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STABILITY OF 11,12-BENZOFLUORANTHENE CHOLEIC ACID DERIVED BY PRESSURE DATA

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ABSTRACT

Vaporization studies on pure 11,12-benzofluoranthene (benzo[*k*]fluoranthene, hereafter referred to as BKF) and the BKF-choleic acid (DCABKF) were performed by using the torsion effusion method. The pressure of the vapor in equilibrium with the condensed phase was determined for BKF as

$$\log P(\text{kPa}) = (11.37 \pm 0.18) - (6257 \pm 77)/T$$

and for DCABKF as

$$\log P(\text{kPa}) = (11.81 \pm 0.44) - (6497 \pm 300)/T$$

By the second-law treatment of the vapor pressure data, $\Delta H^0_{428} = 120 \pm 10$ and $\Delta H^0_{434} = 124 \pm 6$ kJ mole^{-1} were obtained for BKF vaporization from the pure compound and from DCABKF, respectively.

INTRODUCTION

Inclusion compounds of the "channel" type are formed by 3α,12α-dihydroxy-5β-cholan-24-oic acid (deoxycholic acid, hereafter indicated as DCA) with a wide variety of guest molecules and are termed choleic acids. Orthorhombic, tetragonal and hexagonal crystal phases have been studied so far and the crystal structures of some of them have been solved (ref. 1 and references cited therein). Since DCA inclusion compounds have many potential applications, it is very useful to establish an "affinity scale" between DCA and guest molecules in order to foresee both the probability of formation of the choleic acids and which molecules can be preferably occluded. In this connection, it was considered interesting to measure the enthalpy changes (ΔH_r^0) associated with the release of guest molecules from the choleic acid crystals. Therefore, vapor pressure measurements have been

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recently obtained on styrene- [2], naphthalene- [2], phenanthrene- [3] and 1,2-benzanthracene- [3] choleic acids, hereafter referred to as DCASTY, DCANAF, DCAPHE and DCABAN, respectively. All these choleic acids belong to the orthorhombic crystal system, which presents the most powerful clathrating ability.

This paper deals with the study of another orthorhombic choleic acid containing BKF.

EXPERIMENTAL AND RESULTS

DCA was obtained from Merck (99% pure) and was used without further purification. BKF was kindly supplied by Prof. L. Zoccolillo, who determined its purity as greater than 99.95% by gas liquid and high-pressure liquid chromatography. Crystals of DCABKF were grown by slow evaporation from an ethanolic solution. The crystals were subsequently washed with benzene in order to remove the excess of BKF (DCA and DCABKF are practically insoluble in benzene).

The composition of the DCABKF was checked by gas chromatography and proton NMR; the DCA:BKF ratio obtained was 3:1. The melting point, measured at atmospheric pressure by means of a Leitz heating plate 350, was 456–458 K. Powder photographs were taken, using CuK_α radiation, with a Debye–Scherrer camera having a diameter of 114.6 mm, since no suitable single crystals were available. These photographs were very similar to those of DCAPHE, whose crystal structure is known [4]. The DCABKF unit cell constants were derived as $a = 26.8$, $b = 13.6$, $c = 7.2$ Å, which were nearly equal to those of DCAPHE ($a = 26.81$, $b = 13.60$, $c = 7.22$ Å).

The vapor pressure was measured by using the torsion effusion technique. The basis of the method is well known [5]. When the vapor of the sample contained in an effusion graphite cell suspended at a tungsten wire in the isothermal region of the furnace effuses under vacuum, its pressure can be derived by measurement of the torsion angle, α, of the cell from

$$P = \frac{2K\alpha}{a_1 l_1 f_1 + a_2 l_2 f_2}$$

where K is the constant of the torsion wire (30 μm in diameter and 35 cm in length), a_1 and a_2 are the areas of the effusion holes, l_1 and l_2 are the respective distances from the rotation axis and f_1 and f_2 are the corresponding force correction factors. In this study, the force correction factors are derived from the equation [6]

$$\frac{1}{f} = 0.0147\left(\frac{R}{r}\right)^2 + 0.3490\left(\frac{R}{r}\right) + 0.9982$$

where r and R are the radius and the thickness of the effusion hole,

TABLE 1

Constants of the cells employed in the torsion effusion technique

Cell	Orifice area 10^{-3} ($\pm$0.05) cm^2		Moment arms $\pm$(0.01) cm		Freeman's factors [6]	
	a_1	a_2	l_1	l_2	f_1	f_2
A graphite	7.39	7.39	0.845	0.840	0.559	0.562
B graphite	17.67	17.67	0.850	0.850	0.614	0.614
C graphite	31.42	31.42	0.835	0.860	0.780	0.724

respectively. The temperature of the cell was measured by a calibrated chromel–alumel thermocouple inserted in a second cell below the torsion crucible. The experimental assembly was described in a previous work [9].

