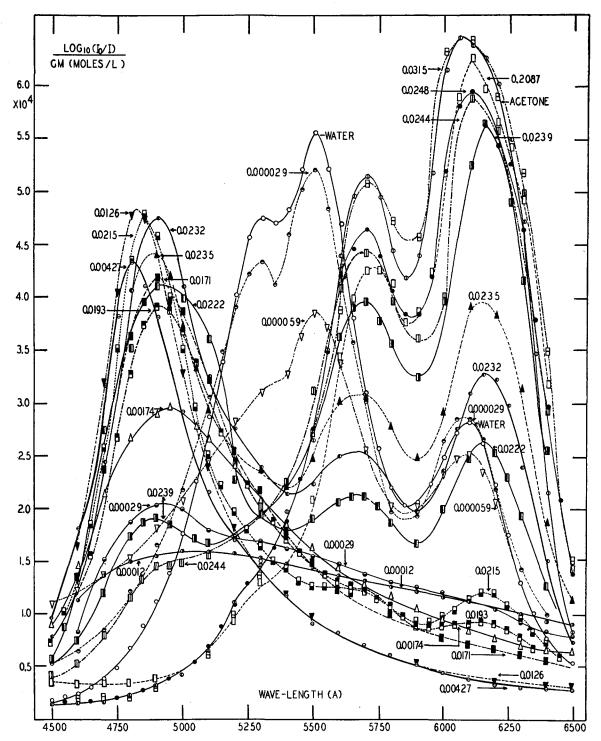


Fig. 1. Effect of varying potassium laurate concentration on the absorption spectra of $1 \times 10^{-4}~M$ pinacyanol chloride in aqueous solution.

It has been shown by Sheppard¹⁰ that the absorption spectrum of pinacyanol chloride obeys

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

Beer's law in organic media while deviating from such behavior in water. Furthermore, the over-all nature of the spectrum is markedly different for

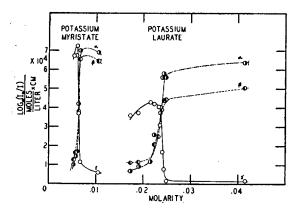


FIG. 2. Intensity of band maxima versus soap concentration for potassium laurate and myristate.

the dye in a non-polar environment than in water. This has been attributed to the existence of a dimerized form of the dye in water and the monomeric form in organic solvents. Sheppard and Geddes11 observed that the spectrum of this dye in aqueous solutions of the cationic soap, cetyl pyridinium chloride, is favorable to the "organic spectrum." This was explained on the basis of a partition of the dye between water and colloidal micelles with the dye in the latter environment showing the spectrum characteristic of its solutions in non-polar solvents. As indicated below, the change in spectrum in solutions of anionic soaps is far greater than that in solutions of cationic soaps as reported by Sheppard and Geddes.

Considerable evidence has been advanced for the existence of micelles in which a solubilized material is dissolved between the non-polar ends of detergent molecules.¹² It thus appears probable that pinacyanol chloride is likewise dissolved in such a hydrocarbon-like layer and that the concentration at which its absorption spectrum in soap solutions changes toward that typical of its solutions in organic solvents marks the critical concentration for the formation of micelles.

In Fig. 1 are plotted the absorption spectra at 25.8° C of 1×10^{-4} molar pinacyanol chloride

solutions of varying concentration with respect to potassium laurate. The effects are extremely remarkable. With minute amounts of soap, the water bands at 5200A and 5500A disappear and a new band appears at about 4800A. At a potassium laurate concentration of 2.3×10^{-2} molar, this short wave-length band begins to diminish in intensity and simultaneously the intensity of absorption bands at 5700A and 6150A increases rapidly. These latter two bands are characteristic of pinacyanol chloride solutions in organic solvents. The change may be made more striking by plotting the extinction coefficients at the band maxima against the soap concentration. Following Sheppard's notation, the bands are designated as α , β , and γ in order of decreasing wave-length. The data are presented in Table I and plotted in Fig. 2. The abrupt change in spectra at a soap concentration of $2.3-2.4\times10^{-2}$ molar is clearly demonstrated in Fig. 2. Although no authentic value for the critical concentration of potassium laurate is reported in the literature, the value given above may be compared to those obtained for sodium laurate. By conductivity Ekwall^{1b} reports 2.8 × 10⁻² molar, while Long and Nutting¹³ obtained a value of 2×10^{-2} molar by the surface tension-time effect on a buffered system. The

