The Solubilization of Long-Chain Alcohols in Association Colloid Solutions below the Critical Concentration for Micelle Formation

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Fig. 1. The turbidities of sodium laurate solutions containing n-decanol.

1. 21   mole per cent decanol.
2. 15.7   »   »   »   »
3. 10.5   »   »   »   »
4. 7.35   »   »   »   »
5. 5.25   »   »   »   »
6. 3.20   »   »   »   »

It is possible to follow with the microscope the solubilization of the in water sparingly soluble n-decanol by aqueous solutions of sodium laurate. A compact layer of a double-refracting liquid-crystalline substance is seen to form and grow on the surface of each drop of decanol. A similar phenomenon is observed even when the concentration of the sodium laurate solution is below the critical concentration for micelle formation, C.M.C., of sodium laurate, e. g. at 40° C down to approximately 0.006 M.

The turbidities of laurate solutions containing a constant mole-fraction of n-decanol vary with the laurate concentration as shown by the nephelometric curves given in Fig. 1. Two turbidity ranges may be distinguished. The turbidity range at low concentrations terminates with an abrupt upper limit, at 40° C at a laurate concentration of 0.006 — 0.007 M. In ths other turbidity range, the turbidity ie much weaker; its upper limit or its maximum is near the critical concentration, 0.024 — 0.030 M.

The turbidity in the first range is due to emulsified decanol. In the second range the substance causing the turbidity is of a different nature. The substance is evidently highly dispersed and is difficult to observe with the microscope; at higher decanol concentrations double-refracting spheres of a liquid-crystalline substance are noted, at least above the C.M.C. Above the C.M.C. the precipitated substance goes into solution w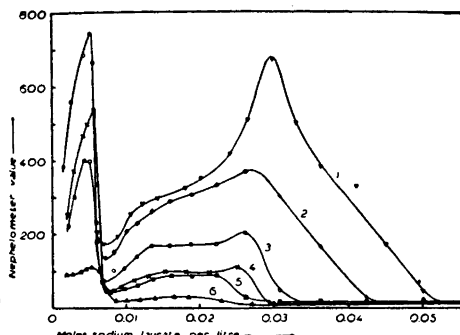hen the temperature is raised. The turbidity observed between the C.M.C. and the lower limit of the turbidity range is very little affected by a change in temperature. The upper limit of the first turbidity range shifts upwards rapidly with increasing temperature and the phenomenon is reversible.

These experiments thus show that the interaction between decanol and laurate which above the C.M.C. leads to a solution of the alcohol in the micelles continues at laurate concentrations as low as 0.006 M, i. e. down to the so-called limiting concentration (limiting association concentration, L.A.C.) of sodium laurate [1-2]. Between the C.M.C. and L.A.C., the interaction leads to the formation of a poorly soluble substance which separates as a fine suspension.

The equivalent conductivity of sodium laurate below the L.A.C. is not affected by the addition of decanol. Above the L.A.C., however, the equivalent conductivity is altered considerably by the addition. When approximately 250 moles per cent have been added, the equivalent conductivity has lowered to approximately the value at the L.A.C. in the absence of

the alcohol. This indicates that the inter-action between decanol and laurate extends down to the L.A.C., but no further.

The interaction results in an increased solubility of the decanol. Beginning at the L.A.C., the solubility increases at first slowly, but attains already at the critical concentration a value that is many times higher than at the L.A.C. Above the C.M.C. the solubility of decanol rises rapidly with increase in the laurate con-centration. The solubilization of decanol thus begins already at the L.A.C.

A similar interaction is noted between decanol and the other fatty acid soaps. In all the cases studied this was observed to take place below the C.M.C., down to the L.A.C. of the soaps. Similar inter-actions take place in the case of n-octanol and n-hexanol.

Analogous observations have previously been described for another group of polar-nonpolar compounds, the fatty acids. Under the microscope the reaction between lauric acid and laurate solutions can be followed at temperatures above the melting point of the acid. In this case a liquid-crystalline acid laurate is formed. The reaction continues down to the limiting concentration of sodium laurate, 0.006 M[4-6]. Two turbidity ranges are observed in laurate solutions containing lauric acid[2-5, 7], one immediately below the L.A.C. in which the turbidity is due to free lauric acid and the other between the L.A.C. and C.M.C. in which range acid laurate is responsible for the turbidity. Above the C.M.C., fairly large quantities of lauric acid are dissolved, colloid acid laurate being formed[2, 3]. The equivalent conductivity also varies in a manner simi-lar to that described above[1, 2].

