

The Critical Concentration for the Formation of Micelles as Indicated by the Absorption Spectrum of a Cyanine Dye

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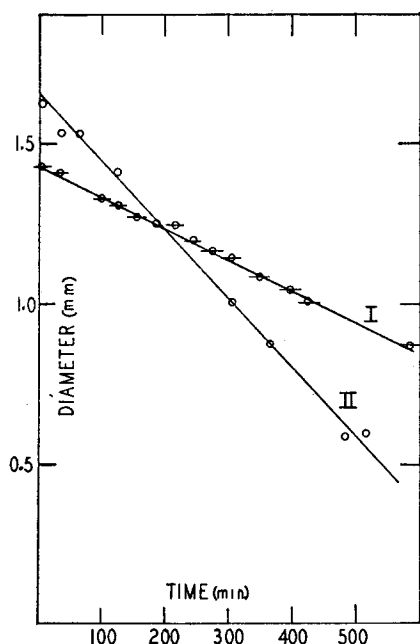


FIG. 1. Diffusion of ethyl benzene into latex solutions at 25°C. Curve I: 98 percent conversion. Curve II: 67 percent conversion.

Experiments were carried out in which polymer particles were substituted for the soap micelles used in the earlier work. The polymer particles were formed from a mixture of 75 percent isoprene and 25 percent styrene in a soap solution with an initial soap concentration of 3 percent and 100 parts monomer to 180 parts water. Samples of latex were used at 67 and 98 percent conversion to polymer. The former already contained 33 percent and the latter only 2 percent of monomer.

The rate of diffusion at 25°C from a drop of ethyl benzene with an initial diameter of 1.5 mm but calculated as the slope of the best straight line was found to be 2×10^{-3} mm decrease of diameter per minute in the polymer solution of 67 percent conversion and 1.0×10^{-3} mm in that of 98 percent conversion. These diffusion rates are not very accurate on account of the difficulty encountered in the observation of the boundary of the drop due to the opacity of the solution. Within the limits of Fig. 1 the rate of decrease of diameter of the drop is linear, but it seems probable that the rate will be found to increase as the drop decreases still further in diameter.

In these polymer solutions no micellar soap and very little dissolved soap is present. On account of the extremely great area of the latex particles almost the whole of the soap is adsorbed at the interface between the latex particles and the aqueous phase.

The relations presented in this and in the preceding letter are often neglected in the development of the kinetics of emulsion polymerization. When 3 percent soap with 100 g of monomer and 180 g of water is used, all free monomer commonly disappears by solution in the polymer particles by the time the yield of polymer reaches about 60 percent.

¹ W. D. Harkins, *J. Chem. Phys.* 13, 381 (1945); 14, 47 (1946).

The Critical Concentration for the Formation of Micelles as Indicated by the Absorption Spectrum of a Cyanine Dye *

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February 7, 1946

RECENTLY Sheppard and Geddes¹ reported that the absorption spectrum of aqueous pinacyanol chloride is shifted from that exhibited in aqueous solution to that characteristic of its solutions in non-polar solvents by the addition of cetyl pyridinium chloride. They consider that the "addition of a micelle-forming hydrophile colloid effects conversion of the dye from an aggregated—probably dimeric—to a monomeric state." We have determined the absorption spectra of the same cyanine dye in aqueous solutions of potassium laurate and potassium myristate of varying soap concentration at a dye concentration of 1×10^{-4} molar and a temperature of 25.6°. The extremely rapid change in the spectrum in each of these soap solutions is found to occur at the critical concentration for the formation of micelles, and this appears to give the simplest method for the determination of the critical concentration.

With increasing soap concentration, the observed spectra show a very pronounced shift over a short range of concentration to the form typical of the dye solutions in a non-polar medium. With potassium laurate the spectrum is markedly different from that of the dye in water at a soap concentration of 1×10^{-3} molar. In more concentrated solutions a band appears at 4800Å; this band disappears

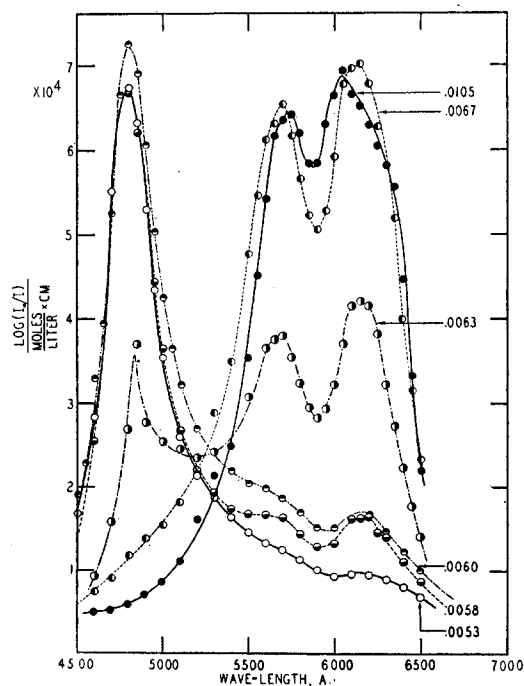


FIG. 1. Absorption spectra of 1×10^{-4} pinacyanol chloride in aqueous potassium myristate solutions.

and two bands at 5700Å and 6150Å appear when the soap concentration is varied from 2.3×10^{-2} to 2.4×10^{-2} molar; these latter higher wave-length bands are typical of pinacyanol chloride solutions in organic solvents. The behavior of potassium myristate as indicated in Fig. 1 is similar to that of the laurate. The transition of the former occurs at a soap concentration of 6.0×10^{-3} molar.

