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STUDY OF THE PALMITIC–CHOLEIC ACID BY VAPOUR PRESSURE MEASUREMENTS AND VAN DER WAALS' ENERGY CALCULATIONS

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ABSTRACT

Vaporization studies in pure palmitic acid ($CH_3(CH_2)_{14}COOH$; hereafter referred to as PAL) and the PAL–choleic acid (DCAPAL) were accomplished by resorting to the torsion effusion method. The vapour pressure in equilibrium with the condensed phase was determined for PAL as

$$\log P\ (\text{kPa}) = (9.77 \pm 0.16) - (4677 \pm 62)/T$$

and for DCAPAL as

$$\log P\ (\text{kPa}) = (25.28 \pm 0.56) - (12355 \pm 224)/T$$

By the second-law treatment of the vapour pressure data, $\Delta H^0_{379} = 89 \pm 2$ and $\Delta H^0_{445} = 237 \pm 5$ kJ mol^{-1} were derived for PAL vaporization from the pure compound and from DCAPAL, respectively.

Moreover, van der Waals' energy calculations were performed on DCAPAL to obtain an empirical correlation between the host–guest interaction energy and the enthalpy change associated with the release of PAL from the crystal of DCAPAL.

INTRODUCTION

3α,12α-Dihydroxy-5β-cholan-24-oic acid (deoxycholic acid, $C_{24}H_{40}O_4$; hereafter referred to as DCA) is a typical bile acid, whose main property is its great clathrating ability. DCA forms well-defined molecular compounds, termed choleic acids, with guest molecules such as, for example, fatty acids, aliphatic and aromatic hydrocarbons, alcohols, esters, ketones, aminoazodies and vinyl monomers.

Choleic acids are inclusion compounds of the "channel" type, in which guest components are trapped in channels formed by the host lattice of the DCA molecules. Known choleic acids crystallize in orthorhombic, hexagonal and tetragonal phases. The orthorhombic ones are the most interesting and some of these, including aromatic hydrocarbons or their derivatives, were previously studied [1–4] by means of vapour pressure measurements, in order to obtain information about their stabilities. The results allowed us to

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explain the observed stabilities on the basis of choleic acid structures and the number of aromatic rings in the guest molecule.

Our purpose is now to investigate the relative stabilities of some choleic acids containing fatty acids. We have begun to study palmitic–choleic acid because its crystal structure is known [5]. We have performed van der Waals' energy calculations on DCAPAL, to achieve information that we hope to be useful in the analysis of choleic acids containing fatty acids with different numbers of carbon atoms.

EXPERIMENTAL AND RESULTS

Commercially available DCA from Merck (99% pure) was used withput further purification. PAL was obtained from Fluka (99% pure). DCAPAL was crystallized at room temperature firstly from absolute ethanol and then from acetone. Prismatic, colourless crystals were grown by slow evaporation. The melting point, measured at atmospheric pressure by means of a Leitz heating plate 350, was 455–457 K. The stoichiometric ratio DCA : PAL : acetone of 8 : 1 : 1 was indicated to be very probable by crystal structure refinement and agrees with the measured density (1.12 g cm^{-3}). To measure the vapour pressure we used a torsion effusion apparatus. The method and experimental assembly have been described previously [6]. At each experimental temperature the pressure value was derived from measurement of the torsion angle, α, of the tungsten wire, to which the cell is suspended, by the relationship [7] $P = K\alpha$, where K is an instrument constant also including the geometrical parameters of the used cell. The temperature was determined by a calibrated iron–constantan thermocouple inserted in a second cell placed below the torsion cell. In order to check the reliability of the instrument constant K, vapour pressures of pure standard substances (zinc and naphthalene) were measured and compared with selected data reported in the literature [8,9]. The cells with different geometrical constants were employed in this study.

PAL

At present the only vapour pressure values of pure PAL are apparently the following: old data reported by Stull [10] in a review in 1947, one equation over the solid phase at low temperature in the Handbook of Chemistry and Physics [11] and, finally, more recent data measured by De Kruif et al. [12]. We have determined a new set of the vapour pressure values of this compound in the temperature range 354–404 K in two runs. The experimental data are reported in Fig. 1.

