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STUDY OF THE VAPORIZATION PROCESS OF THE RUBIDIUM DEOXYCHOLATE CRYSTAL AND FIBRE

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ABSTRACT

The vaporization behaviour of rubidium deoxycholate (RbDC) is investigated. In the first stage, the evaporation of crystallization water occurs and an average enthalpy change $\Delta H^0_{325} = 34 \pm 4$ kJ mol^{-1} is derived by a second-law treatment of the vapour data. In the fibre the vaporization of the residue crystallization water presents slower kinetics than in the crystal. In the RbDC, as in the sodium salt, no vaporization is observed until its melting point. Above this temperature (594–596 K) the vapour, constituted by various decomposition products, shows almost reproducible values.

INTRODUCTION

In a previous communication [1] a thermal and X-ray study of the sodium salt of 3α,12α-dihydroxy-5β-cholan-24-oic acid (sodium deoxycholate, NaDC) crystal and macromolecular fibre are considered in order produce information on the structure of NaDC micelles. Unfortunately, attempts to determine the NaDC crystal structure at atomic resolution were unsuccessful, although the occurrence of 6_5 helices and their packing mode have been established. Thus, crystals of rubidium deoxycholate (RbDC) were prepared, which has a behaviour in aqueous solution similar to that of NaDC, in the hope of obtaining crystals of the NaDC type to apply the heavy-atom method. We succeeded in solving the RbDC crystal structure, which is strictly related to that of NaDC, characterized by 2_1 helices mainly stabilized by hydrogen bonds and coulombic and ion–dipole interactions [2]. The interior of a helix is filled with Rb^+ ions surrounded by water molecules, whereas the outer surface is covered by non-polar groups (see Fig. 1). Moreover, macromolecular fibres were drawn from RbDC aqueous solutions which give rise to a detailed X-ray diffraction pattern very similar to that of the NaDC fibre. Therefore, a vaporization study of the RbDC crystal and fibre was undertaken in order to compare their behaviour with that of the corresponding NaDC phases and to check the similarity of the structures.

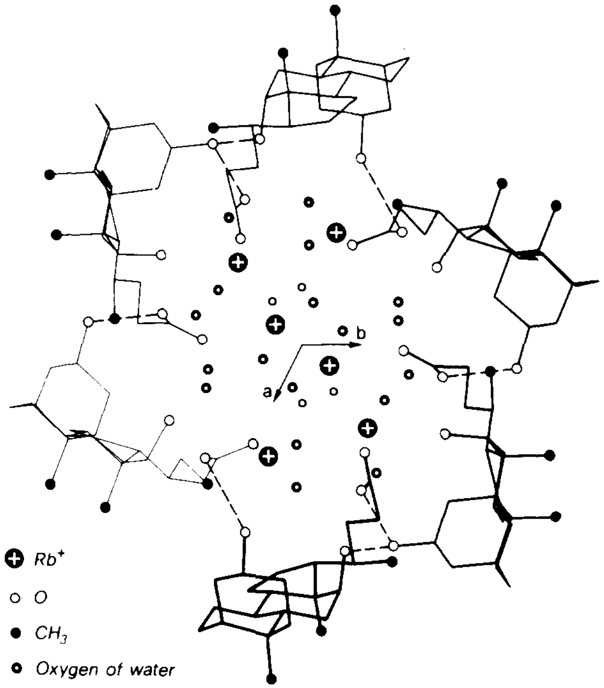

Fig. 1. A view of a RbDC helix along the 2_1 axis. Only the hydrogen bonds among deoxycholate anions are indicated by broken lines. The thin circles represent oxygen atoms of water molecules with a site-occupation factor of 0.5.

TABLE 1

Weight losses of RbDC crystal and fibre due to water vaporization

Sample	Initial weight (mg)	Time of vaporization (min)	Temp. (°C)	Pressure condition	Weight loss (%)
Crystal					
A[a]	139	~ 45	150	vacuum	8.8
A	118	35	45	room pressure	7.6
A	356	~ 180	60	vacuum	7.7
B	191	~ 60	75	vacuum	7.1
B[b]	234	~ 65	95	vacuum	7.5
B	188	~ 2 days	25	vacuum	7.3
B	380	60	75	room pressure	6.8
A	136	~ 60	130	vacuum	8.9
Fibre					
[c]	204	~ 60	170	vacuum	6.6
[c]	73	90	70	vacuum	7.1
[c]	165	60	135	vacuum	7.0

[a] Measured during run 2.
[b] Measured during run 10.
[c] Measured during run 3.