For this study, three different cells were employed and their geometrical constants are reported in Table 1. In order to test if thermodynamic equilibrium exists within the used cells and that the temperature measurements are reliable, the vapor pressure of a standard element (zinc) was determined and the obtained data compared with those selected by Hultgren et al. [7].

Apparently no vapor pressure for pure BKF has been reported in the literature, so that the vapor pressure of this compound was determined. Its vaporization was studied in the temperature range 403–453 K in two different runs and the experimental data are reported in Fig. 1.

From the least squares treatment of the vapor values, the equation

$$\log P(\text{kPa}) = (11.37 \pm 0.18) - (6257 \pm 77)/T$$

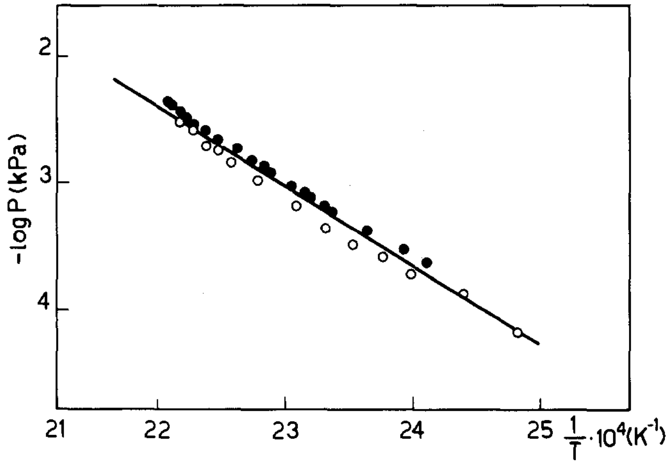

Fig. 1. Vapor pressure–temperature dependence of BKF. ○, Run 81.05 (cell B); ●, run 81.09 (cell C).

TABLE 2

Vapor pressure–temperature equations of DCABKF[a]

Run	Cell	log P(kPa) = $A - B/T$	
		A	B
81.04	A	11.40±0.27	6269±116
81.07	C	11.95±0.90	6544±387
81.14	B	12.07±0.25	6659±111

[a] The associated errors are standard deviations.

where the errors are standard deviations, was derived. From this equation, the second-law enthalpy associated with the vaporization process $\Delta H^0_{428} = 120$ kJ mole^{-1} was derived; the error should not exceed 10 kJ, taking into account the overall errors in the measurements.

The vaporization of DCABKF was carried out in the temperature range 414–454 K. The vapor pressure values were reproducible in the first step of the vaporization process but, when 30–40% of the initial sample had been vaporized, its value decreased.

By considering only the initial points, pressure–temperature dependence was derived by treating the data using the least squares method and the results are reported in Table 2. Considering the slopes and intercepts obtained in each run, the equation

$$\log P(\text{kPa}) = (11.81 \pm 0.44) - (6497 \pm 300)/T$$

was obtained. The associated errors represent the semidispersion of the data and should reflect the estimated uncertainties in the temperature measure-

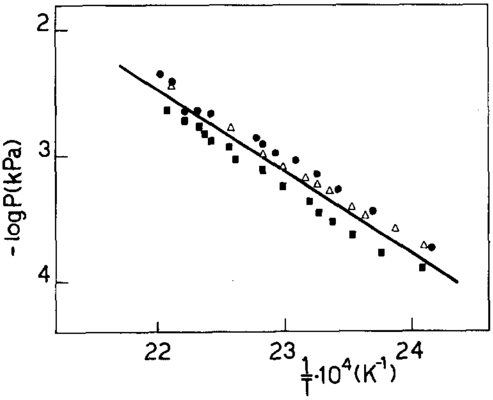

Fig. 2. Vapor pressure–temperature dependence of DCABKF in the first step of the vaporization. ●, Run 81.04; ■, run 81.14; △, run 81.07.

ments and in the calibration constants. The pressure data are plotted as a function of temperature in Fig. 2. From the slope, the second-law $\Delta H^0_{434} = 124 \pm 6$ kJ mole^{-1} was derived. At the end of the vaporization of the guest, the vapor pressure of pure DCA was observed [2].

