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Estimation of the Surface Area of Solid Particles

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and two bands at 5700A and 6150A 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 16A 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 $\times 10^{-2}$ 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 5×10^{-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]

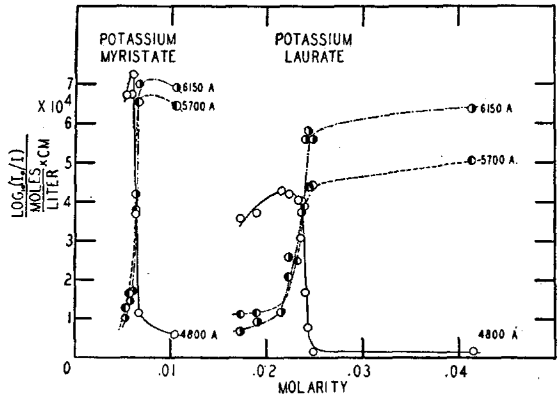

FIG. 2. Intensities of band maxima *vs.* soap concentration.

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.

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[*] 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.

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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 Jura[2] 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 observations[3] 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.

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