EXPERIMENTAL AND RESULTS

Samples of crystal RbDC were obtained by adding to pure DCA (Merck) a little less than the equivalent amount of RbOH (Alfa) solution and filtering the resulting suspension. Acetone was added at 40°C until the solution became cloudy. The RbDC crystals grown by cooling were separated by filtering and then dried. The fibre samples were prepared by adding hydrogen iodide (0.015 M) to a RbDC aqueous solution (0.1 M), following the procedure described for the preparation of NaDC fibres [1].

RbDC crystal

Two RbDC crystal samples were studied (A and B). Their vaporization behaviour was investigated by heating at room pressure and under vacuum. In both pressure conditions (see Table 1), by varying the temperature in the range 45–95°C the weight-losses of the samples are about 7.3 ± 0.3% the original weight. These weight-losses can be explained as a loss of six water molecules (6.8%) and the partial loss of another water molecule from the asymmetric unit (3 RbDC · 10 H_2O). When the sample was heated at temperatures higher than 100°C, a further vaporization of the residue water was noted with slower kinetic.

The water vapour pressure was measured by a torsion effusion apparatus as previously described [3]. The pressure at each temperature was derived from the torsion angle of the effusion cell by the relation [4] $P = K\alpha$ (where K is the instrument constant taking into account the torsion constant of the wire from which the cell is suspended, and the constants of the cell used). Four cells with different effusion holes were employed. Checks on the reliability of the corresponding instrument constants were performed by measuring the absolute vapour pressure of some pure elements (mercury and cadmium) and comparing the values obtained with those selected by Hultgren [5]. The agreement of the data also showed that thermodynamic equilibrium conditions exist in the cells used. The water pressures over the RbDC crystal samples were measured in the temperature range 289–370 K. After the first step of the vaporization, when the samples were vaporized to about 2–3% of the original weight (two or three molecules of crystallization water), the pressure data were not reproducible. Therefore, only the initial points of each run have been taken into account and plotted in Fig. 2. The corresponding slopes and intercepts of the pressure–temperature equations as derived by a least-squares treatment of the data are summarized in Table 2. The associated errors are standard deviations. It is interesting to note that when the analysed samples are original, even if the absolute vapour pressure is not the same (probably due to the different size of the samples used), their slopes are equal within the standard deviations. This leads to the average value $\Delta H^0_{330} = 32 \pm 2$ kJ mol^{-1} for the vaporization enthalpy of the crystalli-

TABLE 2

Summary of the constants of the water pressure–temperature equation measured in the first stage of the RbDC crystal and fibre vaporization

Sample	Run	No. of points	ΔT (K)	$\log P$ (kPa) = A − B/T	
				A	B
Crystal					
A	2	12	289–322	3.04±0.09	1774± 28
A	3	12	293–318	2.98±0.18	1768± 39
A	5	11	294–323	2.44±0.07	1671± 23
B	6	9	305–336	2.85±0.06	1801± 21
B	10	13	311–334	2.80±0.06	1812± 21
B [a]	11 [a]	6	310–354	2.53±0.07	2020± 22
A	14 [b]	5	311–349	2.50±0.12	2012± 40
B	15 [c]	6	328–370	2.06±0.15	1991± 52
Fibre	13	13	299–329	3.23±0.07	1939± 21
	16	11	303–329	3.78±0.15	2025± 46
	17	13	301–335	2.95±0.34	1889±125

[a] Residue of run 6.

[b] Sample residue of a previous vaporization of about 7.1% of the original weight.

[c] Residue of run 5.

