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Study of the Stability of the Phenanthrene- and 1,2-Benzanthracene-Choleic Acids by Vapor Pressure Measurements

Daniela Ferro, Patrizia Imperatori, and Claudio Quagliata*

Istituto di Chimica Fisica, Università di Roma, 00185 Rome, Italy

The stability of the phenanthrene- and 1,2-benzanthracene-choleic acids (DCAPHE and DCABAN, respectively) was studied by measuring their vapor pressure by means of the torsion-effusion method. The temperature dependence of the gaseous guests over their channel complexes was determined: DCAPHE, log P(kPa) = (13.09 ± 0.50) - (6740 ± 300)/T; DCABAN, log P(kPa) = (12.46 ± 0.70) - (6600 ± 400)/T. From the second-law vaporization enthalpy change, the enthalpy of the reaction $3DCA(s) + X(g) \rightarrow (DCA)_3X(s)$ was derived, where DCA and X represent deoxycholic acid and aromatic hydrocarbon, respectively. The results are compared with those obtained previously for similar choleic acids containing styrene and naphthalene.

Introduction

$3\alpha,12\alpha$-Dihydroxycholanic acid (deoxycholic acid, to be abbreviated as DCA hereafter; see Figure 1) gives rise to crystalline inclusion compounds of the "channel" type with a wide variety of molecules. Orthorhombic, tetragonal, and hexagonal crystals, named choleic acids, have been obtained so far and the crystal structures of some of them have been solved (*1*). Most of the choleic acids belong to the orthorhombic system, characterized by an assembly of DCA bilayers (host lattice) and by empty spaces between them, in which guest molecules can be accommodated.

In order to establish the affinity between DCA and enclathrated molecules, we first undertook a study of the stability of some orthorhombic choleic acids, containing aromatic hydrocarbons, by means of vapor pressure measurements. Some results on the styrene- and naphthalene-choleic acids (abbreviated as DCASTY and DCANAF, respectively) have been previously reported (*2*). This paper deals with the phenanthrene- and 1,2-benzanthracene-choleic acids (DCAPHE and DCABAN, respectively; see Figure 1) with the aim of ascertaining the trend of the host-guest interaction energy by increasing the number of the condensed rings. The crystal structure of DCAPHE is known (*3*). In order to derive the formation enthalpy of DCABAN, we measured the vapor pressure of 1,2-benzanthracene. In the case of DCAPHE the vapor pressure of the liquid aromatic hydrocarbon is known (*4*, *5*).

Experimental and Results

Commercially available DCA (Merck Co., 99% pure), phenanthrene (Carlo Erba Co., 99% pure), and 1,2-benzanthracene (Fluka Co., 99.9% pure) were used.

Prismatic crystals of DCAPHE (colorless) and DCABAN (pale yellow), elongated along c, were grown from ethanolic solutions by slow evaporation. Their unit-cell dimensions, together with some other relevant data, are reported in Table I. The unit-cell dimensions and the space group of DCAPHE and DCABAN were derived by Weissenberg photographs, using Cu Kα radiation. Their densities were measured by flotation in cyclohexane and carbon tetrachloride. The melting points were determined at atmospheric pressure by a Leitz 350 heating plate.

The vapor pressures of pure phenanthrene and 1,2-benzanthracene and of DCAPHE and DCABAN were measured by using the torsion-effusion technique. The basis of the method and the experimental procedure have been reported previously (*7*, *8*). The vapor pressure of the sample is measured by the torsion angle α of the effusion cell by employing the relation $P = 2K\alpha/(a_1l_1f_1 + a_2l_2f_2)$, where K is the torsion constant of the tungsten wire (0.346 ± 0.003 dyn cm rad^{-1}), 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 derived from the equation (*9*) $1/f = 0.0147(R/r)^2 + 0.3490(R/r) + 0.9982$, where r and R are the radius and the thickness of the effusion hole, respectively. The temperature of the cell was measured by a calibrated chromel-to-alumel thermocouple inserted in a second cell placed below the torsion cell. The measurements were carried out by using four cells with different geometrical constants (see Table II). Using these cells, we measured the vapor pressure of pure zinc as the standard element.

The obtained data were compared with those selected by Hultgren (*10*) in order to test if the thermodynamic conditions, the temperature measurements, and the used geometrical factors are reliable.

Before studying the orthorhombic channel complexes, we measured the vapor pressures of the pure guests. As concerns the phenanthrene, we carried out one run in the temperature range 317-362 K, obtaining the following equation:

$$\log P(\text{kPa}) = (9.37 \pm 0.21) - (4204 \pm 72)/T \quad (1)$$

where the reported errors are the standard deviations. This equation is plotted in Figure 2 for comparison with the slopes derived from vapor data measured over the melted phase.

