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ENTHALPIES OF FUSION AND SOLID–SOLID TRANSITION OF EVEN-NUMBERED PARAFFINS $C_{22}H_{46}$, $C_{24}H_{50}$, $C_{26}H_{54}$ AND $C_{28}H_{58}$

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ABSTRACT

Enthalpies and temperatures of fusion have been measured by differential scanning calorimetry for some *n*-paraffins (docosane, tetracosane, hexacosane, octacosane). Heat capacity differences between the solid and liquid at the melting point (ΔC_{pm}) have been derived from the experimental results.

By temperature scanning starting from 260 K the enthalpies and temperatures of solid–solid transitions have also been detected.

INTRODUCTION

Normal paraffins exhibit solid–solid transitions from crystalline phases at low temperature to disordered phases at high temperature some degrees below the melting point. The early works of Müller suggest that the transitions are related to rotation of molecular chains about their long axes [1,2]. The atomic structure of the low-temperature "crystalline" phase of even-numbered paraffins has been determined [3–10]. More recently the main structural features of the high-temperature "rotator" phases have been established [8,9,11,12]. These studies, performed mainly by X-ray diffraction techniques, show that the molecules in crystalline phases stack together, forming a layered structure with the long molecular axes tilted with respect to the normal to the layer planes. The paraffins with carbon atom number, n, less than 26 (docosane, tetracosane) crystallize in a triclinic lattice. For $n > 26$ (octacosane) the lattice is monoclinic. Coexistence of monoclinic and triclinic phases is observed for hexacosane.

All even-numbered paraffins with $n \geqslant 22$ present an intermediate "rotator" phase at temperatures between the crystal and the liquid phase, in which a high degree of orientational disorder of the molecules is observed.

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The lattice associated with the rotator phase in even paraffins C_{22}, C_{24}, C_{26} is hexagonal (R_{II} or R_I = quasi-hexagonal) and for C_{28} monoclinic. The amplitude of the molecular longitudinal motion in the rotator phase increases with molecular length. This amplitude is temperature independent in rotator phases of even paraffins with $22 \leqslant n \leqslant 26$. The voids between molecular layers in the crystalline phase of even paraffins are narrower than those of odd paraffins, indicating a closer packing of layers in systems in which molecules are tilted.

In addition, some thermodynamic properties of odd and even normal alkanes have been reported in the literature [5,13–18].

In connection with many years of study of solid–liquid equilibria of *n*-alkanes with different solvents we have prepared a series of pure even-numbered alkanes (C_{22}, C_{24}, C_{26}, C_{28}) to determine temperatures and enthalpies of fusion and solid–solid transitions and especially heat capacity changes during the melting process.

In view of the fact that some of our data on the physical constants of these compounds differ slightly from those reported by earlier investigators, it was felt desirable to publish our results.

EXPERIMENTAL

Materials

Hydrocarbons C_{22} and C_{28} (Fluka AG) and C_{24} and C_{26} (ICN Pharmaceuticals, Inc., Plainview, NY), all purum grade materials, were fractionally recrystallized three times from the melt.

Calorimetric measurements

Determination of transition and fusion enthalpies, transition and fusion temperatures and ΔC_{pm} for even carbon-number alkanes, C_{22}–C_{28}, were carried out in a differential scanning calorimeter DSC-1B, associated, for integrating purposes, with a Kipp and Zonen BD-2 integrator, Kipp and Zonen micrograph BD-5 and electronic self-made counter with 10^9 count rate.

Preliminary thermal analysis of the substances under investigation revealed that the smaller the scan rate and the more numerous the subsequent melting-crystallization steps, the better the separation of the two peaks (Fig. 1).

Enthalpy of fusion experiments were carried out at a scan rate of 1° min^{-1}, power sensitivity of 4 mcal s^{-1}, recorder sensitivity 5 mV and nitrogen flow rate 25 ml min^{-1}. The instrument was calibrated against 99.9999 mol% purity indium and gallium samples.