The linear least-squares treatment of the data of each run gives two P–T equations from which the following equation was selected

$$\log P \text{ (kPa)} = (9.77 \pm 0.16) - (4677 \pm 62)/T$$

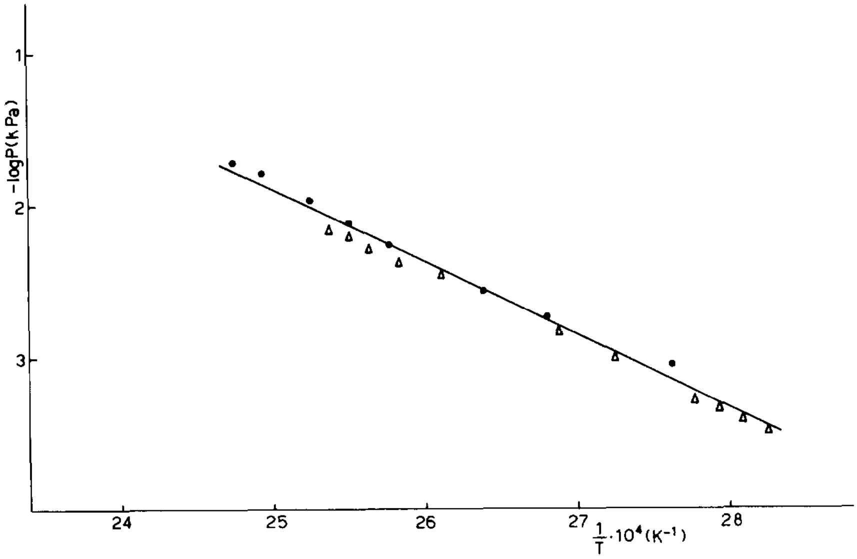

Fig. 1. PAL vapour pressures. (●) Run 13.01; (△) run 13.02; (———) selected $P-T$ equation.

where the errors are standard deviations. From this equation the second-law enthalpy change $\Delta H^0_{379} = 89 \pm 2$ kJ mol^{-1} was derived. In Fig. 2 our equation is drawn for comparison with those reported in the literature.

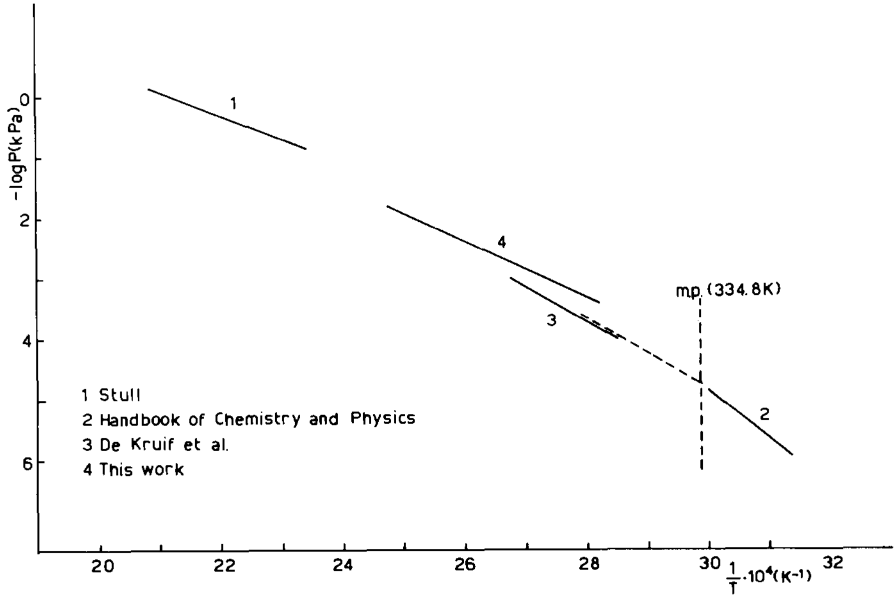

Fig. 2. Comparison of PAL vapour pressures.

DCAPAL

Vapour pressures are not initially reproducible, probably due to the loss of small amounts of acetone, used in the samples' preparation and occluded in the channels of DCAPAL. Non-reproducible data have prevented us from deriving an enthalpy value associated with acetone release, but it was pointed out that the fugacity of this compound rapidly decreases as its vaporization proceeds inside the channels.

After practically all the acetone has been vaporized, PAL vaporization begins. Typical vaporization behaviour of DCAPAL (run 10.04) is plotted in Fig. 3.

