STUDY OF THE 4:1 INCLUSION COMPOUND BETWEEN DEOXYCHOLIC ACID AND (E)-*p*-DIMETHYLAMINOAZOBENZENE BY VAPOUR PRESSURE MEASUREMENTS

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ABSTRACT

Vaporization studies on pure (E)-*p*-dimethylaminoazobenzene (hereafter indicated as DAB) and the DAB-choleic acid (DCADAB) were accomplished by means of the torsion effusion method. The pressure of the vapour in equilibrium with the solid phase was determined for DAB as

$$\log P(\text{kPa}) = (15.05 \pm 0.18) - (6887 \pm 500)/T$$

and by the second-law treatment of the vapour pressure data a $\Delta H_{381}^0 = 132 \pm 8$ kJ mol^{-1} was obtained for DAB vaporization from the pure compound.

Since the tensimetric data of DCADAB lie at the limit of the instrument's working range only a rough value of $\Delta H_{435}^0 = 138$ kJ mol^{-1} was obtained for DAB vaporization from DCADAB. This finding agrees with the strong DAB–DCA interactions found in the DCADAB crystal structure.

INTRODUCTION

Vaporization studies on orthorhombic inclusion compounds of the "channel" type formed by 3α, 12α-dihydroxy-5β-cholan-24-oic acid (deoxycholic acid, hereafter indicated as DCA) and some aromatic hydrocarbons have already been carried out [1–3]. The main purpose of these studies is to determine which molecules can be included preferentially in the DCA host lattice in order to establish an "affinity scale" between DCA and guest molecules, very useful in the possible applications of the DCA inclusion compounds, termed choleic acids [4].

Since vapour pressure measurements allow one to obtain the enthalpy changes (ΔH_r^0) associated with the release of guest molecules from the choleic acid crystals, it is possible to obtain information on the strength of the host–guest interactions. DCA forms with DAB a 4:1 choleic acid which crystallizes in the orthorhombic $P2_1 2_1 2_1$ space group, as do the choleic acids previously investigated [1–3]. The DCADAB crystal structure was solved by X-ray methods coupled with van der Waals energy calculations which permit

location of the guest molecule [5,6]. Only one possible arrangement was found for the DAB molecule. The DCADAB crystal packing (see Fig. 1) is common to the choleic acids containing acetic and palmitic acid, acetone, ethyl methyl ketone, diethyl ketone, chloroacetone and acetophenone [4] and populates the A minimum of the choleic acids α group [7]. Strong host–guest interactions freeze the DAB molecule in the channels of the host lattice and are responsible for the remarkable stability of DCADAB, reflected by its high melting point, about 33 K higher than that of the DCA.

EXPERIMENTAL

Materials

DCA was obtained from Merck (99% pure) and was used without further purification. DAB, purchased from Fluka (m.p. 388–390 K), was crystallized
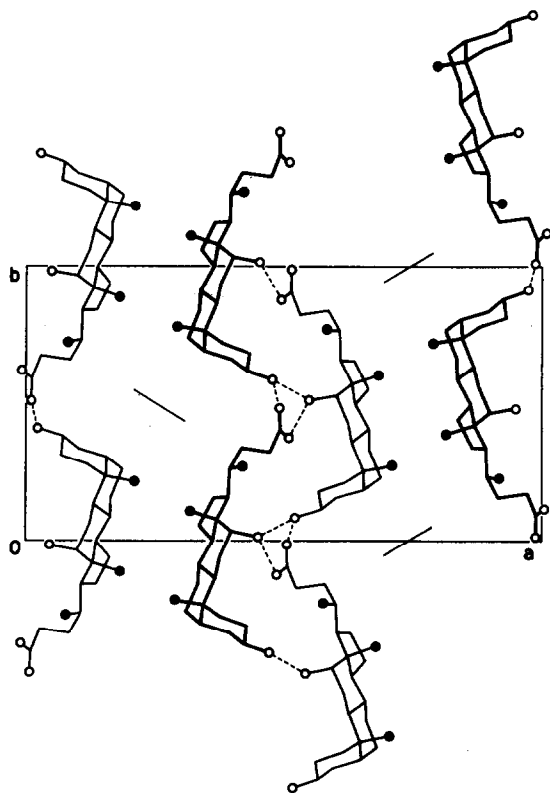

