Studies on the Interaction of Paraffin Chain Alcohols and Association Colloids

X.   The Solubility of Decanol-1 in Sodium Oleate Solutions Containing Sodium Chloride

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The maximum amounts of decanol solubilized until sodium oleate solutions containing sodium chloride become turbid have been determined. The solubility of decanol decreases rapidly with increasing sodium chloride concentration. The general shape of the solubility curve is not altered by the addition of 0.05 M NaCl. The break point in the solubility curve occurs at a lower oleate concentration in salt-containing than in salt-free solutions. The break point is known to occur at the so-called "2nd critical concentration"; this limit is hence not only a function of the concentration of the micelle-forming hydrocarbon-chain ions in the solution, but also a function of the concentration of the gegenions. This indicates that the changes in the micellar structure that take place here do not depend solely on the fact that the micelles come so near each other that disturbances occur in their electrical double layers. The factors responsible for the decrease in the solubility of decanol are discussed.

Investigations of the effects of inorganic salts on the solubilization of simple nonpolar and polar-nonpolar substances have shown that the addition of salt increases the solubilization of nonpolar compounds [1-3], but decreases the solubility of polar-nonpolar substances, *e.g.*, long-chain alcohols [2-5]. This difference has been explained by assuming that nonpolar and polar-nonpolar molecules are incorporated in different regions of the micelles.

In studies of the effect of inorganic salts on the solubilization of very complicated organic molecules, such as dyes, it has been established that in most cases the added salt causes an increase in the solubilizing power of the colloid [6].

In Part I [7] of this series, data were given on the solubility of decanol in oleate solutions at the turbidity point where the separation of a mesomorphic phase begins. It was found that the solubility curve increases linearly up to a colloid concentration of about 0.12 M, then curves upwards and finally

downwards as the oleate concentration is increased further. The purpose of the present investigation was to study the effect of sodium chloride on the solubility of decanol in oleate solutions and to determine whether the shape of the solubility curve remains the same as for oleate solutions containing no added salt. It was also of interest to determine whether the breakpoint in the solubility curve at the so-called "2nd critical concentration" is displaced when salt is added.

MATERIALS AND METHODS

The same substances and methods have been used as in Part I [7] of this series. The sodium chloride employed was a product from E. Merck.

The experimental error of the solubility values has been estimated to be about ± 0.2 ml of decanol per litre.

The concentrations of sodium oleate and sodium chloride are given in moles per 1 000 g of oleate solution (salt-free) and are denoted by M.

EXPERIMENTAL RESULTS

The solubility of decanol at the turbidity point in 0.100 M sodium oleate solutions containing different amounts of sodium chloride is shown in Fig. 1. The solubility decreases very rapidly with increasing sodium chloride concentration. The solubility of decanol could not be measured when the sodium chloride concentration exceeded about 0.15 M, because the solutions became very viscous, nearly gel-like. The curve has the same form as Klevens has found for the system octanol-potassium myristate-potassium chloride [3].

The solubility of decanol in sodium oleate solutions containing 0.05 mole of sodium chloride per litre is shown by curve a in Fig. 2. Curve b gives the solubility of decanol at the turbidity point in salt-free oleate solutions (Part I [7]). The form of the solubility curve is similar for salt-containing as for salt-free oleate solutions. At lower oleate concentrations, the solubility increases linearly with the oleate concentration, then begins to increase a little faster, but finally the curve becomes concave against the concentration axis. In the presence of sodium chloride, the departure from linearity occurs at a lower concentration (at about 0.08 M oleate) than in salt-free solutions (at about 0.12 M oleate);
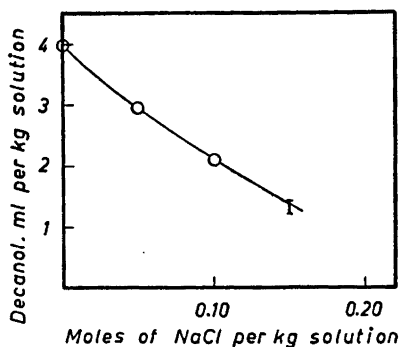

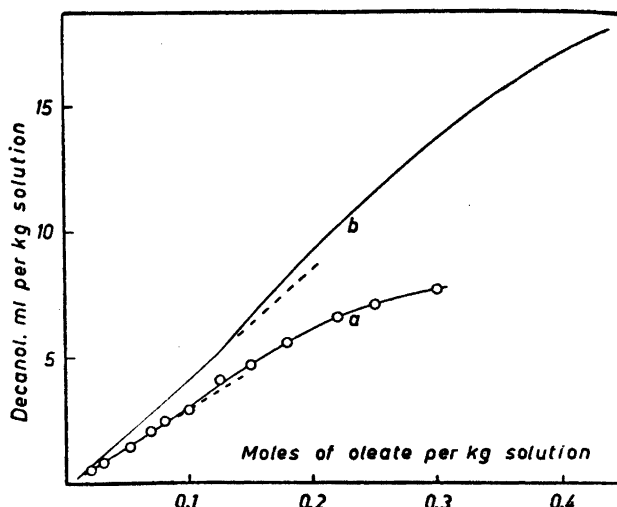Fig. 1. The effect of sodium chloride on the solubility of decanol in a 0.100 M sodium oleate solution. 40°C.