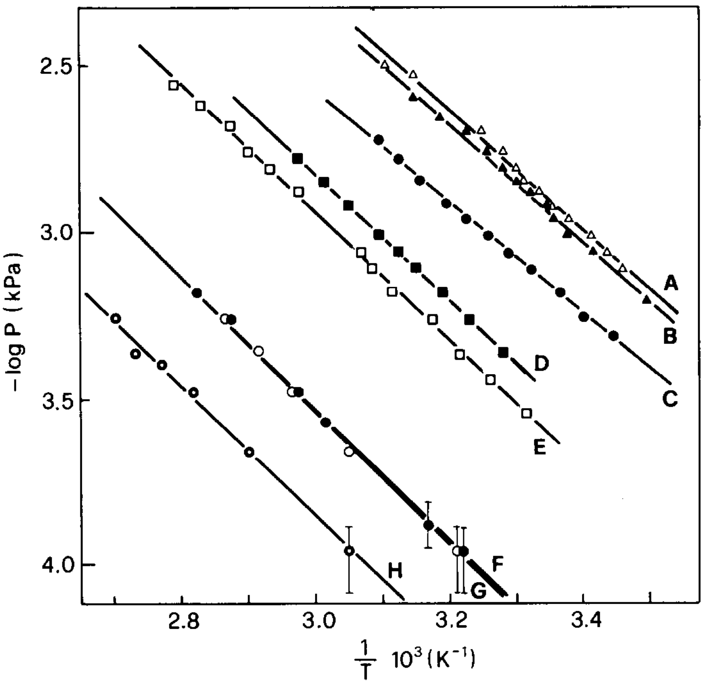

Fig. 2. Crystallization water vapour pressure over RbDC crystal. (A) run 2; (B) run 3; (C) run 5; (D) run 6; (E) run 10; (F) run 11; (G) run 14; (H) run 15.

zation water molecule. Samples of the RbDC crystal residue of previous vaporizations and the original were studied under vacuum at room temperature for several hours so that the first water molecules are vaporized from the sample. In this case, the residue water is less volatile, and its vaporization enthalpy is slightly higher (about 7 kJ mol^{-1}) than that found in the first step of vaporization.

By reheating the crystal samples it was noted that the vapour pressure over the samples dropped below the instrument sensitivity ($\sim 10^{-4}$ kPa) and increased at about 600 K. A panoramic illustration of the vaporization of a crystal RbDC sample is plotted as log P vs. $1/T$ in Fig. 3.

All the experimental data determined above the m.p. of RbDC (594–596 K) are plotted in Fig. 4 and fitted to a straight line by least-squares, the corresponding equation being

$$\log P(\mathrm{kPa}) = 39.32 \pm 1.33 - (26297 \pm 828)/T \qquad (1)$$

In the same figure the curve from the study of pure DCA vaporization [6] is also plotted. In contrast to that previously observed for NaDC [1], the slope represented by eqn. (1) is greater than that found for pure DCA during this step of the vaporization. There is no simple explanation for this behaviour.

RbDC fibre

In the first step of the experiments (299–335 K) the vaporization

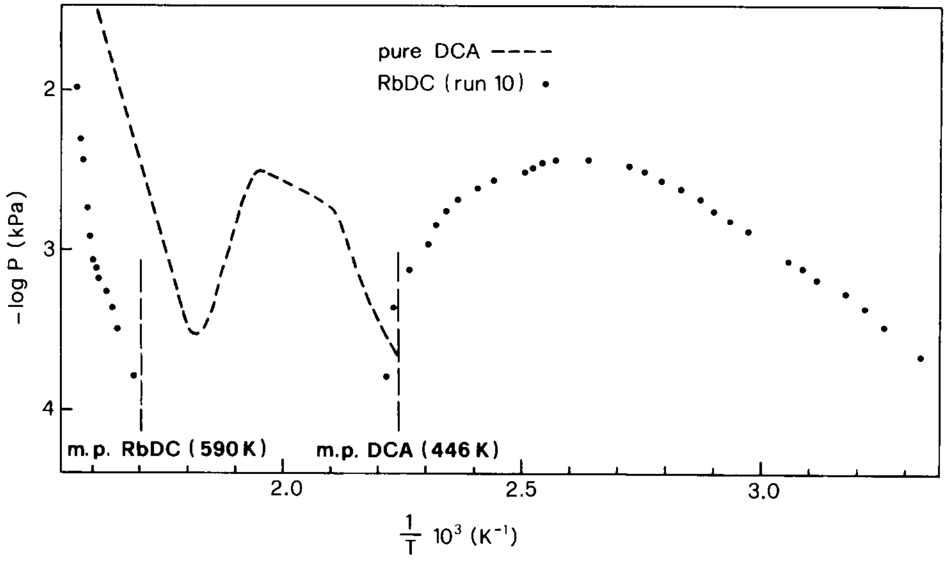

Fig. 3. Typical vaporization behaviour of the RbDC crystal compound compared with pure DCA.