Fig. 1. DCADAB crystal packing view along c. (●) Methyl groups, (○) oxygen atoms. (— — —) Hydrogen bonds, (———) projection of the DAB molecular planes.

several times from ethanol (Merck, Uvasol). DCADAB was prepared by adding the azo dye in excess to a hot ethanolic solution of DCA.

Prismatic orange crystals of DCADAB, grown by very slow evaporation (m.p. 479–480 K), were washed with benzene in order to remove excess DAB (DCA and DCADAB are practically insoluble in benzene). Their composition was checked by density and ^{1}H NMR measurements. The density, measured by flotation in n-hexane and carbon tetrachloride (1.17 g cm^{-3}), was in agreement with that calculated from the unit cell constants ($a = 25.676$, $b = 13.731$, $c = 7.160$ Å) assuming a DCA : DAB ratio of 4 : 1 (1.18 g cm^{-3}). The same ratio was found by NMR using $(CD_3)_2SO$ as solvent.

Methods

The X-ray data were recorded on a Syntex P2$_1$ automated diffractometer with graphite-monochromatized Mo$K\alpha$ radiation and on a precession camera with Cu$K\alpha$ radiation.

The melting points were measured at atmospheric pressure by means of a Leitz 350 heating plate.

The amount of DAB in the crystals of DCADAB after vaporization was determined by its molar extinction coefficient at $\lambda_{max} = 410$ nm, since no appreciable change was found at this wavelength either for DAB or DCADAB in ethanolic solutions. UV spectra were recorded at room temperature with a Varian Cary 219 spectrophotometer.

The study of the vaporization behaviour and the vapour pressure measurements were carried out by a torsion effusion apparatus. The method and experimental assembly have been described in a previous work [8]. At each experimental temperature the vapour pressure was determined by measuring the torsion angle, α, of the torsion wire from which the effusion cell is suspended by the well known equation $P = K\alpha$ where K includes the length and the torsion constant of the tungsten torsion wire, the areas and the distances from the rotation axis of the two effusion holes and empirical correction factors [9]. The K value was determined experimentally by vaporizing standard pure elements (Zn, Pb) with known vapour pressure [10].

RESULTS

Before studying the DCADAB system, the vapour pressure of pure DAB was measured since no tensimetric data of this compound are reported in the literature.

Two torsion assemblies, differing in the diameter of the torsion wire and in the area of the effusion holes in the cell, were used.

For each run the data were treated by the method of least squares in order to obtain the corresponding pressure–temperature equations. Weighting the slopes and intercepts proportionally to the number of points the following equation for the overall temperature range 356–407 K was selected

$$\log P(\text{kPa}) = 15.05 \pm 0.18 - (6887 \pm 500)/T$$

where the associated errors are estimated considering the uncertainties in the temperature measurements. This equation is plotted in Fig. 2 with the experimental values. From the slope of this equation the second-law vaporization enthalpy change $\Delta H^0_{381} = 132 \pm 8$ kJ mol^{-1} was derived.

