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Short Communications

Some Differences between Solubilization in Bile Salt and Paraffin Chain Salt Solutions

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Similarly as other association colloids, the bile acid salts are good solubilizers of lipophilic substances, but there exist clear differences between the solubilization processes in solutions of the bile salts and the association colloids of the paraffin chain salt type. In both cases solubilization of hydrocarbons begins at a well-defined low colloid concentration and proceeds stepwise as the colloid concentration is increased [1-4]. The concentrations separating the solubility ranges are more or less clearly definable even when substances other than hydrocarbons are solubilized (but in some cases slightly displaced owing to the interaction between the solubilized substance and the colloid). In other respects marked differences are noted when polar-nonpolar substances such as straight-chain alcohols and fatty acids are solubilized. Whereas the solubilization of these substances begins in the bile salt solutions at the same concentration as the solubilization of hydrocarbons, in paraffin chain salt solutions the solubilization begins, although in a limited degree, at a concentration, the L.A.C., that is far below that where the hydrocarbon solubilization begins [4-6]. In the bile salt solutions the solubilization of alcohol continues until the micelles become saturated with alcohol, after which the excess of alcohol separates in the free form. In the paraffin chain salt solutions the solubilization in many cases ends when a mesomorphic phase composed of alcohol, association colloid and water separates. The added long-chain alcohols do not influence the conductances of the bile salt solutions (as far as we have investigated), but do alter the conductances of the paraffin chain salt solutions (Fig. 1 A). In the latter case even small amounts of alcohol bound by the micelles in the solutions alter the conductance, but a rapid decrease in the conductance occurs as soon as the system becomes heterogeneous [6-7]. Similar differences are also noted when fatty acids are solubilized by bile salt and fatty acid soap solutions.

The fact that the conductances of bile salt solutions are not altered by the alcohols (in any case not by small amounts of the additive) suggests that the charge distribution on the surface of the bile salt micelle does not change when alcohols are incorporated in the micelles, whereas the charge distribution is, however, altered when the alcohols are incorporated in fatty acid soap and alkyl sulphate micelles. That the mesomorphic phase does not separate from bile salt solutions may possibly be due to the fact that hydrophilic properties of the micelle surface of the bile salt micelles are not diminished to the same extent by alcohols and fatty acids as when the latter are incorporated in the paraffin chain salt micelles.

The polar-nonpolar compounds mentioned are known to increase the power of paraffin chain colloids to solubilize hydrocarbons [5,8]. This is illustrated by the curves 1 a and 1 b in Fig. 1 B which shows that the solubility of *p*-xylene in 0.04 M sodium myristate solution increases as much as 60—70 % when increasing amounts of decanol or myristic acid are added to the solution. In bile salt solutions the effect of the addition is the opposite. This is evident from curve 2 which shows the influence of added decanol on the solubility of *p*-xylene in a 0.1 M sodium cholate solution, and from curves 3 a and 3 b (in Fig. 1 B) which

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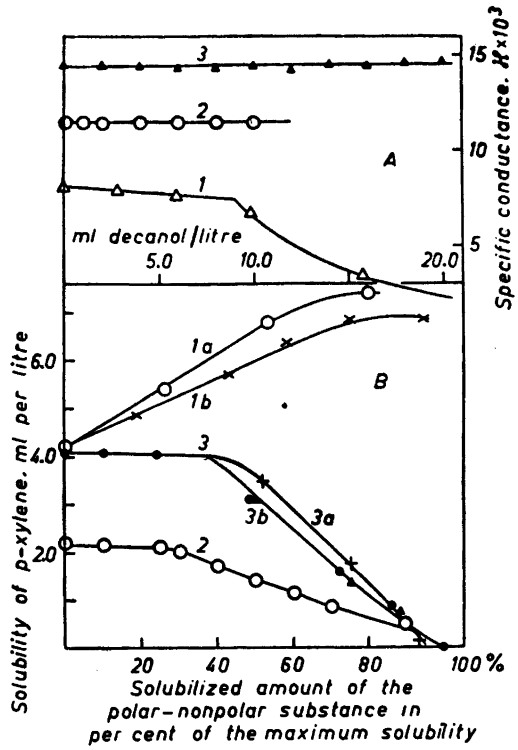

Fig. 1 A. The effect of added decanol-1 on the conductance of association colloid solutions. 40° C