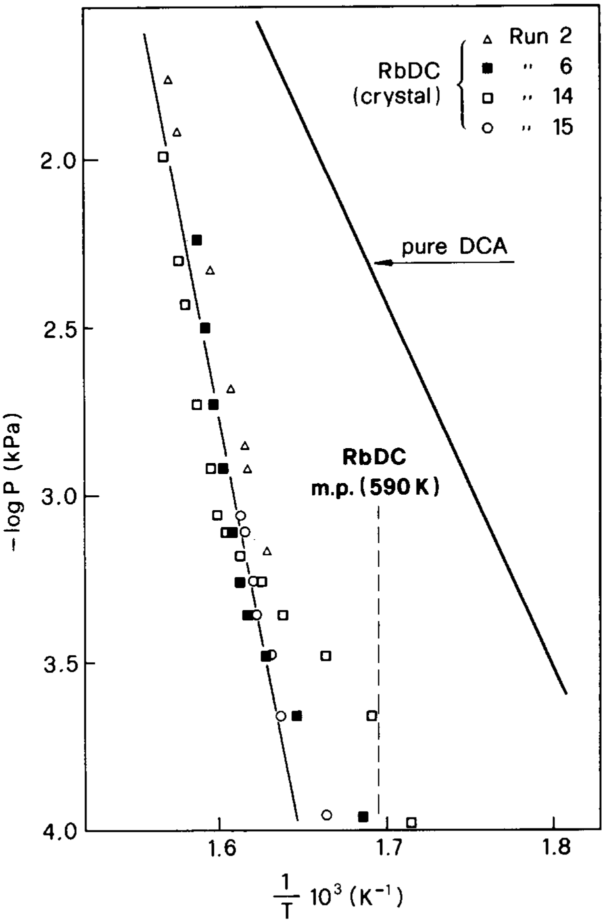

Fig. 4. Vapour pressure of the RbDC crystal above its m.p. (590 K).

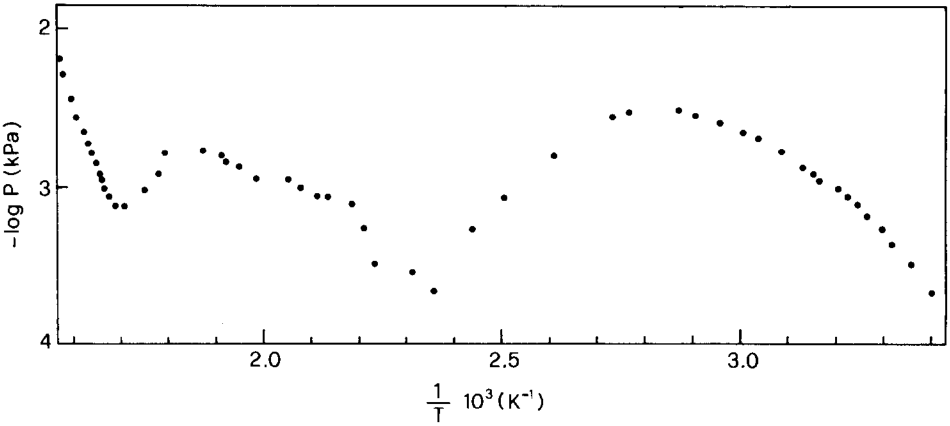

Fig. 5. Typical vaporization of RbDC fibre sample.

