

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 shown² 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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Received February 1, 1952.

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

PER EKWALL and KARL SMEDS

*Institute of Physical Chemistry,
Åbo Akademi, Åbo, Finland*

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 micelles¹⁻³. 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.

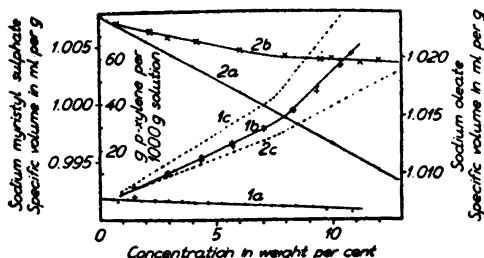


Fig. 1. The specific volumes of sodium oleate and myristyl sulphate solutions.

- 1 a. Pure sodium oleate solutions.
- 1 b. Sodium oleate solutions saturated with *p*-xylene.
- 1 c. The amounts of *p*-xylene solubilized by sodium oleate solutions.
- 2 a. Pure sodium myristyl sulphate solutions.
- 2 b. Sodium myristyl sulphate solutions saturated with *p*-xylene.
- 2 c. The amounts of *p*-xylene solubilized by sodium myristyl sulphate solutions.

We have also measured the specific volumes of aqueous solutions of these colloids in which *p*-xylene had been solubilized. The specific volumes of series of colloid solutions saturated with *p*-xylene are shown in Fig. 1, curves 1 b and 2 b. The curves are seen to be formed of two almost straight lines which meet at an angle. Calculations based on the measured values show that the break points are due to the fact that the micellar substance is able to solubilize more xylene per mol colloid above than below this concentrations (1 c and 2 c). The break point occurs in the oleate solutions at an oleate concentration of about 7 % (0.23 *M*) and in the case of sodium myristyl sulphate at about 7.2 % (0.22 *M*). These concentrations are approximately the same as those which according to earlier solubilization studies⁴ represent the 2nd critical concentrations of these associationscolloids.

The data thus confirm that the micelles present below and above the 2nd critical concentration possess different properties as far as their ability to solubilize hydro-

carbons is concerned. Since the partial specific volumes of the colloids in their pure aqueous solutions (without added xylene) are not found to undergo any marked changes in this region, it must be assumed that the packing within the micelles remains unaltered when the mentioned concentration limit is exceeded even though the structures and/or sizes of the micelles may undergo changes.

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Received February 1, 1952.

Dipole Moment Measurements of α , β , γ , δ and ϵ Benzene Tetrachloride

O. BASTIANSEN and JOAR MARKALI

Universitetets Kjemiske Institutt,
Blindern — Oslo, Norway

By the photochlorination of benzene in the presence of catalytic quantities of iodine, G. Galingaert, A. J. Kolka, H. D. Orloff *et al.* of the Ethyl Corporation, Detroit, have succeeded in isolating five compounds having the structure 3,4,5,6-tetrachlorocyclohexene-1^{1,2}. These five benzene tetrachlorides (BTC) were designated as α , β , γ , δ and ϵ , in the order of their characterization, and the difference between the various isomers was believed to be of the same kind as that known from the benzene hexachlorides (BHC)^{3,4}. Adopting the ideas and designations used for cyclohexane derivatives⁵ the possible configurations of the BTCs can be characterized by the scheme given in Table 1. The "conversion forms" containing more than two ϵ bonds (in parentheses in Table