*Fig. 2. The solubility of decanol at the turbidity point. 40°C. a) Sodium oleate solutions
0.05 M in sodium chloride. b) Salt-free oleate solutions.*

the departure is less marked than in salt-free oleate solutions, but exceeds the
experimental variation in the solubility determinations. The effect of the salt
varies in different concentration ranges; in the linear range below 0.08 M oleate,
the solubility is decreased by about 26 %, at higher oleate concentrations, the
decrease is larger and amounts to about 33 % in the 0.2 M and about 44 %
in the 0.3 M oleate solution.

<div align="center">DISCUSSION</div>

As pointed out earlier [7,8], the solubility curve gives the maximum amount
of decanol dissolved by the micelles before the system becomes heterogeneous.
The slope of the solubility curve at each point gives the proportion of decanol
and soap in the mixed micelles formed at the soap concentration in question.
The curve a in Fig. 3 and the values in Table 1 show how the decanol content
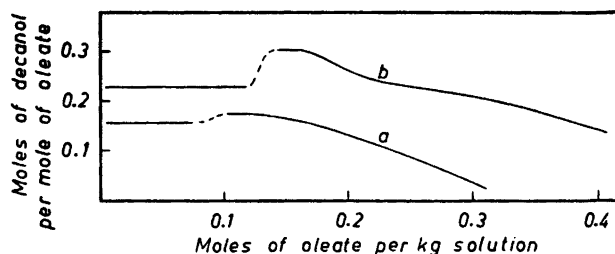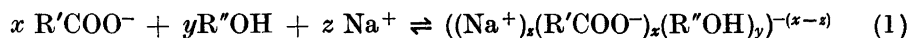of the mixed micelles (in moles of decanol per mole of oleate) varies with the

*Fig. 3. The decanol content per mole of association colloid in the mixed micelles. 40°C.
a) Sodium oleate solutions 0.05 M in NaCl. b) Salt-free oleate solutions.*

Table 1. *Composition of the mixed micelles at the turbidity point in sodium oleate solutions containing sodium chloride.*

Concentration of sodium oleate	Maximum proportion of decanol in moles of decanol per mole of oleate		
	Concentration of sodium chloride		
	0.05 M	0.10 M	0.15 M
0.005 − 0.08 M	0.16	(0.11)	(0.07)
0.12 M	0.18		
0.20 M	0.13		
0.30 M	0.04		

oleate concentration in solutions 0.05 M in sodium chloride. (The values given in parentheses in Table 1 have been calculated on the basis of only one experimental solubility value and are therefore only approximate.) Curve b in Fig. 3 shows the corresponding curve for salt-free oleate solutions. It is seen that in the former case the decanol content of the mixed micelles remains constant at approximately 0.16 mole of decanol per mole of oleate up to an oleate concentration of about 0.08 M. The relative decanol content then increases to a low maximum which is about 0.18 mole of decanol per mole of oleate, and finally decreases to a very low value. The addition of sodium chloride seems to smooth out the course of the solubility curve.

We wish to stress the following factors which we hold responsible for the fact that the system becomes heterogeneous at a lower decanol content when salt is present than when the solutions are salt-free. As we pointed out in Part IX [8] of this series, the process that precedes the formation of the new phase can be represented by an equation of the type:

$$x \text{ R}'\text{COO}^- + y\text{R}''\text{OH} + z \text{ Na}^+ \rightleftharpoons ((\text{Na}^+)_z(\text{R}'\text{COO}^-)_x(\text{R}''\text{OH})_y)^{-(x-z)} \quad (1)$$

$$\frac{[((\text{Na}^+)_z(\text{R}'\text{COO}^-)_x(\text{R}''\text{OH})_y)^{-(x-z)}]}{[\text{R}'\text{COO}^-]^x [\text{R}''\text{OH}]^y [\text{Na}^+]^z} = K \quad (2)$$