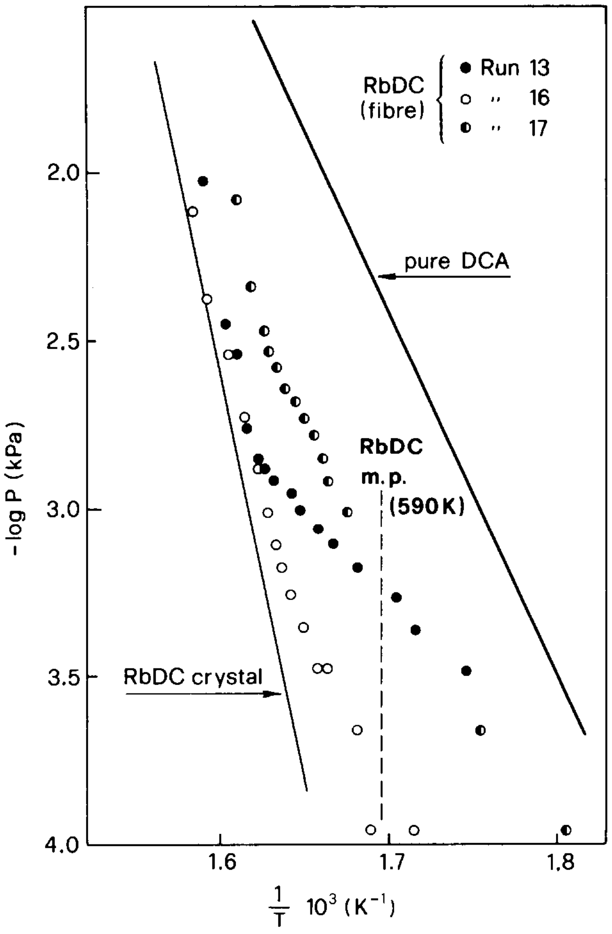

Fig. 6. Vapour pressure of RbDC fibre above its m.p. (590 K).

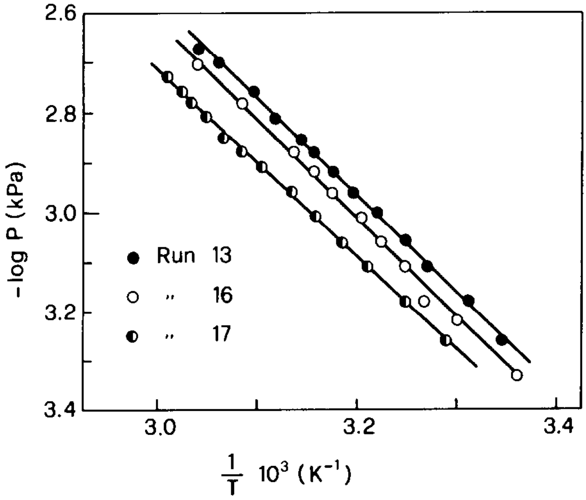

Fig. 7. Crystallization water vapour pressure over RbDC fibre.

behaviour of the fibre samples is similar to that found for the crystal, and the losses are about 6–7% of the original weight. The vaporization of the residue water occurs at a higher temperature than that found for the crystal.

A panoramic illustration of the vaporization behaviour of the RbDC fibre is plotted in Fig. 5. After melting, practically all the crystallization water is vaporized, as seen by the fact that the weight loss of the samples at this temperature is about $10.5 \pm 1.0\%$ and the water is 11.2% its original weight.

The pressure data determined above the melting point of RbDC present a different trend to those obtained for the crystal (see Fig. 6). This could be due to the vaporization of very small amounts of residue water. In fact, when a fibre sample is heated for some hours at temperatures below the melting point (run 16), the behaviour is very similar to that of the crystal. The water pressures measured in the first step of the vaporization runs are plotted in Fig. 7 and reported in Table 2.

The water vaporization enthalpy change derived from a second-law treatment of the data ($\Delta H^0_{320} = 37$ kJ mol^{-1}) is similar to the average of the two values found for the RbDC crystal.

CONCLUSION

The results found in this work show that the vaporization process of crystal and fibre RbDC samples is practically identical. In the first step of their vaporizations the loss of the crystallization water molecules was observed with the second-law enthalpy change $\Delta H^0_{325} = 34$ kJ mol^{-1}. The error associated with this change should not exceed 4 kJ mol^{-1}, taking into account the uncertainties in the temperature determination. In the temperature range of the vaporization of the residue water, the associated vaporization enthalpy of the crystal sample is slightly higher (about 39 kJ mol^{-1}), while for the fibre samples a vaporization tail was observed at a higher temperature. This behaviour shows that the interactions of the water molecules in the 3 RbDC · 10 H_2O asymmetric unit are not equal, confirming previous predictions [2]. It is interesting to note that the vaporization enthalpy of the water from RbDC is much lower than that found for the sodium salt ($\Delta H^0_{318} = 74 \pm 6$ kJ mol^{-1} [1]). This indicates that the water interactions in the latter compound are stronger than those present in RbDC.

As far as the second step of the vaporization is concerned, the rubidium salt does not present an appreciable vapour pressure in the approximate temperature range 450–600 K. In this range the pure acid begins to vaporize and decompose probably also losing a CO_2 molecule. This behaviour is similar to that found for the NaDC [1], confirming the presence of interactions between alkali ions and $-COO^-$ groups in these salts. On increasing the temperature above the melting point of both NaDC and RbDC a decomposition of these compounds occurs. The total vapour pressure measured might be due to the contributions of the various fragments, e.g., CO_2 (which in the acid is lost at a lower temperature), alkali metal and/or alkali-containing molecules, and, possibly, other decomposition products.

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