1. *0.207 M sodium oleate solution containing decanol-1*
2. *0.180 M sodium cholate solution containing decanol-1*
3. *0.250 M sodium desoxycholate solution containing decanol-1*

Fig. 1 B. Solubility of p-*xylene at 40° C in association colloid solutions.*

1. *0.04 M potassium myristate solutions containing*
   a) decanol-1 O—O
   b) myristic acid ×—×
2. *0.10 M sodium cholate solutions containing decanol-1*
3. *0.09 M sodium taurodesoxycholate solutions containing*
   a) decanol-1 +—+
   b) nonylic acid ●—●
   heptylic acid ▲—▲

show the influence of decanol, nonylic acid and heptylic acid on the solubility of *p*-xylene in 0.09 M sodium taurodesoxycholate solution. As long as the amount of polar-nonpolar additive is relatively small, the xylene solubility either remains constant or decreases slowly, but when the amount added exceeds a certain value, the solubility of xylene decreases rapidly. (In order to facilitate the comparison, the content of the polar-nonpolar compound has been expressed as a percentage of the maximum solubility of the compound in the pure colloid solution in question).

It has, as known, been concluded (above all on the basis of X-ray studies) that the solubilized hydrocarbon molecules are built in between the palisade layers of the paraffin chain colloid micelles (or in the centre of the

spherical or spheroidal micelles); the molecules of the alcohols and fatty acids are, however, incorporated between the colloid molecules in the palisade layers and thus increase the amount of micelle-forming matter. Solubilization data of the type on which curves 1 a and 1 b in Fig. 1 B are based have been considered to support this view and to prove the existence of two loci of solubilization in the micelles [8,9].

The experiments described in curves 2 and 3 in Fig. 1 B show that the alcohols and fatty acids on one hand and hydrocarbons on the other, are initially solubilized quite independently by the bile salt micelles. This can be considered to indicate that the polar-nonpolar compounds and hydrocarbons are solubilized in different loci in the bile salt micelles. A marked difference as compared with the paraffin chain colloids is, however, that the polar-nonpolar compounds are built in the bile salt micelles in such a manner that the power of the micelles to solubilize hydrocarbons is not increased; on the contrary, the incorporation of larger amounts of the polar-nonpolar compounds progressively diminishes the power to solubilize hydrocarbons. It is thus evident that the mode in which the polar-nonpolar compounds are built in the micelles differs for the bile and paraffin chain salts.

One of the present authors has called attention to the fact that the maximum amounts of fatty acids that sodium taurocholate solutions are able to solubilize are so great [3] (from about 2 moles of nonylic acid to 5 moles of caproic acid per mole of taurocholate in 0.09 M solution) that it must be assumed that the structure of the micelles is altered to such an extent that mixed micelles with completely new properties are formed. Also the maximum amounts of long-chain alcohols solubilized by bile salt micelles are fairly large (1—2 moles per mole of the bile salt). According to the data presented here altered properties of the micelles become apparent only after the mole ratio of polar-nonpolar compound and bile salt exceeds a certain value, which is about 0.14 for decanol and sodium cholate, 0.34 for decanol and sodium taurodesoxycholate, and 0.8 for nonylic and 1.3 for heptylic acid and sodium taurodesoxycholate. A change in micellar structure apparently occurs only after these values of the ratio are exceeded.

All the above mentioned data show that there exist important differences in the solubilization mechanism in the case of bile salts and paraffin chain salts, particularly in regard to the location of solubilized molecules in the micelles and the interaction between the solubilizer and solubilizate. This is evidently connected with essential differences in the structures of the micelles of the two types of association colloids.

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Can Micelles be Treated as Ideal Mixtures of Ions and Neutral Molecules?

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In the last few years, attempts have been made in this Institution to study equilibria involving micelles of carboxylic acids such as lauric acid, $C_{11}H_{23}COOH$ = HL, and amines like dodecyl amine $C_{12}H_{25}NH_2$ = D. Emf titrations have been made (using glass or hydrogen electrodes, sometimes Ag, AgL electrodes) with a practically constant ionic medium, in order to keep the activity factors constant. In each titration, the total concentration $B = [HL]_t + [L^-]_t$ or $[D]_t + [DH^+]_t$ has been kept constant, and the data have been given in the shape of a plot $Z(\log h)_B$,