When the ratio of alcohol to soap, y/x, exceeds a certain value, a new phase is formed. This ratio is, as we have shown above, lower in the salt-containing than in salt-free solutions. We have previously assumed that a smaller number of sodium ions are bound per fatty acid ion in the mixed micelles containing alcohol than in the pure soap micelles, *i.e.* the ratio of gegenions to fatty acid anions, z/x, is assumed to be lower in the former case than in the latter. The presence of sodium chloride must lead to an increase in the number of bound gegenions, *i.e.* to a higher z/x-value. The conditions for the formation of the new phase are fulfilled in the salt-containing solutions when mixed micelles with a higher gegenion content (z/x) but smaller alcohol content (y/x) than those present in salt-free oleate solutions are formed. The observed decrease in the solubility of decanol on addition of salt can be explained fairly well on the basis of the law of mass action, eqn. (2), when certain simplifying assumptions are made. Plausible results are also obtained with an equation of the "solubility
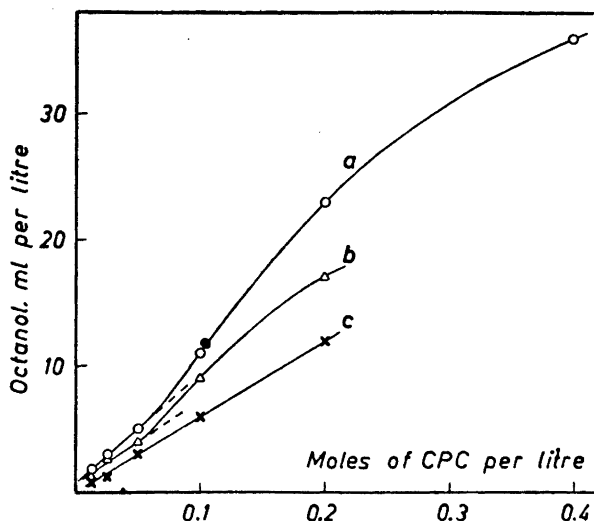
Fig. 4. The solubility of octanol at the turbidity point. 40°C. a) Salt-free cetylpyridinium chloride solutions, b) Cetylpyridinium chloride solutions 0.125 M in NaCl, c) Cetylpyridinium chloride solutions 0.500 M in NaCl (Richards and McBain [2])

product" type (see eqn. (4) in Part IX [8]). It should be noted that in salt-containing soap solutions the C.M.C. is lower and hence the activities of simple ions (R'COO⁻) are lower than in salt-free solutions.

Also other changes in the structure of the micelles than the above-mentioned, such as changes in their shapes and sizes, may occur when salt is added; this is indicated by light-scattering [9-11] and viscosity [12] measurements.

In Parts I—IV [7,13-15], it was shown that when the oleate concentration of 0.1—0.2 M is exceeded, so many important changes occur in the properties of oleate solutions that one has to assume that a change also takes place in the micellar substance and that therefore it is justified to speak of a concentration limit, called the "2nd critical concentration". In Part IX [8] it was shown that similar phenomena occur also in solutions of sodium caprate, laurate and myristate and that the concentration limit mentioned is displaced toward lower soap concentrations when the number of carbon atoms in the hydrocarbon chain increases. Our investigations have shown that the solubility of decanol is one of the properties that undergo a characteristic change at this limit. Our present measurements show that the limit is displaced to lower oleate concentrations when sodium chloride is added. The position of this limit is hence not only a function of the amount of the micelle-forming hydrocarbon-chain ions and molecules in the solution, but also a function of the concentration of gegenions (as is the case for the critical concentration). This indicates that the changes in the micellar structure that take place in this concentration range do not depend, solely at least, on the fact that the micelles come so near each other that disturbances occur in their electrical double layers.

We have examined the data on the solubility of alcohols in association colloid solutions published by other workers and have found that in all cases when the measurements have been carried out with sufficient accuracy and when a sufficient number of measurements has been made, the solubility curves (solubility in ml/l, g/l or moles/l plotted against the concentration of association colloid in moles per litre) are linear over a relatively wide concentration range above the C.M.C., then show a breakpoint, slope upwards and finally, in some cases, become concave against the concentration axis [1,2,16]. This is shown especially clearly by the solubility curve for octanol in cetylpyridinium chloride solutions according to measurements of Richards and McBain [2] (Fig. 4, curve a*). Our opinion is therefore that the type of solubility curve that we have found for the solubility of decanol in solutions of fatty acid soaps and of alkyl sulphates is characteristic for at least all the long-chain primary alcohols and all association colloids of the paraffin-chain type.

Richards and McBain reported also some data on the effect of salt on the solubility of alcohol [2]. The effect of 0.125 M sodium chloride on the solubility of octanol in cetylpyridinium chloride solutions (Fig. 4, curve b) is completely analogous to that found by us for sodium oleate solutions 0.05 M in sodium chloride. Our conclusion that a larger addition of salt smooths out the solubility curve is also verified (Fig. 4, curve c). The picture given by Figs. 2 and 4 of the effect of salt on the solubility of long-chain alcohols in solutions of association colloids may therefore be regarded as typical.

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* The variation of the solubility of alcohol in colloid solutions is in Fig. 4 plotted in another coordinate system than in the original paper.