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**Note**

# STUDY OF THE VAPORIZATION PROCESS OF SODIUM AND RUBIDIUM DEOXYCHOLATE LYOPHILIZATES

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The sodium and rubidium salts of deoxycholic acid (hereafter abbreviated to NaDC and RbDC, respectively) form micellar aggregates in aqueous solutions [1]. The size of the molecular aggregates increases on lowering the pH [2] and temperature [3], and on increasing the ionic strength [2] and the pressure [3]. Under suitable conditions these aggregates can give a gel from which a macromolecular fibre can be drawn [2]. Crystals containing helices of NaDC and RbDC can be obtained from these macromolecular fibres by ageing [4–6]. The X-ray patterns of the crystals, macromolecular fibres, gels and aqueous solutions show maxima of intensity in the same $\theta$ regions [4]. Thus, it is probable that all these phases are composed by very similar structural units of helical shape. X-ray and NMR studies carried out on NaDC confirm this hypothesis [7].

In order to verify the similarity of the structures occurring in the solid state and in solution, thermal measurements on lyophilizates of NaDC and RbDC were made to establish how their vaporization behaviour compares to that of the corresponding crystals and macromolecular fibres [4,6].

NaDC and RbDC lyophilizates were prepared, in the hope that they would retain the structure of the micellar aggregates in aqueous solution, since the X-ray patterns of the aqueous solution and of the lyophilizates are identical.

## EXPERIMENTAL AND RESULTS

NaDC and RbDC (Calbiochem) were opportunely lyophilized under vacuum at about $-203$ K from 0.1 M aqueous solutions with pH varying from 8.4 to 7.4.

The pressures of the vapour in equilibrium with these salts were measured by a torsion–effusion apparatus. The method and assembly have been described previously [8]. Two pyrophyllite cells with different geometrical constants were employed in this work.

Six vaporization runs of NaDC lyophilizate were carried out. In the first step of the heating a reproducible increase in the vapour pressure was observed in every run, as in the vaporization study of the crystal samples [4]. A typical vaporization behaviour of NaDC lyophilizate and crystal samples is reported in Fig. 1.

The average second-law enthalpy change associated with this vaporization process, $\Delta H_T^0 = 66 \pm 10$ kJ mol$^{-1}$, is equal, within the estimated error, to that found for the vaporization of the crystallization water from the NaDC crystal and fibre ($74 \pm 6$ kJ mol$^{-1}$ [4]). This can be taken to prove that crystallization water molecules are also present in the NaDC lyophilizate.

On heating again, the vapour pressure is sufficiently constant in a large temperature range for the vaporization of adsorbed water in the porous samples. At about 465 K a new increase in the vapour pressure was observed. Since the importance of this phenomenon depends on the pH of the solution from which the lyophilizate was obtained and the measured vapour pressures are similar to those found studying the pure acid [9] (see Fig. 1), this vapour was ascribed to the decomposition of the deoxycholic acid (DCA). This acid was probably generated during the lyophilization process when HI was added to the NaDC aqueous solution in order to vary the pH. The presence of some DCA in the lyophilizate obtained at low pH (7.4) was also confirmed by analysis with a Leitz 350 heating plate, showing the melting of small parts of the sample at about 433 K, a temperature close to the melting point of some DTA inclusion compounds. Increasing the temperature, at about 573 K the lyophilizate melts with a rapid increase in vapour pressure values as observed in the crystal samples and in the pure acid and explained as vaporization of decomposition products.

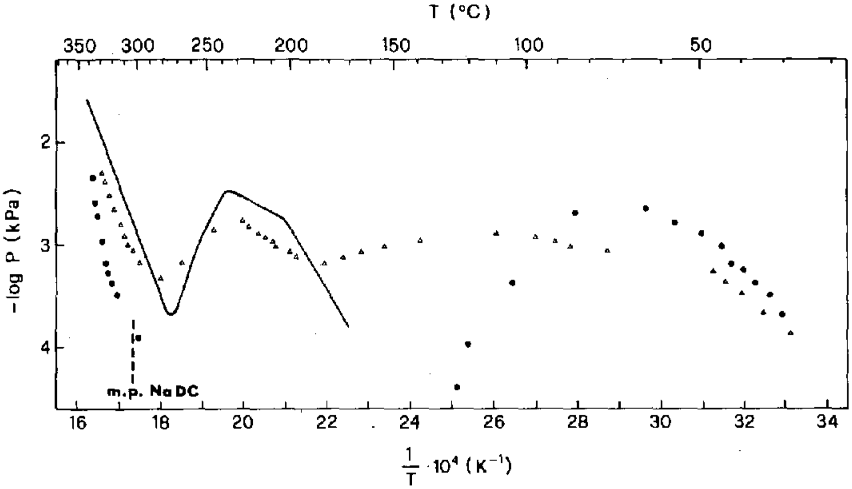

Fig. 1. Vaporization behaviour of NaDC lyophilizate (△) and crystals (●); pure DCA (——).