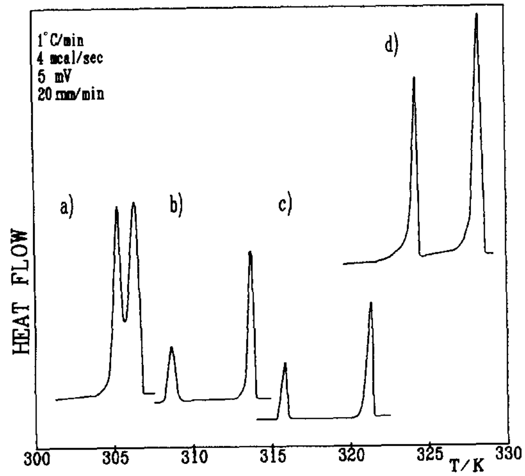

Fig. 1. DSC diagrams of *n*-alkanes: docosane (a), tetracosane (b), hexacosane (c) and octacosane (d).

Crystal samples which had been recrystallized several times and finally conditioned were ground in a micro agate mortar equipped with a system to remove static electricity produced by grinding. Samples (0.3–3 mg) were weighed on a Cahn model Gram electrobalance (± 0.004 mg) in volatile pans, fitted with aluminium discs placed over the sample material before sealing up the pan.

The ΔC_{pm} values were obtained from heat capacity measurements carried out from at least 50 °C below the transition temperatures to 50 °C above melting temperatures with thorough care to eliminate the pre-melting range. Three to five runs were performed on each compound to reveal the existence of solid-to-solid phase transitions.

RESULTS

Experimental data on fusions and solid–solid transitions are reported in Table 1. Columns 2 and 3 list the mean values of five onset temperatures of the fusion/transition peak in K, whilst columns 4 and 5 give the average fusion/transition enthalpy in kJ mol^{-1}. In column 6 the mean values of the *n*-alkane heat capacity differences between the solid and liquid at the melting temperature are presented in J mol^{-1} K^{-1}. Five calorimetric runs led to more precise average values of the heat capacity. The C_{p} values for docosane and hexacosane deviate from the smoothed curve less than for other *n*-alkanes, as shown in Fig. 2. However, these measured data are sufficiently reliable to provide a baseline for the heat capacity changes during the melting point calculations. As shown in Table 1 the ΔC_{pm} data are in good agreement with the literature value for hexacosane [17], the

TABLE 1

Experimental data on temperature, enthalpy and heat capacity change of *n*-alkanes at melting and solid–solid transitions

n	T_m (K)	T_{tr} (K)	ΔH_m (kJ mol^{-1})	ΔH_{tr} (kJ mol^{-1})	$\Delta H_m + \Delta H_{tr}$ (kJ mol^{-1})	ΔC_{pm} (J mol^{-1} K^{-1})	Ref.
22	315.20	314.45	39.76	36.35	76.11	58.50	–
	317.15	316.15	48.95	28.20	77.15		16
			48.95	28.87	77.82		13
	316.85				78.43		5
24	323.65	318.90	57.31	27.68	84.99	66.60	–
	323.75	321.25	54.90	31.30	86.20		16
	322.85				86.78		5
	323.45				85.77		15
26	329.18	324.40	63.92	30.36	94.28	78.30	–
	329.25	325.50	60.70	33.42	94.12	74.53	17
	329.45	326.45	59.50	32.20	89.09		16
			58.74	35.02	93.76		13
	329.55						14
28	333.98	330.40	66.52	33.66	100.18	118.90	–
	334.35	331.15	64.60	35.44	100.08		16
	334.45				94.98		15

difference being 5%. The data for other *n*-alkanes are published for the first time, so they cannot be verified.