TABLE I. The intensity of band maxima at various soap concentrations for 1×10^{-4} molar pinacyanol chloride in potassium laurate solutions at 25.8°C.

Soap concentration	Extinction coefficient $\left(\frac{\log_{10}(I_0/I)}{\text{cm (mole/l)}}\right)$			
(molar)	α×10 ⁴	$\beta \times 10^4$	γ×10 ⁴	
2.90 ×10 ⁻⁵	2.63ь	5.19	4.31	
5.88×10^{-5}	2.33b	3.84	3.07ª	
1.22×10^{-4}	1.02b	1.28 ^b	1,56	
2.90×10^{-4}	1.03b	1,35 ^b	1.99	
1.74×10^{-3}	$0.74^{\rm b}$	1.27b	2.97	
4.25×10^{-3}	$0.31^{\rm b}$	0.61^{b}	4.27	
1.262×10^{-2}	0.35 ^b	0.69b	4.74	
1.710×10^{-2}	0.65^{b}	1.26b	4.16	
1.930×10^{-2}	0.92	1.18ª	3.89	
2.153×10^{-2}	1.19	1.23a	4.76	
2.225×10^{-2}	2.52	2.09	4.08	
2.321×10^{-2}	3.27	2.50	4.72	
2.350×10^{-2}	3.90	3.06	4.56	
2.394×10^{-2}	5.61	3.94	1.87	
2.436×10^{-2}	5.87	4.41	1.43a	
2.478×10^{-2}	5.89	4.63	0.29ь	
4.154×10^{-2}	6.38	5.06	0.17ь	
2.088×10^{-1}	6.26	4.24	0.31 в	

 $^{^{\}rm a}$ Step-out. $^{\rm b}$ No band but a wave-length of corresponding band maxima at other soap concentrations.

¹¹ S. E. Sheppard and A. L. Geddes, J. Chem. Phys. **13**, 63 (1945).

¹² This evidence is summarized and literature references given in W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Am. Chem. Soc. 68, 220 (1946) and W. D. Harkins, R. W. Mattoon, and M. L. Corrin, J. Colloid Science 1, 105 (1946).

¹³ G. C. Long and F. A. Nutting, J. Am. Chem. Soc. **63**, 84 (1941).

Table II. The intensity at band maxima at various soap concentrations for 1×10^{-6} molar pinacyanol chloride in potassium laurate solutions at 25.8°C.

Soap concentration (molar)	Extinction coefficient $\left(\frac{\log_{10}\left(I_0/I\right)}{\text{cm (mole/l)}}\right)$			
	α×104	$\beta \times 10^4$	γ×104	
2.023×10 ⁻²	2.58	2.86ь	7.45	
2.055×10^{-2}	3.04	3.04^{b}	6.50	
2.104×10^{-2}	4.07	3.65	6.27	
2.146×10^{-2}	5.23	4.41	6.99	
2.173×10^{-2}	7.72	5.53	3.75	
2.202×10^{-2}	9.79	6.54	2.27ª	
2.285×10^{-2}	11.55	7.42	2.07b	
2.402×10^{-2}	12.74	7.23	1.36b	
2.809×10^{-2}	12.68	6,48	0.70 ^b	

 $^{{}^{\}rm a}$ Step-out. ${}^{\rm b}$ No band but at wave-length of corresponding band maxima at other soap concentrations.

presence of buffering salts would, however, tend to render this value low. With 1×10^{-5} molar pinacyanol essentially the same results were obtained; the data are given in Table II.