The DCADAB vaporization was studied employing the same assemblies used for pure DCA. Some runs were carried out with a very thin (~ 15 μm diameter) torsion wire in order to increase the instrument's sensitivity and to observe the first step of the sublimation process since the vapour pressure values over DCADAB, under about 330–340 K, are close to the sensitivity limit of the conventional assembly. Figure 3 reports the data obtained studying this step of vaporization. It was observed that the first pressure values are not reproducible and that the values measured above about 450 ± 5 K show slopes similar to that obtained studying pure DCA [1]. In particular under this temperature, during an isothermal run, the vapour pressure decreases as a function of time and the extrapolation at zero time gives results that are not very reliable taking into account the furnace hysteresis. Notwithstanding this, the greater part of the tensimetric data reported in Fig. 3 above about 450 K was obtained from the extrapolation of isothermal vaporization (see Fig. 4), but, of course, the few and rather
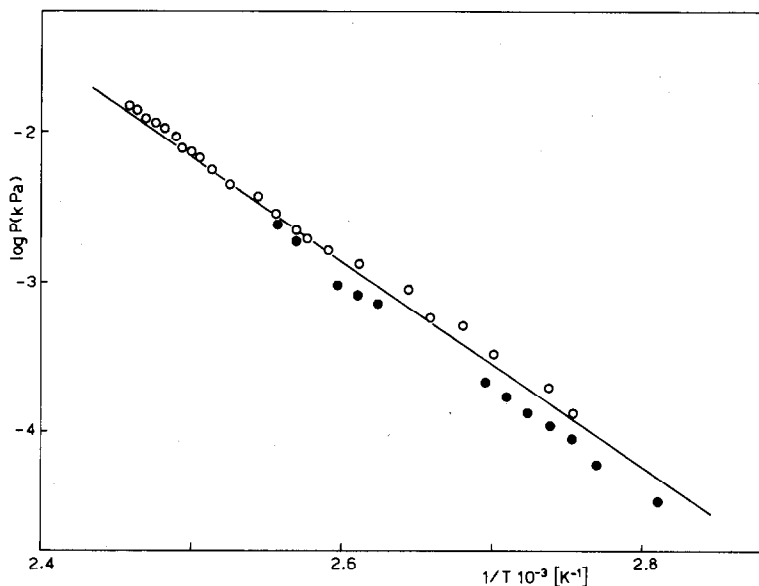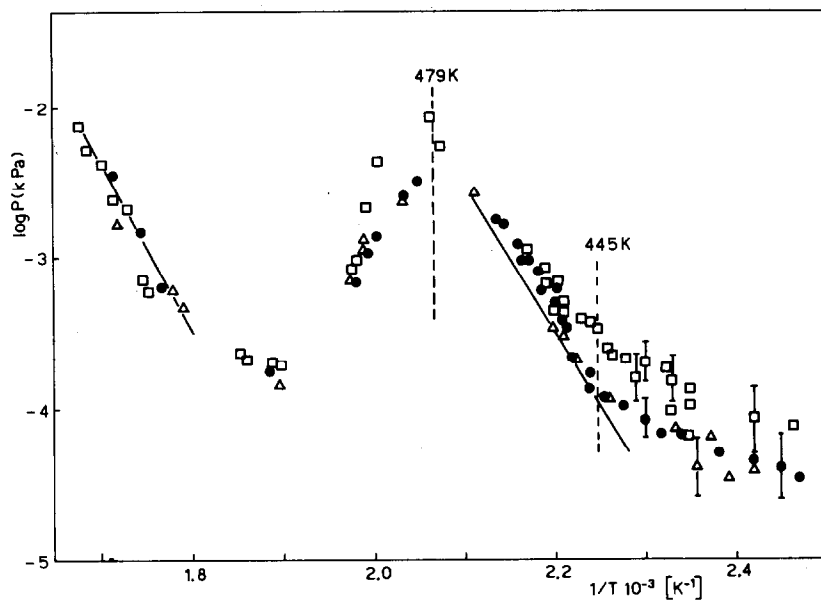