As regards the 1,2-benzanthracene, apparently no vapor pressure values have been reported in the literature up to now, so that pressures of this compound have been determined in the temperature range 377-426 K by using two different cells. The data are plotted as log P vs. $1/T$ in Figure 3. The least-squares treatment of the results yields the following equations:

$$\log P(\text{kPa}) = (10.71 \pm 0.59) - (5404 \pm 239)/T \quad \text{(run 1)} \quad (2)$$

$$\log P(\text{kPa}) = (10.65 \pm 0.13) - (5441 \pm 55)/T \quad \text{(run 2)} \quad (3)$$

where the errors are standard deviations. Weighting the corresponding slopes and intercepts proportionally to the number of the experimental points, we propose the following equation for the 1,2-benzanthracene vaporization process:

$$\log P(\text{kPa}) = (10.66 \pm 0.50) - (5430 \pm 200)/T \quad (4)$$

The associated errors were estimated by taking into account the uncertainties associated with the temperature measurements and the calibration factors.

DCAPHE. The vaporization was investigated in the temperature range 403-441 K by using three different cells. In

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Table I. Some Crystal Data of DCAPHE and DCABAN

a, Å	b, Å	c, Å	Z	d_c, g cm^{-3}	d_m, g cm^{-3}	space group	host/guest	mp, K
				DCAPHE				
26.81 ± 0.04	13.60 ± 0.02	21.66 ± 0.03[a]	4	1.14 ± 0.02	1.15 ± 0.02	$P2_12_12_1$	3:1	457 ± 2
				DCABAN				
26.99 ± 0.04	13.69 ± 0.02	7.29 ± 0.01	4	1.15 ± 0.02	1.15 ± 0.02	$P2_12_12_1$	3:1[b]	473 ± 2

[a] The translation period of the DCA molecules along c is 7.22 Å. [b] This value was reported in ref 6.

Table II. Physical Constants of the Used Torsion-Effusion Cells

		cell A	cell B	cell C	cell D
10^3(orifice area),[a] cm^2	semicell 1	49.09	31.41	7.09	17.67
	semicell 2	49.09	31.41	7.38	17.67
force correction factors[b]	semicell 1	0.786	0.780	0.558	0.614
	semicell 2	0.795	0.724	0.562	0.614
moment arm,[c] cm	semicell 1	0.83	0.84	0.85	0.85
	semicell 2	0.90	0.86	0.84	0.86

[a] ±0.05 × 10^{-3} cm^2. Measured by photographic enlargement. [b] See text. [c] ±0.01 cm.

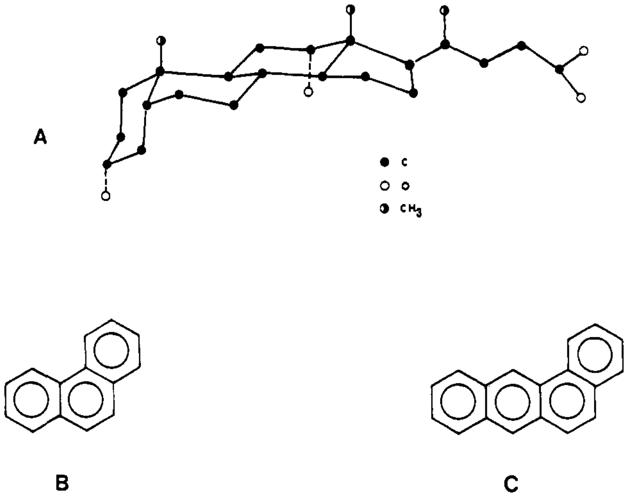

Figure 1. A–C refer to DCA, phenanthrene, and 1,2-benzanthracene molecules, respectively.

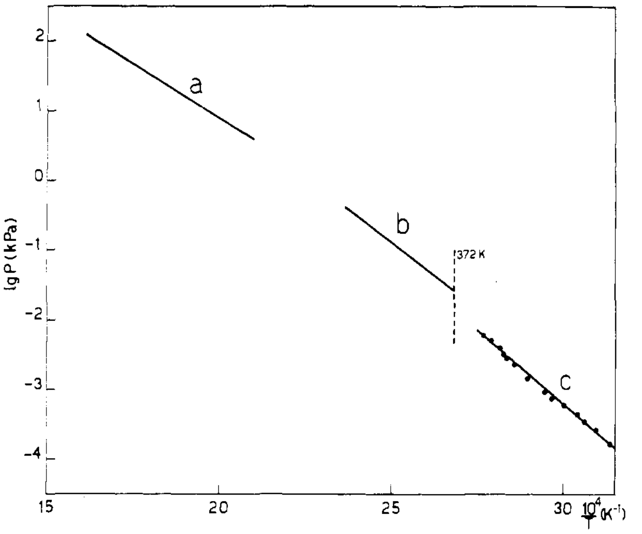

Figure 2. Vapor pressure of phenanthrene: (a) ref *5*; (b) ref (*4*); (c) our data.