The slightly lower critical concentration obtained with the lower dye concentration is probably caused by the increased sensitivity obtained in that the partition of the dye between the micelles and water tends to mask the "organic spectrum" when but little of the dye can enter the micelles.

Similar results are obtained with potassium myristate as indicated in Fig. 2 and Table III. In this case the critical concentration at 25.8°C and in the presence of 1×10^{-4} molar pinacyanol chloride is 6×10^{-3} molar. A value of 7.0×10^{-3} molar for sodium myristate has been reported by Ekwall.^{1b}

With sodium cetyl sulfate it was found necessary to decrease the dye concentration to 1×10^{-5} molar in order to fix sharply the critical concentration. The value obtained, $3.6-5.2\times10^{-4}$ molar at 35.8° C (Fig. 3), compares favorably with that reported by Lottermoser and Puschel⁴ of $4-6\times10^{-4}$ molar on the basis of conductivity and a value of 4×10^{-4} molar by Nutting, Long, and Harkins^{7b} by surface tension-time measurements. The data are given in Table IV.

The critical concentration for potassium dehydroabietate at 25.8° C is $2.5-3.2\times10^{-2}$ molar. The spectral change with this soap is less sharp than in the case of the potassium soaps of the straight chain acids as indicated in Fig. 3 and Table V.

The behavior of potassium oleate and of

TABLE III. The intensity of band maxima at various soap concentrations for 1×10^{-4} molar pinacyanol chloride in potassium myristate solutions at 25.8°C.

Soap concentration (molar)	Extinction coefficient $\left(\frac{\log_{10}\left(I_0/I\right)}{\text{cm (mole/l)}}\right)$			
	$\alpha \times 10^4$	β×10⁴	γ×104	
5.31 ×10 ⁻³	0.96	1.13 ^b	6.74	
5.82×10^{-3}	1.62	1.63ª	6.68	
6.02×10^{-3}	1.66	1.85 ^b	7.25	
6.31×10^{-3}	4.21	3.80	3.70	
6.65×10^{-3}	7.02	6.55	1.19b	
1.048×10^{-2}	6.94	6.43	0.59ь	

a Step-out. b No band but at wave-length of corresponding band maxima at other soap concentrations.

potassium dilinoleate prepared by the dimerization of linoleic acid differs from that of the soaps described above. With potassium oleate, a new band appears at 5200-5400A after the disappearance of the 4800A band. This band persists during the development of the 6250A band. The absorption spectra are given in Fig. 4, the intensities of the maxima at various soap concentrations in Fig. 5 and Table VI. The variation in the 5700A band is more or less masked because of the proximity of the broad 5400A band. In this instance it is difficult to assign a critical concentration, and a provisional value of 7-12×10⁻⁴ molar corresponding to the point of rapid development of the long wave-length band has been taken. No value for the critical concentration of this soap is found in the literature, although Ekwall^{1b} has determined the conductivity of its solutions. The development of colloidal micelles would seem, from the spectroscopic evidence, to occur over a wide concentration range.

With potassium dilinoleate at 25.8°C the

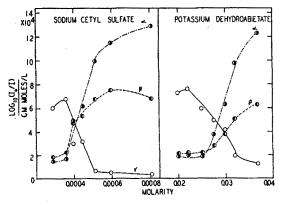


Fig. 3. Intensity of band maxima versus soap concentration for sodium cetyl sulfate and potassium dehydroabietate.

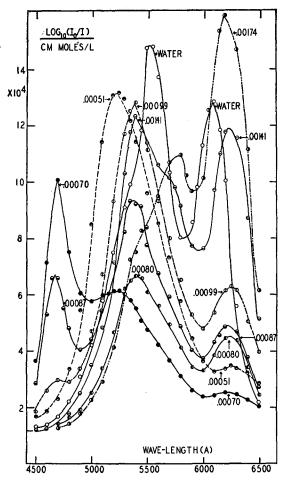


Fig. 4. Effect of varying potassium oleate concentration on the absorption spectra of pinacyanol chloride in aqueous solution.