Fig. 2. Vapour pressure of pure DAB.
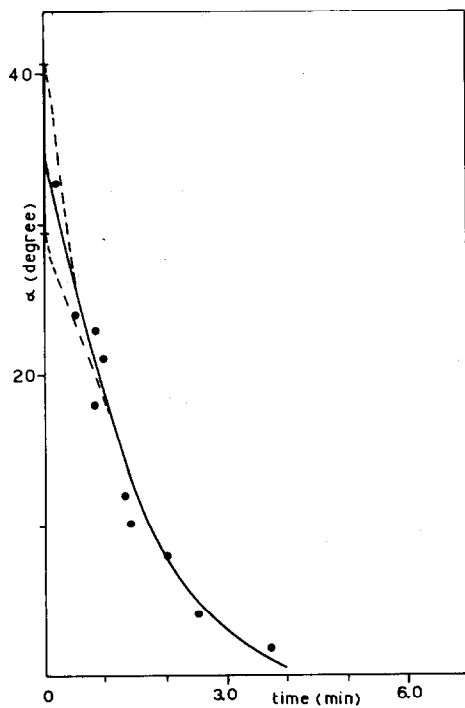
Fig. 3. Vaporization behaviour of DCADAB.

Fig. 4. Torsion angles of DCADAB as a function of time at 450 K.

unreliable results cannot be utilized to derive a pressure–temperature equation and a vaporization enthalpy of the DAB from DCADAB.

Weight losses and analyses of samples heated at about 460–470 K showed that, in addition to DAB, a large amount of DCA also vaporizes. This observation suggests that below 450 K the DAB near the surface of the crystals vaporizes, but because of the strong DAB–DCA interactions inside the channels and a probable collapsing of the DCA lattice, the DAB diffusive process through the crystal surface is slow so that the DAB fugacity decreases. In this step, the surface shell of the crystals is formed by almost pure DCA and melts at about 450 K near the melting point of pure DCA (~ 446 K). Above 453 K the vapour pressure of the sample yields values similar to those of pure DCA, owing to the DCA composition and to release of a water molecule [11]. A small amount of DAB, that diffuses more easily through the melted surface, contributes to a slight increase in the vapour pressure of pure DCA. As the temperature rises to 479 K (m.p. of DCADAB) the sample core also melts and the residue DAB present in the sample completely vaporizes. At this stage the sample is composed almost entirely of DCA and the vaporization behaviour is similar to that found in the study of pure DCA [1].

CONCLUSION

The vaporization behaviour of pure DAB and of DAB released from DCADAB was studied. The corresponding enthalpy change for pure DAB was determined by means of tensimetric data. Unfortunately, that of DAB released from DCADAB was not measured because the tensimetric data lie at the limit of the working range of the instrument. Their values decrease as a function of time since the amount of DAB in the crystal surface progressively decreases. Therefore, a reliable value of the vaporization enthalpy change associated with the process

