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Short Communications

The Solubilization of Hydrocarbons by Association Colloids Below and Above the Second Critical Concentration for Micelle Formation

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In general the opinion prevails that the curves representing the solubilities of hydrocarbons such as hexane, benzene etc. in solutions of association colloids rise with increasing colloid concentration and are convex toward the concentration axis (see, for example, the review entitled Solubilization by Klevens [1]). One of the present authors, however, proved in 1947 that in the case of several paraffin chain salts the solubility curves for hydrocarbons follow linear courses over a wide concentration range [2]. This means that after a limited transition range immediately above the critical concentration for micelle formation the saturation capacity of the micellar substance is practically constant over the whole of the so-called small micelle concentration range. In the paper mentioned [2] it was, however, indicated that the saturation capacity has a higher value above the so-called roentgengraphic concentration for micelle formation than below this concentration limit. These observations have now been confirmed.

In the experiments saturated solutions of *p*-xylene in aqueous solutions of sodium oleate and sodium myristyl sulphate were prepared at 40° C and the amounts of solubilized *p*-xylene were determined with a Zeiss-Löwe interferometer for liquids. Fig. 1 shows the forms of the solubility curves. In oleate solutions the solubility of xylene increases linearly up to an oleate concentration of 0.19 *M*. At this concentration there is a break point in the curve and above this point the solubility increases more rapidly than below. Below 0.19 *M* the saturation capacity of the micellar substance is 189 ml xylene per mol oleate and above this concentration it rapidly increases to 300–330 ml xylene per mol oleate. A similar behaviour is observed in the case of the sodium myristyl sulphate solutions. In the latter case the break point occurs at a concentration of 0.19–0.20 *M*. Below this concentration the saturation capacity for xylene is 127 ml per mol myristyl sulphate and above this concentration 184 ml xylene per mol myristyl sulphate.

These experimental results show that the power of the micellar substance to solubilize xylene differs on both sides of a definite concentration limit, *i.e.* the micelles have different properties in this respect on both sides of this limit.

A comparision of our results with those of earlier X-ray studies shows that it was in the same concentration region that the so-called roentgenographic concentration for micelle formation was believed to lie [3–6]. The existence of such a concentration limit is however queried by recent X-ray studies of American investigators [7,8]. Nevertheless, the so-called I-band which seems to

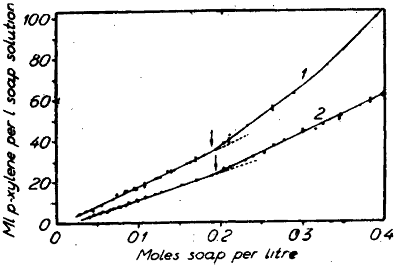

Fig. 1. The solubilization of p-xylene in sodium oleate and sodium myristyl sulphate solutions below and above the 2nd critical concentration.

1. *The solubility of xylene in sodium oleate solutions.*
2. *The solubility of xylene in sodium myristyl sulphate solutions.*

represent the distance between the centres of similar micelles or between similar layers within the micelles has never been observed below this concentration region.

It was in this same concentration range that an equivalent conductivity minimum was observed already long ago. The equivalent conductivity was observed to increase above a concentration of approximately 0.2 M in the case of sodium oleate (18° C)[9] and above a concentration of about 0.1 M in the case of sodium myristyl sulphate (60° C)[10]. One of the present authors has shown [2] that this increase in the equivalent conductivity can in the case of sodium oleate be explained by assuming that increasing amounts of water are immobilized between the hydrophilic interfaces within "large micelles" of some kind.

Many investigators are now of the opinion that large micelles do not exist. Among those who believe that there is such a concentration limit separating two different micellar regions this limit is known as the second critical micelle concentration (*2nd* C.M.C.). The present study provides proof that such a concentration limit actually exists.

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The Specific Volumes of Association Colloid Solutions Below and Above the Second Critical Concentration

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Previous studies have shown that the partial specific volumes of association colloids undergo marked changes in the region of the first critical concentration at which the molecules or ions associate to form micelles [1–3]. As far as we have been able to determine, no data are available in the literature concerning any changes undergone by the partial specific volume in the region of the second critical concentration. We have now studied the variation of the specific volume of sodium oleate and sodium myristyl sulphate solutions in this concentration range. As shown by curves 1 a and 2 a of Fig. 1, the specific volumes vary linearly with the colloid concentration over the whole of the concentration range studied. Thus no changes are observed in the partial specific volumes of these colloids when their 2nd critical concentrations at 0.19—0.20 M are exceeded.