4800A band fails to appear. The intensity of the band maximum at 5300A goes through a maximum at a soap concentration of 1.7×10-4 molar simultaneously with a constant intensity of the 6200A band. The 6200A band increases in intensity with soap concentration at soap concentrations greater than 2.5×10^{-4} molar. The data are given in Fig. 5 and Table VII. When the specific conductance of this material is plotted against the concentration, as suggested by Tartar, a break occurs at 3.0×10^{-4} molar as indicated in Fig. 6.

Since the color changes occurring at the critical concentration are very marked, it has been found possible to employ a visual rather than spectrophotometric method for such determinations. A soap solution of known concentration and containing pinacyanol chloride may be titrated with a solution of the dye in water and the critical concentration determined with a deviation of less than 1 percent of that determined spectroscopically. The titration technic affords an excellent means for the rapid and unambigu-

TABLE IV. The intensity at band maxima at various soap concentrations for 1×10^{-6} molar pinacyanol chloride in sodium cetyl sulfate solutions at 35.8°C.

Soap concentration	Extinction coefficient $\left(\frac{\log_{10}\left(I_0/I\right)}{\text{cm (molc/I)}}\right)$			
(molar)	α×10⁴	β×10 ⁴	γ×104	
2.88×10 ⁻⁴	1.52	1,90a	5,99	
3.57×10^{-4}	1.75	2.23	6.80	
3.97×10^{-4}	4.92	4.80	3.04	
4.45×10^{-4}	6.18	5.35	3,21	
5.13×10^{-4}	9.96	6.78	0.71 ^b	
5.94×10^{-4}	11.51	7.14	0.56 ^t	
8.11×10^{-4}	12.89	6.78	0.35 ^t	

^b No band but at wave-length of corresponding band maxima at other soap concentrations.

Table V. The intensity at band maxima at various soap concentrations for 1×10^{-5} molar pinacyanol chloride in potassium dehydroabietate solutions at 25.8°C.

Soap concentration (molar)	Extinction coefficient $\left(\frac{\log_{10}(I_0/I)}{\text{cm (mole/I)}}\right)$			
	$\alpha \times 10^4$	β×10⁴	γ×104	
1.99×10^{-2}	1,92	2.12ъ	7.28	
2.21×10^{-2}	2.17	2.20ь	7.64	
2.51×10^{-2}	1.88	2.20	5.95	
2.76×10^{-2}	3.81	2.82	4.96	
3.00×10^{-2}	6.34	3.83	4.18	
3.19×10^{-2}	9.79	5.09	1.93	
3.68×10^{-2}	12.32	6.29	1.25 ^t	

Table VI. The intensity at band maxima at various soap concentrations for 2×10^{-6} molar pinacyanol chloride in potassium oleate solutions at 25.8°C.

Soap concentration	Extinction coefficient $\left(\frac{\log_{10}(I_0/I)}{\text{cm (mole/I)}}\right)$				
(molar)	$\alpha \times 10^4$	β×104	ω×10 ⁴	γ×104	
5.06×10 ⁻⁴	3.47	7.33ь	13.07	2.30b	
5.93×10^{-4}	3.39	5.00b	12.33	2.27b	
6.98×10^{-4}	2.53	3.66b	6.13	1.01b	
8.02×10^{-4}	4.45	4.91 ^b	6.65	1.41b	
8.72×10^{-4}	4.86	5.90b	9.22	6.58	
9.24×10^{-4}	5.40	7.24 ^b	11.36	4.54	
9.94×10^{-4}	6.30	8.02b	12.84	3.00	
1.10×10^{-3}	8.00	9.32ь	14.24	1.64b	
1.26×10^{-3}	9.96	9,59ь	13.10	1.55b	
1.40×10^{-3}	5.88	5.07*	6.17	0.73ъ	

 $^{^{\}rm a}$ Step-out. $^{\rm b}$ No band but at wave-length of corresponding band maxima at other soap concentrations.

 $^{^{\}mathrm{a}}$ Step-out. $^{\mathrm{b}}$ No band but at wave-length of corresponding band maxima at other soap concentrations.