Interaction with the formation of acid salt takes place between other fatty acid soaps and the corresponding fatty acids down to the L.A.C. of the soaps[1, 2]. This interaction has been considered evidence for the belief that association in soap solu-

tions begins already at the limiting con-centration[1, 2, 8, 9] and not at the critical concentration, as it has been previously assumed, and as it is still frequently suggested. The solubilization of alcohols beginning at the L.A.C. furnishes additio-nal support for this assumption.

At 40° C decanol is solubilized by sodium myristyl sulphate solutions in a manner analogous to that described above. This takes place down to a myristyl sulphate concentration of 0.0003 M; the C.M.C. of the sample of myristyl sulphate was 0.0012 M. In hexadecyltrimethylam-monium bromide solutions, the solubili-zation of decanol extends down to a con-centration of 0.0004 M (C.M.C. : 0.001 M). This phenomenon thus seems to be quite general, and indicates that in the case of the association colloids of the paraf-fin chain type, premicelle formation begins to take place at a limiting association concentration which is below the C.M.C.

Harkins and co-workers[10-12] have shown it to be probable that the solubilization of polar-nonpolar compounds occurs through the incorporation of the latter in the palisade layers of the micelles. This pro-cess they have termed penetration. The difference between the solubilization of hydrocarbons and that of alcohols, fatty acids, etc., is clearly shown by our experi-ments. When the substances of the former type are added in excess, the unchanged hydrocarbon separates, sometimes in the form of an emulsion; when polar-nonpolar substances are added in excess, these substances separate along with the asso-ciation colloid until the concentration of the latter is reduced to a value close to the L.A.C. The incorporation of the molecules of the polar-nonpolar substances in the micelles makes the latter less hydrophilic, and thus leads to a decrease in the solu-bility of the micellar substance.

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Chemical Nature of the Thiobarbituric Acid Test for the Oxidation of Unsaturated Fatty Acids

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Thiobarbituric acid was used by Kohn and Liversedge[1] as a reagent for a compound formed by aerobic incubation of tissue suspensions. It was found by Bernheim et al.[2] that the colors obtained upon addition of thiobarbituric acid to incubated tissues are due to a product of oxidation of unsaturated fatty acids, especially linolenic acid. Subsequently, Wilbur et. al.[3] studied further thiobarbituric acid as a reagent for oxidized fatty acids. They found that the strongest colors were produced with oxidized linolenic acid, weaker with oxidized linoleic and arachidonic acids. Furthermore, while oxidized fatty acids gave orange-red colors, various sugars and aliphatic aldehydes gave yellow colors, and glyoxylic acid a pink color.

As stated by Wilbur et al. the chemical reaction underlying the thiobarbituric acid reaction has not been completely elucidated. However, a comparison of thiobarbituric acid with phloroglucinol with respect to chemical properties will probably contribute to its explanation. The two compounds show some similarity with respect to chemical structure, including an analogous tautomerism and both are used as sensitive reagents for the quantitative determination of aldehydes, especially furfural. Furthermore, phloroglucinol is used as a reagent for the detection of oxidative changes of fats in the well-known Kreis-test[4]. The question therefore arises whether thiobarbituric acid is a reagent for the presence of the same chemical structures.

In order to investigate this question we have compared the two reactions using a number of fatty acids and other products of various origin. The thiobarbituric acid reaction was carried out as described by Wilbur et al. In order to facilitate the comparison of the results, the Kreis-test was carried out in a one phase-system using the modification of Pool et al.[5]. Finally, the peroxide values of the substances were determined by Hartmann and Glavind's colorimetric method[6].

Some representative results are given in Table 1. The colors were measured on the Beckman spectrophotometer at the respective wave-lengths. For presentation in the table they are calculated as the extinctions obtained in the three methods by the same amount of substance in the same final volume of 10 ml using a 1 cm cuvette.

It can be seen from the table that a minute amount of purified methyl oleate hydroperoxide gave a strong color in the thiobarbituric acid reaction. Such a strong color cannot be explained by the presence in the oleate of small amounts of linolenate. This observation does not agree with the statement by Wilbur et al. that thiobarbituric acid is a reagent for oxidized linolenic acid alone.

A study of the table further shows that the thiobarbituric acid reaction and the Kreis-test follow each other rather closely,