The contribution of the partial pressure of pure DCA to the total vapor pressure is practically negligible in the temperature range covered by our measurements.

CONCLUSIONS

From vapor pressure data, the vaporization enthalpy change of pure BKF and DCABKF were derived. Combining these values, it was found that the heat of formation of DCABKF is very small (4 ± 16 kJ mole^{-1}). It was also noted that the guest in DCABKF is at near unit activity in the first step of vaporization, but its value decreases during its vaporization. This effect could be ascribed to the collapse of the DCABKF canals, which empty during the releasing of the guest molecules, so that the remaining occluded molecules are trapped and decrease their fugacity.

The orthorhombic choleic acids give rise to four packing motifs, corresponding to as many minimum regions in the potential energy calculations

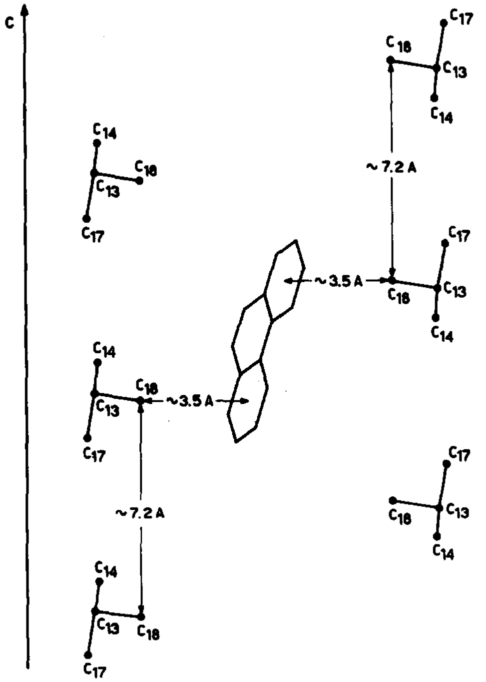

Fig. 3. A schematic diagram showing the interactions between C_{18} methyl groups and phenanthrene. The atomic numbering of steroids is adopted.

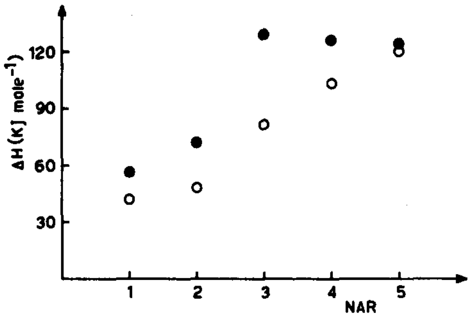

Fig. 4. Enthalpy changes associated with the release of the guest molecule from choleic acid (●) and with the vaporization of the pure guest molecules (○) as a function of the increasing number of aromatic rings (NAR).

performed for the crystals [8]. One of these regions, indicated as B, is populated by choleic acids, as DCASTY, DCANAF, DCAPHE and DCABAN, including aromatic hydrocarbons, which are sandwiched between side chains and rings D of DCA molecules.

The lattice parameters of DCABKF and the close similarity of its X-ray powder diagram to that of DCAPHE allow assignment of DCABKF choleic acid to the B minimum region of the α structures. The strongest interactions between DCA and guest molecules, in the case ofthe B region choleic acids, are due to C_{18} methyl groups of DCA and to the π charge cloud of the aromatic hydrocarbon. The number of C_{18} engaged depends on the length of the aromatic hydrocarbon (see Fig. 3 for explanation). It is reasonable to suppose that styrene and naphthalene are bound to one C_{18} methyl group, whereas phenanthrene, 1,2-benzanthracene and BKF are bound to two C_{18} methyl groups. In fact, the greater length of 1,2-benzanthracene and BKF with respect to phenanthrene is not sufficient to permit further interactions with other C_{18}, which are about 7 Å away from those engaged with phenanthrene. This hypothesis is supported by the ΔH_r values reported in Fig. 4, which shows a very similar behaviour for DCASTY and DCANAF on the one hand and for DCAPHE, DCABAN and DCABKF on the other. Moreover, as expected, the vaporization enthalpy change of the pure guest molecules increases with the number of condensed rings (see Fig. 4).

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