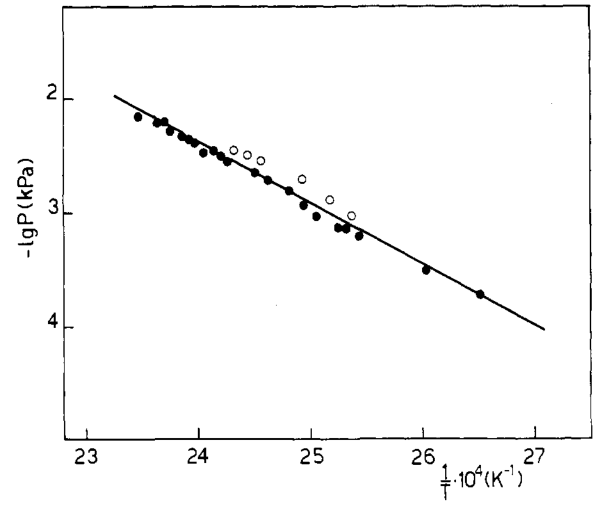

Figure 3. Vapor pressure of 1,2-benzanthracene: open and black circles refer to runs 1 and 2, respectively.

Table III. Pressure-Temperature Equation of DCAPHE and DCABAN Measured in the First Step of the Vaporization

run	cell	temp range, K	log P(kPa) = $A - B/T$[a] A	 B
		DCAPHE		
A.23	B9	403–424	12.98 ± 0.39	6713 ± 160
A.26	B8	403–403	13.55 ± 0.21	6976 ± 89
A.30	D12	407–441	12.05 ± 0.47	6322 ± 199
A.33	C11	404–438	13.20 ± 0.48	6694 ± 204
A.34	A12	408–440	14.03 ± 0.23	7131 ± 99
A.39	A9	406–430	12.82 ± 0.27	6666 ± 114
		DCABAN		
E.12	D9	410–429	12.66 ± 0.19	6644 ± 181
E.16	B8	405–418	11.60 ± 0.59	6279 ± 241
E.20	B10	410–421	13.08 ± 1.04	6896 ± 431

[a] The associated errors are standard deviations.

these measurements are taken into account only the data measured in the first step of the vaporization when the composition of the choleic acid is practically constant. In fact, when the guest in the sample is vaporized for about 40% of the original amount, its activity decreases rapidly. Even if the number of the vapor pressure values is small, the pressure–temperature equations for each run were derived by the least-squares treatment of the data and the corresponding equations are reported in Table III. When all the guest was vaporized from the channel complex, the residue showed a vaporization behavior similar to that found for pure orthorhombic DCA (*2*).

DCABAN. The vaporization of 1,2-benzanthracene from DCABAN was studied in the temperature range 405–429 K in three runs. The procedure in the measurements is similar to that followed for the DCAPHE channel complex. The obtained results, treated by the least-squares method, are reported in Table III. Also for this choleic acid the residue of the vaporization practically consists of pure orthorhombic DCA. In both cases, in the temperature range covered by the vapor pressure measurements of the guest, the contribution of DCA to the total vapor is negligible (*2*).

Discussion

From the corresponding pressure–temperature equations, the second-law sublimation enthalpies of pure phenanthrene and 1,2-benzanthracene, $\Delta H°_{340}$ = 80 ± 2 kJ mol^{-1} and $\Delta H°_{351}$

Table IV. Enthalpy Changes of Reactions 7 and 8[a] of the Studied Choleic Acids

system	ΔT, K	$\Delta H^\circ_T(7)$, kJ	$\Delta H^\circ_{298}(8)$, kJ	ref
DCASTY	353-414	57 ± 5	15 ± 5	*2*
DCANAF	361-419	72 ± 5	24 ± 5	*2*
DCAPHE	403-441	129 ± 6	49 ± 8	this work
DCABAN	405-429	126 ± 8	22 ± 10	this work

[a] See text.

= 104 ± 2 kJ mol^{-1}, respectively, were derived. Our value of the phenanthrene sublimation enthalpy is in agreement with the value determined by Osborn and Douslin (*4*) in the temperature range 373-423 K, $\Delta H^\circ_{398} = 70$ kJ mol^{-1}, and with the value $\Delta H^\circ_{553} = 64$ kJ mol^{-1} reported by Mortimer and Murphy (*5*) (temperature range, 476-630 K), both determined over the liquid phase, considering that this compound melts at 372 K (*4*) and the corresponding ΔH°_{372} (fus) = 16 kJ mol^{-1} (*4*).