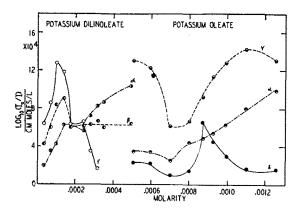


Fig. 5. Intensity of band maxima versus soap concentration for potassium oleate and dilinoleate.

ous investigation of the effect of salts and hydrocarbon additives on the critical concentrations of soaps. At present, the only method available for investigations on the effects of salts is a solubility method described by Tartar and Cadle. The corrections to be applied to conductometric, freezing point, and similar methods are so uncertain in the presence of salts that these technics are of little value.

The critical concentrations of a few soaps are given in Table VIII.

EXPERIMENTAL

Materials.—Potassium laurate was prepared by saponification of a carefully fractionated

Table VII. The intensity at band maxima at various soap concentrations for 1×10^{-5} molar pinacyanol chloride in potassium dilineoleate solutions at 25.8°C.

Soap concentration	Extinction coefficient $\left(\frac{\log_{10}\left(I_{\theta}/I\right)}{\text{cm (mole/l)}}\right)$			
(molar)	$\alpha \times 10^4$	$\beta \times 10^4$	ω×10 ⁴	
3.52×10^{-5}	1.96ª	4.25ª	6.40	
7.04×10^{-5}	3.54	6.00a	8.57	
9.85×10^{-5}	4.25	8.36ª	12,80	
1.41×10^{-4}	6.22	9.07 a.	11.88	
1.76×10^{-4}	6.29	6.33	6.02	
2.46×10^{-4}	5.65	6.61	6.14	
2.81×10^{-4}	7.26	6.29	3.56 ^b	
3.17×10^{-4}	8.24	6.61	1.70ь	
3.52×10^{-4}	8.64	6.00	3.02b	
4.93×10^{-4}	10.33	6.40	3.02b	
5.63×10^{-4}	11.65	6.72	2.12b	
7.04×10^{-4}	12.52	6.61	1.70b	
1.06×10^{-3}	13.00	6.61	1.87b	
1.76×10^{-3}	19.60	12.28	3.73ь	

^a Step-out.
^b No band but at wave-length of corresponding band maxima at other soap concentrations.

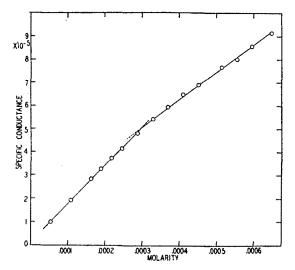


Fig. 6. Conductivity of dilute solutions of potassium dilinoleate.

sample of methyl laurate. The soap was twice recrystallized from ethanol and washed with acetone. It was dried in a vacuum.

Potassium myristate was obtained by the neutralization in hot ethanol with alcoholic potassium hydroxide of Eastman myristic acid which had been twice recrystallized from ethanol and once from acetone and which had been subjected to hydrogenation at 3 atmospheres over Adams platinum oxide catalyst. The soap was recrystallized twice from alcohol and washed with acetone.

Potassium oleate was prepared from a sample of oleic acid purified by Professor Reynolds of the University of Cincinnati. The acid, dissolved in hot alcohol, was neutralized with alcoholic potassium hydroxide and the soap recrystallized and carefully washed.

Potassium dehydroabietate was prepared in the same manner from a sample of dehydroabietic acid supplied by Dr. Shepherd of the University of Illinois.

The sodium cetyl sulfate was of the same lot employed by Nutting, Long, and Harkins in their investigation of surface tension-time effects. The potassium dilineoleate was supplied by the Eastern Regional Laboratories of the Department of Agriculture and labelled NRRL-1731-9.

Solutions.—All solutions were prepared by weight. The weighed sample of soap was dis-

¹⁴ H. V. Tartar and R. D. Cadle, J. Phys. Chem. **43**, 1173 (1939).

solved in a known amount of dye solution of proper concentration.