The observed phenomena can be illustrated in a more striking fashion by plotting the intensities of the three characteristic bands as a function of soap concentration as in Fig. 2. The smallness of the concentration range over which the change occurs is quite clearly indicated.

The simplest explanation that may be offered considers the change in nature of the absorption spectra as due to the formation of soap micelles which solubilize the dye.² In water an equilibrium exists between the monomer and dimeric forms of the dye.³ When soap micelles are present, however, the dye may be solubilized within their hydrocarbon layers. It is thus in a non-polar environment, even though separated from water by only the length of a soap molecule (about 16Å in case of the laurate). The dye will then be partitioned between the water and micelles with increasing dye solubilization as more micelles are formed.

Thus, the soap concentration at which the spectral transition occurs may be considered the critical concentration for the formation of micelles. The critical concentration at 25°C as determined by this method is 2.3 to 2.4×10^{-2} molar for potassium laurate and 6.0×10^{-3} molar for potassium myristate. Unfortunately, no accurate published data by other methods on such values for potassium myristate are available for comparison.

The sharp nature of the change offers evidence that a considerable portion of ionic soap present before micelles are formed is transformed into micelles, once the proper soap concentration is attained. It would be improbable, for example, that the addition of 2×10^{-4} mole of potassium myristate per liter of solution could form enough micellar material to cause a spectral change so pronounced as that observed in going from a 5.8×10^{-3} to 6.0×10^{-3} molar solution of the soap.

The behavior of the soap-dye system in very dilute soap solutions (below $5 \times 10^{-3} M$ for laurate) is quite complicated and is not, as yet, amenable to any simple explanation. It is hoped, however, to clarify this situation by further

investigation. It is possible that soap solutions may exhibit some solubilizing properties at concentrations lower than those at which the marked spectral change occurs. If this is found to be true, it would indicate some micellar organization in these solutions in conformity with the views of McBain.⁴

Further studies on the effect of temperature, dye concentration, and similar variables are in progress and will be presented together with a more complete discussion of the theory in a subsequent paper. The modification of the spectrum of the cationic dye by the anionic soaps is very much greater than that found with cetyl pyridinium chloride. An increase of temperature of 10°C to 35.8°C was found to decrease the critical concentration of potassium myristate only slightly to about 5.7×10^{-3} molar. However, this apparent change in critical concentration with temperature may not be real, but due to a different partitioning with temperature of the dye between the water and the micelles.

* 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.

¹ S. E. Sheppard and A. L. Geddes, *J. Chem. Phys.* **13**, 63 (1945).

² W. D. Harkins, R. W. Mattoon, M. L. Corrin, *J. Colloid Sci.* **1**, (January 1946).

³ S. E. Sheppard, *Rev. Mod. Phys.* **14**, 303 (1942).

⁴ S. A. Johnston and J. W. McBain, *Proc. Roy. Soc. A* **181**, 119 (1943).

Estimation of the Surface Area of Solid Particles

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February 11, 1946

IN replying to my letter of April 14, 1945,¹ Messrs. Harkins and Jura² have submitted data, previously not published, which prove that capillary condensation does not occur when loosely packed titanium dioxide powder is exposed to saturated steam. In the light of Bangham's observations³ on mica it is reasonable to assume that this is also true in the case of tight packing. Accordingly, we have to face the alternative, as pointed out in my letter, that the adsorbent studied is not perfectly wettable, analogous to the behavior of mica. In other words, if the liquid phase were once formed by supersaturation, the contact angle at the vapor-film-liquid boundary would be greater than zero. Consequently, the "surface tension" (if it were measurable!) of the polylayer produced in the saturation procedure must be different from that of normal water. These films, as has been recognized by Bangham and, independently, by Frumkin,⁴ form a phase different from liquid water, and are not "duplex films," as defined by Harkins. Consequently, no prediction of the magnitude of thermal effects resulting from the submersion of such films can be made without further investigation.

In principle, the "absolute method" is open to the same objection as the calculations of Emmett-Brunauer-Teller,⁵ i.e., it contradicts the existence of first-order phase transitions from the adsorbed to the liquid state.

¹ H. M. Cassel, *J. Chem. Phys.* **13**, 249 (1945).

² W. D. Harkins and G. Jura, *J. Chem. Phys.* **13**, 449 (1945).

³ D. H. Bangham and S. Mosallam, *Proc. Roy. Soc. A* **165**, 552 and **A166**, 558 (1938); D. H. Bangham and Z. Sawaris, *Trans. Faraday Soc.* **34**, 554 (1938).

⁴ A. Frumkin, *Acta Physicochimica U.S.S.R.* **9**, 313 (1938).

⁵ H. M. Cassel, *J. Chem. Phys.* **12**, 115 (1944); *J. Phys. Chem.* **48**, 195 (1944).

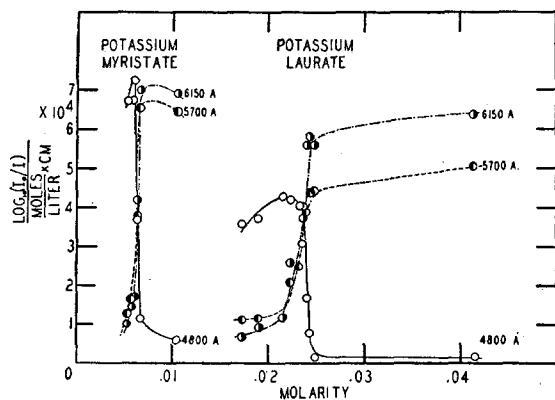


FIG. 2. Intensities of band maxima vs. soap concentration.