In the first step of vaporization the contribution of DCA vapour to the total pressure is negligible. The vapour pressures measured in this step during five runs, in the temperature range 427–463 K, are reported in Fig. 4. From the least-squares treatment of the data, the corresponding P–T equations, reported in Table 1, were derived and the following equation was selected

$$\log P\ (\text{kPa}) = (25.28 \pm 0.56) - (12355 \pm 224)/T$$

The errors are estimated considering the uncertainties associated with the temperature measurements. From the slope the second-law enthalpy change, $\Delta H^0_{445} = 237$ kJ mol^{-1}, associated with the reaction

$$(\text{DCA})_8\text{PAL(s)} \rightarrow 8\text{DCA(s)} + \text{PAL(g)} \qquad (1)$$

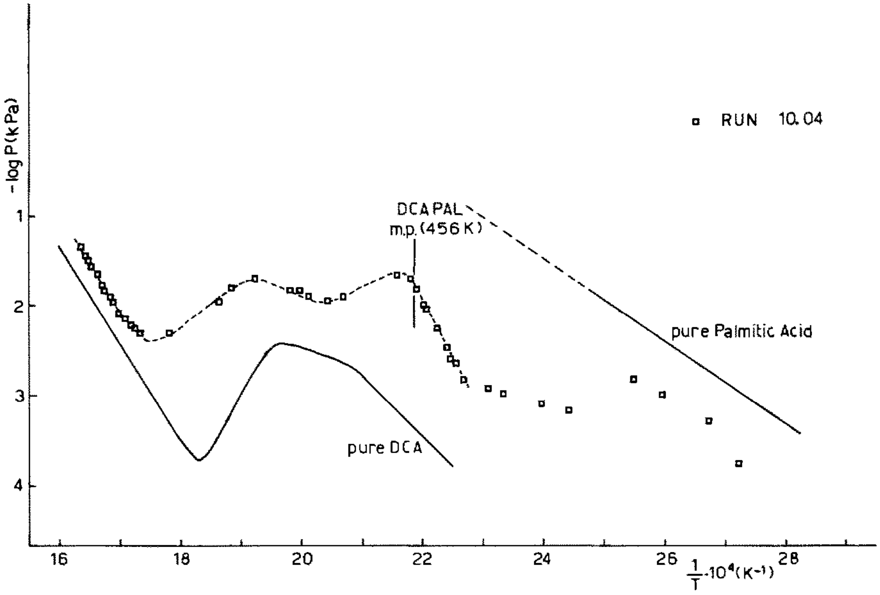

Fig. 3. Typical vaporization of a DCAPAL sample.

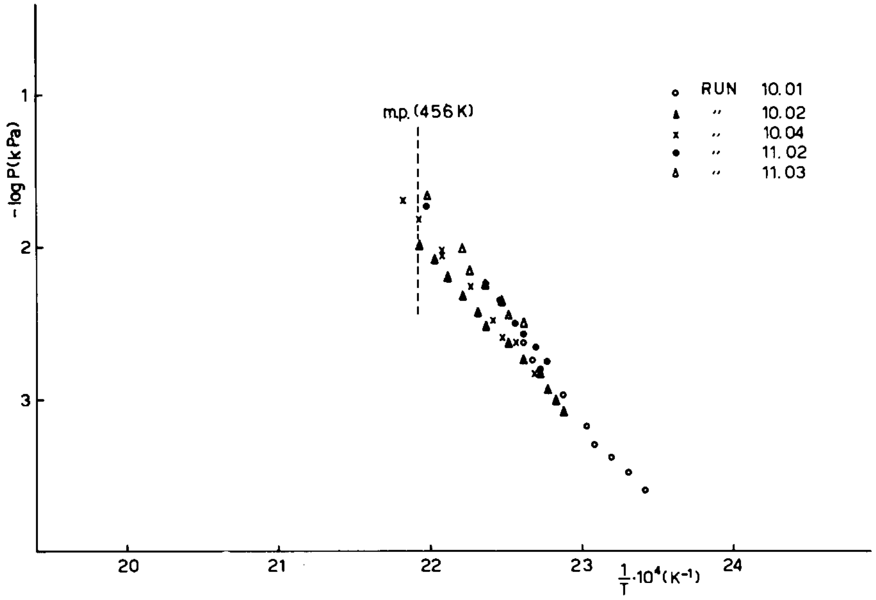

Fig. 4. Vapour pressures measured over solid DCAPAL.

TABLE 1

P–T equations of DCAPAL

Run	Cell	ΔT (K)	Number of points	log P (kPa) = $A - B/T$	
				A	B
10.01	H	427–442	10	24.78 ± 0.62	12130 ± 271
10.02	H	436–456	12	22.46 ± 0.35	11145 ± 352
10.04	H	441–458	9	26.78 ± 0.47	13046 ± 211
11.02	L	439–463	7	26.45 ± 0.27	12822 ± 120
11.03	L	442–460	7	27.75 ± 1.27	13396 ± 57

was derived and the associated overall uncertainty should not exceed 5 kJ mol^{-1}.