Apparatus.—The spectrophotometer employed was that described by Hogness, Zscheile, and Sidwell.15

DISCUSSION

Some evidence may be drawn from the spectroscopic behavior of pinacyanol chloride in soap solutions with respect to the nature of the transition occurring at the critical concentration. Hartley¹⁶ has held that at concentrations below the critical concentration the soap exists in an unaggregated state, i.e., as a completely dissociated electrolyte; the conductometric studies of Scott and Tartar¹⁷ support this view by indicating the sharpness of the break in the conductivity curves at the critical concentration and the conformity of the conductivity relations below the critical concentration with that typical of strong electrolytes. McBain,18 however, has advanced the concept that an equilibrium exists at all times between aggregated and unaggregated soap and that even in extremely dilute solutions "ionic micelles" exist. According to this view, the critical concentration marks the point at which lamellar micelles are first formed.

It would seem, a priori, that the spectral behavior of pinacyanol chloride involving as it does the solubilizing action of lamellar micelles, could give no information concerning solutions in which no such micelles exist. However, the development of the short wave-length, 4800A, band has been observed in all soap solutions investigated with the exception of potassium dilinoleate. The reason for the appearance of this band is as yet unknown. This band does not appear, however, when salts, such as potassium chloride and sodium acetate. or bases, such as sodium hydroxide, are added to pinacyanol chloride solutions. The appearance of

TABLE VIII. Critical concentrations for the formation of soap micelles as determined by pinacyanol in a spectrophotometer.

Soap		Dye con- centration	Tem- pera- ture	Crit concen	
Potassium dilinolea		1 ×10⁻⁵M	25.8°	2.5	×10⁻⁴M
Potassium dehydro	abietate	$1 \times 10^{-5}M$	25.8°	2.5 - 3.2	$\times 10^{-2}M$
Potassium oleate		$2 \times 10^{-6}M$	25.8°	7 -12	×10⁻⁴M
Potassium laurate		$1 \times 10^{-5}M$	25.8°	2.15- 2.20	$\times 10^{-2}M$
Potassium laurate		1 ×10⁻⁴M	25.8°	2.3 - 2.4	X10 ⁻² M
Sodium cetyl sulfat	te	1 ×10⁻⁵M	35.8°	3.6 - 5.2	X10⁻⁴M
Potassium myrista		$1 \times 10^{-4}M$	25.8°	6.0 - 6.7	$\times 10^{-3}M$

the 4800A band has been noted only in soap solutions; this suggests that soap solutions below the critical concentration differ somehow in nature from those of simple, short chain electrolytes.

Another conclusion that may be drawn from the spectral data is that the lamellar, solubilizing micelles are not formed from only the soap present in excess of that required to give the critical concentration. It is improbable, for example, that 1×10^{-4} mole of potassium myristate could form micelles of sufficiently great solubilizing power to account for the pronounced change in spectra occurring on the addition of this amount of soap just at the critical concentration. Owing, however, to the fact that no conclusions can be drawn from the spectra with respect to the partitioning of the dye between the water and the non-polar layers in the micelles, no quantitative inferences may be made with respect to this phenomenon.

The micellar development of potassium myristate, potassium laurate, and sodium cetyl sulfate occurs over a short concentration range, as indicated by the fact that the long wave-length band increases rapidly in intensity. With potassium dehydroabietate this development is more gradual. The data for potassium oleate and potassium dilinoleate, while difficult of interpretation, indicate that with them the formation of lamellar micelles occurs over a wide concentration range.

The writers wish to thank Professor Thorfin R. Hogness for the use of his remarkable spectrophotometer.

¹⁵ T. R. Hogness, F. P. Zscheile, Jr., and A. E. Sidwell, Jr., J. Phys. Chem. 41, 379 (1937).

16 G. S. Hartley, Kolloid Zeits. 88, 22 (1939).

17 A. B. Scott and H. V. Tartar, J. Am. Chem. Soc. 65,

<sup>692 (1943).

18</sup> J. W. McBain, Nature 145, 702 (1940).