ACTA CHEMICA SCANDINAVICA 11 (1957) 568—584

Short Communications

Small-angle Scattering of X-Rays in Aqueous Sodium Desoxycholate Solutions Containing Decanol-1

PER EKWALL and KRISTER FONTELL

Institute of Physical Chemistry, Åbo Akademi, Åbo, Finland

Aqueous bile salt solutions are able to dissolve both hydrocarbons and polar lipophilic compounds. Appreciable amounts of long-chain alcohols, decanol-1 for instance, are solubilized by these solutions. For example, a 0.20 M sodium cholate solution dissolves about 28 ml of decanol per litre of solution at 40°C. A 0.20 m sodium desoxycholate solution dissolves about 55 ml of decanol per 1 000 g solution at 25°C, a 0.35 m solution about 105 ml and a 0.53 m solution about 200 ml[1]. The solubilization process involves two stages, as shown by the fact that when small amounts of decanol are added to cholate solutions, the ability of the latter to solubilize *p*-xylene is not appreciably altered, whereas the solubility of the hydrocarbon rapidly decreases when the molar ratio of decanol to cholate exceeds a certain value [2]. The same has been found to apply also in the case of desoxycholate solutions. This variation of the solubility of *p*-xylene with increasing additions of decanol to a 0.35 m sodium desoxycholate solution is shown in Fig. 1 a; the solubility of *p*-xylene remains almost unaltered as the decanol content increases to 50 ml per 1 000 g of solution, but then falls off rapidly as more decanol is added.

The mentioned variation in the solubility of *p*-xylene is accompanied by changes in the small-angle X-ray scattering by the solutions [3]. The X-ray scattering has been investigated with the same apparatus and technique we have used in our earlier investigations [4]. Fig. 2 shows photometer recordings of the X-ray films obtained with 0.35 m sodium desoxycholate solutions containing different amounts of decanol. As long as the decanol content is below about 40 ml per 1 000 g of solution, the small-angle X-ray pattern remains largely unaltered. As larger amounts of decanol are dissolved the pattern becomes

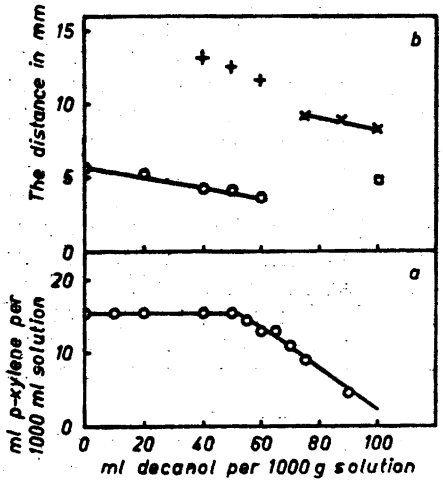

Fig. 1. a) The maximum solubility of *p*-xylene in 0.35 molal sodium desoxycholate solutions containing different amounts of decanol-1. b) The distance of the intensity maxima from the incident beam in the small-angle X-ray patterns of 0.35 m sodium desoxycholate solutions containing different amounts of decanol-1. The inner maximum. Points marked O and □. The outer maximum. Points marked × and +. The intensity maxima + are very vague and blurred.

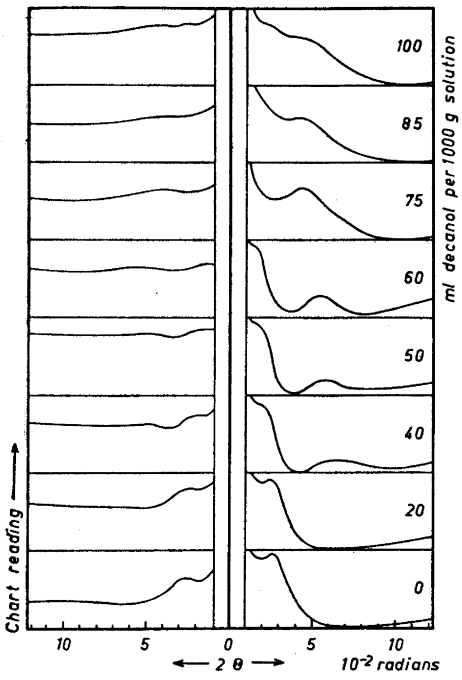

Fig. 2. Photometer recordings of the small-angle scattering by 0.35 M sodium desoxycholate solutions containing different amounts of decanol-1. a) Left side. Recordings obtained with the same photometer sensitivity for all films and with the photometer set to zero for unexposed areas of the films. b) Right side. Recordings obtained when the full-scale reading was set equal to the difference in maximum blackening and background for each film separately.

less and less distinct until it finally fades into the background. At the same time a new very diffuse ring which is located farther from the incident beam gradually becomes evident. When the decanol content is increased further to a high value close to saturation a second inner ring appears at a distance from the incident beam which almost coincides with that of the ring for the original desoxycholate solution or at a somewhat smaller distance. The curves in Fig. 1b show the shift of the intensity maxima with increasing decanol content. — We have found the same phenomenon to occur also with 0.53 m and 0.20 m sodium desoxycholate solutions containing decanol.

Exposures made with an ordinary X-ray powder camera have indicated the occurrence of a similar phenomenon to that described above. At low decanol contents the same pattern is obtained as for pure sodium desoxycholate solutions with Bragg spacings at 2.7—3.3 Å and 6.0—6.2 Å. At higher decanol contents, about 100 ml of alcohol per 1 000 g of a 0.53 m sodium desoxycholate solution, a new ring with a Bragg spacing of 4.5—5.0 Å appears. This spacing corresponds to that of pure decanol; in these quite clear solutions there is no separated decanol and practically all the dissolved decanol is in the solubilized state.

The observation that the original small-angle X-ray pattern for desoxycholate solutions disappears gradually and is replaced by another pattern indicates that decanol effects a radical rearrangement of the micelle structure. It is obvious that desoxycholate micelles are able to incorporate only a limited amount of decanol before their structure undergoes a change. When this critical molar ratio of decanol to desoxycholate is exceeded, the original micelles break down and a new type of mixed micelle composed of bile salt and decanol is formed. These new micelles are not able to solubilize *p*-xylene. It seems probable that the long paraffin chains of the alcohol molecules (alcohol is present in these solutions in molar ratios of decanol to desoxycholate from 1:1 to 2:1) primarily determine the structure of the new micelle. The appearance of a new short spacing at 4.5—5.0 Å possibly indicates the occurrence of parallel-oriented paraffin chains, obviously an arrangement resembling that in micelles of association colloids of the paraffin-chain type.

1. Ekwall, P., Fontell, K. and Sten, A. *Unpubl. results.*
2. Ekwall, P., Sten, A. and Norman, A. *Acta Chem. Scand.* **10** (1956) 681.
3. Ekwall, P. and Fontell, K. *IX Nord. Kemistmötet,* Aarhus 1956.
4. Ekwall, P. and Fontell, K. *Acta Chem. Scand.* **10** (1956) 327.

Received January 21, 1957.