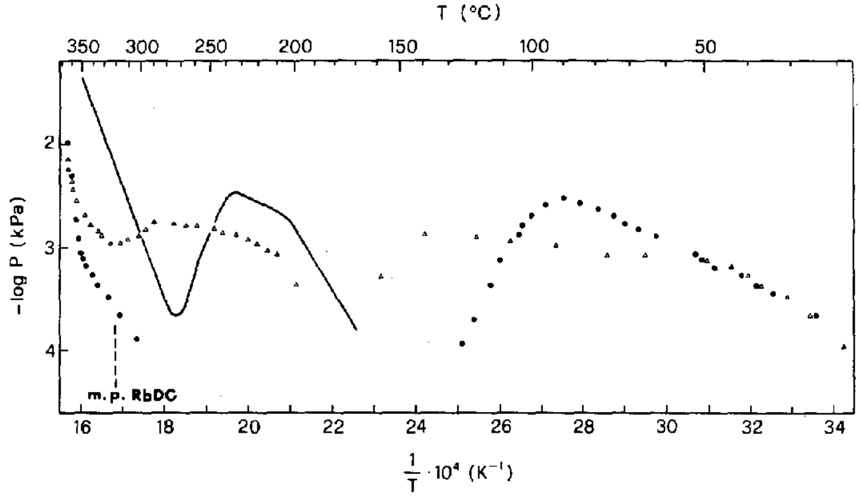

Fig. 2. Vaporization behaviour of RbDC lyophilizate (△) and crystals (●); pure DCA (———).

A similar behaviour was observed during the heating of lyophilized RbDC samples. Preparation and vaporization study are similar to those described for NaDC. Owing to the hygroscopicity of the lyophilizate, particular care was taken in the loading of the cells. The panoramic behaviour of a vaporization run is plotted in Fig. 2. The heat of vaporization in the first step of the experiments, measured in two runs, $\Delta H_T^0 = 40 \pm 8$ kJ mol$^{-1}$, agrees with the vaporization of the crystallization water of RbDC crystal found during the previous study ($\Delta H_T^0 = 34 \pm 4$ kJ mol$^{-1}$ [6]). In this lyophilizate, the presence of pure DCA, probably formed during its preparation, was also observed.

## CONCLUSIONS

The results found in this work show that the vaporization processes of NaDC and RbDC lyophilizates and the corresponding crystal samples are very similar, and that in the lyophilized samples, crystallization water molecules are present, like in the corresponding crystals and fibres. On this basis it is reasonable to suppose that the structures occurring in the solid phases are similar among them and are also similar to that of the micellar aggregates in aqueous solution.

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## REFERENCES

1 D.M. Small, in P.P. Nair and D. Kritchevsky (Eds.), The Bile Acids, Plenum Press, New York, 1971, Chap. 8, pp. 249–356.
2 D.M. Blow and A. Rich, J. Am. Chem. Soc., 82 (1960) 3566.
3 G. Sugihara, T. Neda, S. Kaneshina and M. Tanaka, Bull. Chem. Soc. Jpn., 50 (1977) 604.
4 A.R. Campanelli, D. Ferro, E. Giglio, P. Imperatori and V. Piacente, Thermochim. Acta, 67 (1983) 223.
5 A.R. Campanelli, S. Candeloro De Sanctis, E. Giglio and S. Petriconi, Acta Crystallogr., Sect. C, 40 (1984) 631.
6 S. Candeloro De Sanctis, P. Imperatori, A.R. Campanelli and V. Piacente, Thermochim. Acta, 77 (1984) 77.
7 G. Conte, R. Di Blasi, E. Giglio, A. Parretta and N.V. Pavel, J. Phys. Chem., in press.
8 V. Piacente and G. De Maria, Ric. Sci., 39 (1969) 549.
9 D. Ferro, C. Quagliata, E. Giglio and V. Piacente, J. Chem. Eng. Data, 26 (1981) 192.