$$(DCA)_4 DAB(s) \rightarrow 4DCA(s) + DAB(g) \tag{1}$$
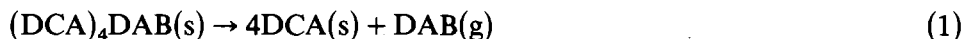
cannot be derived. However, it is possible to obtain an approximate estimate of this value. It is reasonable to suppose that the entropy change of eqn. (1) is comparable with those of the phenanthrene-, 1,2-benzanthracene- and 11,12-benzofluoranthene-choleic acids [2,3] which show similar entropy changes (see Table 1) and that, hence, a rough value of 50 e.u. or more can be assumed. This statement is justified by a comparison of the host–guest interactions in the phenanthrene- and DAB-choleic acids, which show a closer packing for DCADAB [6]. Thus, a value of $\Delta H^0_{435} = 138$ kJ mol^{-1} is calculated, the DAB fugacity being 1.3×10^{-4} kPa at 435 K, the temperature around which most of the experimental points have been determined. By using ΔH^0_{435} for DCADAB together with that for DAB measured in this work the heat of formation of DCADAB is found to be nearly equal to zero.
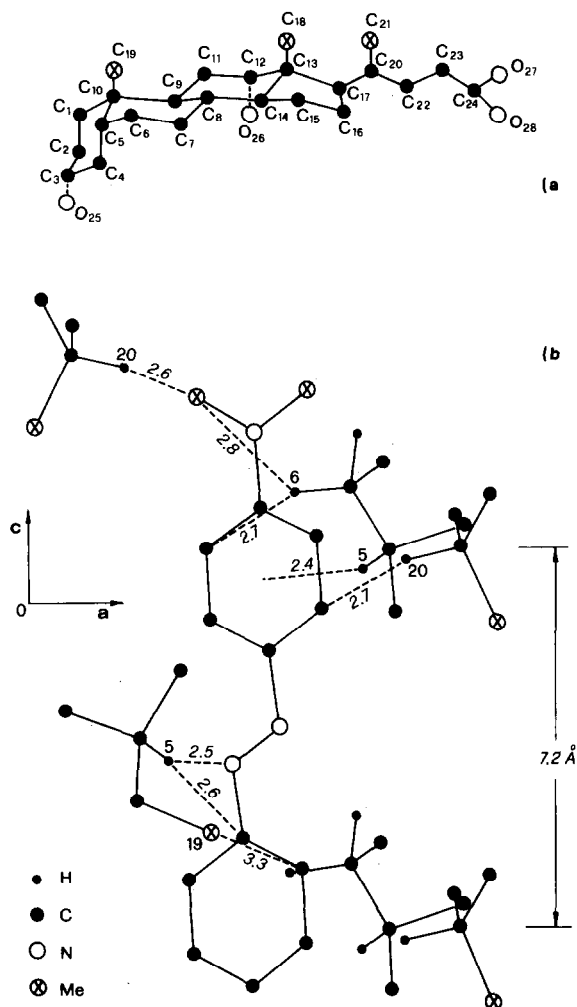
Fig. 5. (a) Atomic numbering of DCA (the hydrogen atoms are omitted); (b) schematic drawing showing the most relevant DCA–DAB interactions (— — —). The hydrogen atoms of DCA have the same numbering as the carbon atoms to which they are attached.

TABLE 1

Thermodynamic parameters of choleic acids (DCA-X) according to the reaction

$DCA_y - X(s) \rightarrow y\,DCA(s) + X(g)$ (X = guest)

X	ΔT (K)	ΔS_T^0 (cal mol^{-1} K^{-1})	ΔH_T^0 (kcal mol^{-1})
Naphthalene	361–419	20.3	17.2 ± 1.2
Styrene	353–414	21.9	13.6 ± 1.2
11,12-Benzofluoranthene	414–454	44.9	29.6 ± 1.4
Phenanthrene	403–441	50.7	30.8 ± 1.4
1,2-Benzanthracene	405–429	48.8	30.1 ± 2.0
DAB	435	50	33

By inspection of Table 1 it may be seen that the ΔH_r^0 value for DCADAB is the highest. This can be expected to occur owing to the shortening of the DCADAB a axis with respect to that of the other choleic acids [1–3], which causes a decrease of the channel cross-sectional area ($\sim 2.8 \times 5.5$ Å). Moreover, the major length of the DAB molecule as compared with that of the other guest molecules gives rise to contact of DAB with a greater number of DCA molecules (Fig. 5). The most relevant contacts are shown in Fig. 5b, where only few atoms of DCA are projected in the ac plane for the sake of clarity [5]. The H_5 atoms play a leading role since the phenyl ring containing the dimethylamino group and the $> C-N=N-$ fragment are firmly anchored to them so that the main interaction between DAB and DCA is due to polarization bonding involving the π charge cloud of DAB. The DAB position, found by means of potential energy calculations [5,6], corresponds to a very sharp minimum, which is the only one with acceptable intermolecular contacts. As a qualitative comparison the minimum energy value for DCADAB and for the phenanthrene-choleic acid are 118 and 113 kJ, respectively. Hence, the minimum energy value of DCADAB is lower than or nearly equal to that of the phenanthrene-choleic acid which is the lowest so far observed. In fact, the number of attachments for DAB is greater than that for the guest molecules of Table 1 (one or two, see ref. 4), since DAB is mainly attached to at least two of the constituents H_5, H_6, H_{20} and C_{19} (see Fig. 5b and ref. 5).

ACKNOWLEDGEMENT

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