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Abstract

Full Text

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CRITICAL REGIONS OF CONCENTRATION IN SOAP SOLUTIONS*

With increasing concentration of solutions of detergents, within a narrow concentration region called the critical concentration of micelle formation (c.c.m.), characteristic for each substance, the true solution passes abruptly into a colloidal one, which is accompanied by a change in the bulk properties of detergent solutions ($^{1-3}$). In addition to the c.c.m., in solutions of individual soaps, when the concentration was raised to 60-90 g/l, a second critical region was observed (^{2,1}). Recently the suggestion was made that other limiting concentrations of association may also be observed in soap solutions (^{4}). Systematic studies in this area have not yet been carried out. The study of limiting concentrations of association in solutions of surface-active substances is of considerable scientific and practical interest for broadening our concepts of the structure and colloid-chemical properties of solutions of associated colloids. Recently the c.c.m. has been used to characterize the hydrophile-oleophile balance of detergents and to determine their practical effectiveness (^{5}).

Fig. 1. Solubilization of toluene in dilute solutions of sodium laurate (1) and potassium laurate (2)

In the present work are presented the results of a study of limiting concentrations of association in solutions of sodium laurate and potassium laurate by the method of determining solubilization. The samples for the investigation were obtained from pure lauric acid and purified alkalis according to the procedure described earlier (^{6,7}). For the entire series of experiments, solutions of the required concentration were prepared from dry powdered sodium laurate and potassium laurate by heating until a homogeneous soap solution formed. The limiting amount of solubilized hydrocarbon in the soap solution was determined from the decrease in volume in the graduated tube of the apparatus (^{8}). A study of the influence of increasing soap concentration on the solubilization ef-

Fig. 2. Critical concentration regions in solutions of sodium laurate (1) and potassium laurate (2)

Figure 2: Fig. 2. Critical concentration regions in solutions of sodium laurate (1) and potassium laurate (2)

fect showed that dissolution of toluene in the soap solution becomes noticeable only at a concentration of sodium laurate and potassium laurate K_1, equal to about 0.026 mol/l (Fig. 1). At lower concentrations the solutions the indicated soaps possess practically no solubilizing capacity. When the concentration of sodium laurate and potassium laurate solutions is increased above K_1, the solubilization of toluene increases unevenly, changing in the region of the limiting concentrations K_2, K_3, and K_4, respectively equal to about 0.28, 0.60, and 0.90 mol/l (Fig. 2). Between the critical concentration regions, the solubilization of toluene in the soap solutions studied changes practically linearly, and it can be characterized by the tangent of the angle of inclination of the experimental curves. For the segments K_1K_2, K_2K_3, and K_3K_4, the tangent of the angle of inclination for sodium laurate is respectively 0.47, 0.81, and 1.11, and for potassium laurate 0.42, 0.43, and 1.00 (Fig. 2). It is interesting to note that the first critical region K_1 is close in value to the critical concentration of micelle formation in solutions of potassium and sodium laurate, determined by other independent methods (3, 5). Consequently, the critical concentration of micelle formation of detergents can be determined with sufficient accuracy by the solubilization method.

Fig. 2. Critical concentration regions in solutions of sodium laurate (1) and potassium laurate (2)

In the concentration interval between the c.m.c. and the second critical region, the solubilizing capacity of sodium laurate and potassium laurate solutions is practically the same. With a further increase in the soap content in solution above K_2, the solubilizing capacity of sodium laurate solutions increases more rapidly than for potassium laurate solutions, i.e., for sodium laurate it is higher than for potassium laurate of the same concentration. The critical concentration regions for potassium and sodium laurate nearly coincide and are represented by similar broken curves (Fig. 2). In concentrated soap solutions there apparently also exist other critical concentration regions in which, owing to the stepwise character of association, a jump-like rearrangement of the internal structure of the solution takes place. In this process more oleophilic micelles are formed, capable of binding larger amounts of hydrocarbon than the micellar structures of less concentrated detergent solutions.

The phenomenon of solubilization can be used for the quantitative characterization of the practical value of detergent solutions (5, 6), the oleophilicity of their

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micellar structure, the critical concentration of micelle formation, and other critical concentration regions.

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