CONCLUSION

Our vapour pressure values of PAL are in satisfactory agreement with those reported by De Kruif et al. [12] and with the slope obtained on extrapolating the P–T equation over the solid phase reported in the literature using the heat of fusion $\Delta H^0_{335} = 42$ kJ mol^{-1} [11]. The agreement could be better taking into account the shift between the data observed over pure DCA residue of DCAPAL vaporizations (see Fig. 3) and the values over pure DCA obtained in a previous work [1].

TABLE 2

Comparison of vapour pressure and standard vaporization enthalpy of pure palmitic acid

Author	ΔT (K)	$\log P$ (kPa) $= A - B/T$		ΔH^0_{298} (kJ mol^{-1})
		A	B	
Stull [10]	427–627	8.14	3847	116
Handbook [11]	319–333	19.34	8069	154
De Kruif et al. [12]	351–374	12.42	5760	152
This work	354–404	9.77 ± 0.16	4677 ± 62	131

Table 2 summarizes for comparison the vapour pressure equations of PAL reported in the literature and the standard vaporization enthalpy changes obtained by the second-law treatment of the data using the above-mentioned heat of fusion value. Even if our absolute vapour pressure values of pure PAL agree well enough with some literature data [11,12], our standard sublimation enthalpy is lower. Unfortunately we cannot critically analyse the results reported in the literature, for lack of experimental data, but we believe that the most probable sublimation enthalpy value of PAL is the average value $\Delta H^0_{298} = 140$ kJ mol^{-1}. Assuming the ΔH^0_{445} of the reaction (1) as standard because the experimental temperatures are very close to 298 K and combining this value with the standard sublimation enthalpy of pure PAL found in this work, the heat of formation of the channel complexes at 298 K according to eqn. (1) was derived as $\Delta H^0_{298} = 97$ kJ mol^{-1}.

The results obtained for DCAPAL can be compared with those relative to six choleic acids containing aromatic hydrocarbons or their derivatives [1–4]. These belong to the same space group of DCAPAL ($P2_12_12_1$) and the van der Waals' packing energy, computed neglecting the guest molecules, is practically the same [5,13], although the size of the channels is greater in cases of choleic acids with aromatic compounds (whose molecules are flat, while PAL is thread-like). The enthalpy changes associated with the release of guest molecules (ΔH_r^0), relative to the six channel complexes previously studied, range between 56.9 and 138 kJ mol^{-1} and are smaller than the above-reported value for DCAPAL (237 kJ mol^{-1}). On the other hand, the host–guest interactions involve, in the first six choleic acids, "polarization bondings" stronger than the simple van der Waals' interactions present in DCAPAL between DCA and PAL molecules. Thus, the difference found depends on the higher number of "contacts" formed by an occluded PAL molecule with DCA, involving the methyl and the fourteen methylenic groups together with the carboxylic one (see ref. 5 for crystal structure discussion).

Potential energy calculations performed in the present study enable us to estimate the contribution of a single group to the host–guest interaction energy. The calculations were accomplished using the same potential functions reported in a previous work [14]. The atoms were generated in the positions corresponding to the final refinement of DCAPAL. All the atom–atom interactions between one PAL and the 28 nearest DCA molecules were computed in a first run, giving an energy value of -202.7 kJ mol^{-1}. In a second run we considered only the PAL carboxyl group with the DCA atoms, obtaining an energy value of -13.2 kJ mol^{-1}. The difference, due to the aliphatic part of PAL, is equal to -189.5 kJ mol^{-1}. In this way, assuming a methyl group equal to a methylene one we estimated the contribution of each methylene group to be given by $-189.5/15 = -12.6$ kJ mol^{-1}.

So, in the case of DCAPAL, the measured ΔH_r^0 of 237 kJ mol^{-1} should be compared with the computed value of 203 kJ mol^{-1}. To verify whether this empirical correlation applies generally, other choleic acids containing fatty acids must be investigated. In this regard, it is possible to foresee that choleic acids containing fatty acids with different numbers of carbon atoms have channels of the same energy, shape and dimensions [13]. Hence, ΔH_r^0 and energy values should depend only on the length of each fatty acid molecule. To test this hypothesis we have prepared other channel complexes of DCA with lauric ($CH_3(CH_2)_{10}COOH$), myristic ($CH_3(CH_2)_{12}COOH$) and stearic ($CH_3(CH_2)_{16}COOH$) acids.

Our aim is to ascertain if the expected decrements or increments of their ΔH_r^0 values with respect to the value found for DCAPAL, can be foreseen, by knowing the contribution to the host–guest interaction energy of a methylenic group.

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