From the intercepts and slopes summarized in Table III the following pressure-temperature equations for DCAPHE and DCABAN were derived:

$$\log P(\text{kPa}) = (13.09 \pm 0.50) - (6740 \pm 300)/T \qquad (\text{DCAPHE}) \quad (5)$$

$$\log P(\text{kPa}) = (12.66 \pm 0.70) - (6600 \pm 400)/T \qquad (\text{DCABAN}) \quad (6)$$

where the errors are estimated on the basis of the uncertainties associated with the measurements. From these equations the enthalpy changes of the reaction

$$\text{DCA}_3\text{X(s)} \rightarrow 3\text{DCA(s)} + \text{X(g)} \qquad (7)$$

were derived, where X represents the guest. The values $\Delta H^\circ_{417} = 129 \pm 6$ kJ and $\Delta H^\circ_{422} = 126 \pm 8$ kJ were determined for DCAPHE and DCABAN, respectively. Considering the temperature dependence of these ΔH°_T negligible and using the sublimation enthalpy of pure guests, we derived the standard enthalpy changes of the condensed-phase reaction:

$$3\text{DCA(s)} + \text{X(s)} \rightarrow \text{DCA}_3\text{X(s)} \qquad (8)$$

The values obtained are $\Delta H^\circ_{298} = 49 \pm 8$ kJ and $\Delta H^\circ_{298} = 22 \pm 10$ kJ for DCAPHE and DCABAN, respectively. On the basis of these data and those reported previously on some choleic acids (*2*), a comparison is possible between them. The most relevant data for DCASTY, DCANAF, DCAPHE, and DCABAN are summarized in Table IV, where $\Delta H^\circ_T(7)$ is the enthalpy change associated with the releasing of the guest molecule from the crystal of the choleic acid, according to eq 7, and ΔH°_{298} (8) is the enthalpy change for production of 1 mol of the choleic acid crystal according to eq 8. All four of those choleic acids belong to the B energy minimum region of the α group (*11*), owing to the values of the crystallographic parameters. In this case the guest molecules are sandwiched within channels of rectangular cross section, with edges of about 5.0 × 7.1 Å. The longest edge of the rectangle is formed by ring D and part of the side chain of DCA (see Figure 4). From this edge protrudes the C_{18} methyl group, which gives rise to the main host-guest interaction. Two methyl groups, pointing approximately toward the centers of the two outer phenanthrene aromatic rings, are engaged in "polarization bonding" with the π charge cloud (*3*). These two methyl groups belong to two DCA molecules related by a 2_1 axis. Steric considerations show that styrene and naphthalene, formed by one and two aromatic rings, interact with just one C_{18} methyl group; phenanthrene and 1,2-benzanthracene, formed by three and four aromatic rings, interact with two C_{18} methyl groups. In fact, although 1,2-benzanthracene has one more ring, the increased length of this molecule, as compared with that of phenanthrene, is not sufficient to bind other C_{18} methyl groups, which are far from those already engaged. Thus, the $\Delta H^\circ_T(7)$ of Table IV are consistent with this explanation, since the values for DCASTY and DCANAF, on one hand, and those for DCAPHE and DCABAN, on the other, are of the same order of magnitude.

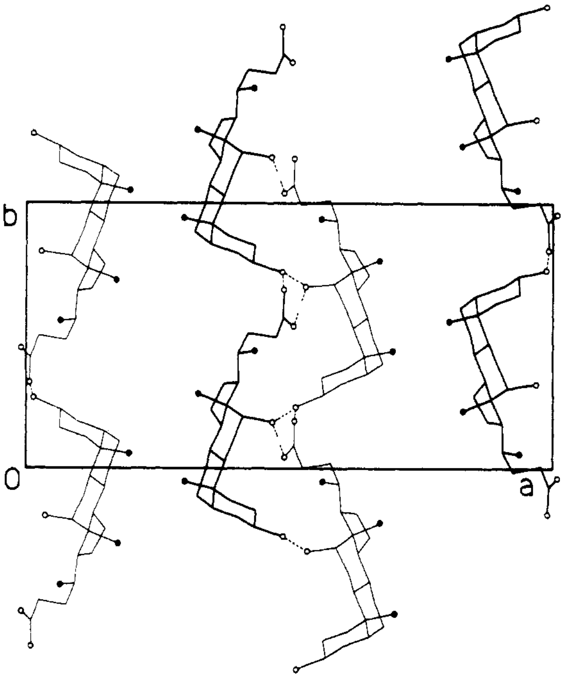

Figure 4. Crystal packing corresponding to the B energy minimum region of the structures viewed along *c*. Black and open circles refer to methyl groups and oxygen atoms, respectively.

Further work is in progress in order to study both choleic acid with larger aromatic hydrocarbons and choleic acids populating the energy minimum regions A and B' of the α and β structures, respectively (*11*).

Registry No. DCAPHE, 16723-86-7; DCABAN, 5928-80-3.

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