The *n*-alkanes C_{22}, C_{24} and C_{26} undergo a solid–solid transition to a hexagonal form and C_{28} to a monoclinic one. The transition takes place a few degrees below the melting point. The hexagonal phase is considerably less stable than the triclinic or monoclinic form and the transition to the hexagonal form, akin to that found in the alkanes, is in principle possible at high temperatures (a triclinic–hexagonal transition as in C_{22}, C_{24} *n*-alkanes is indeed observed in certain polyamides at high temperatures [19]). The enthalpies of the solid–solid transition of docosane and tetracosane should be comparable to each other, in analogy with the triclinic–hexagonal transition. The literature values differ from 28.20 kJ mol^{-1} [16] and 28.87 kJ mol^{-1} [13] for docosane to 31.30 kJ mol^{-1} [16] for tetracosane. Our values are 27.68 kJ mol^{-1} for C_{24} and the unbelievably high value for the enthalpy of transition (36.35 kJ mol^{-1}) comparable with the enthalpy of fusion (39.76 kJ mol^{-1}) for C_{22} (see Fig. 1(a)).

This discrepancy could be due to the difficulty in separating melting and transition peaks, as the phase transition occurs only just 0.75 K below fusion. For kinetic reasons different crystallization conditions lead to different modifications of the hexagonal phase. This could explain the different enthalpy of phase transition found for docosane in our experiment. The

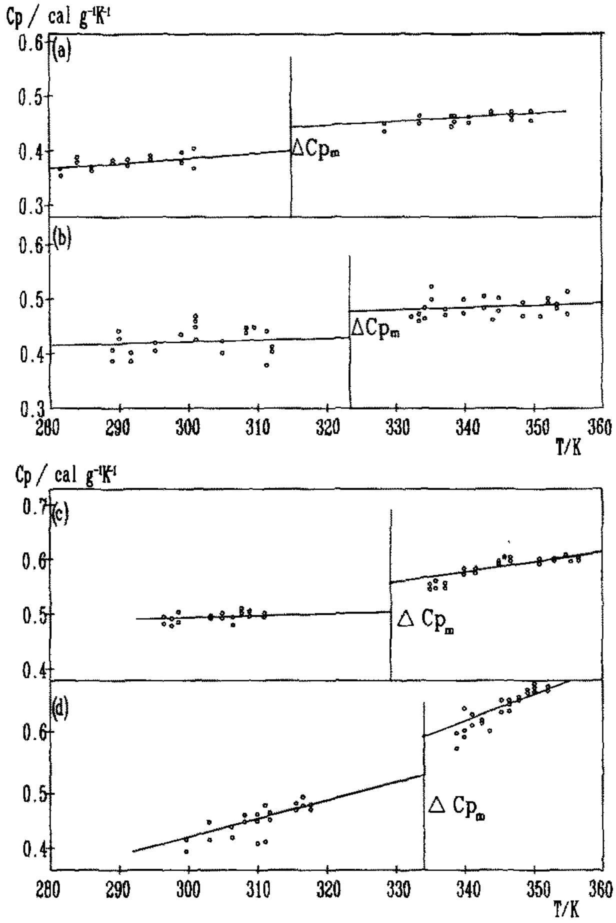

Fig. 2. Specific heat capacity–temperature data for: docosane (a), tetracosane (b), hexacosane (c) and octacosane (d).

discontinuity in the thickness of the interlayer voids at the transition temperature is due mainly to the sharp decrease in molecular tilting angle from the crystalline to the rotator phase. The constancy of the experimental values of the displacement parameter (D_t) for the rotator phase of $C_{22}H_{46}$, $C_{24}H_{50}$ and $C_{26}H_{54}$ within the temperature-stability domain of the hexagonal rotator phase implies that the significant variations in longitudinal molecular displacement are associated with major changes in the mean molecular structure which occur at the transition temperature. The singular behaviour of $C_{28}H_{58}$, which exhibits a clear variation in the displacement parameter within the domain of stability of monoclinic rotator phase, can be explained as a consequence of a variation in molecular tilting angle as was found by means of small-angle X-ray diffraction [10].

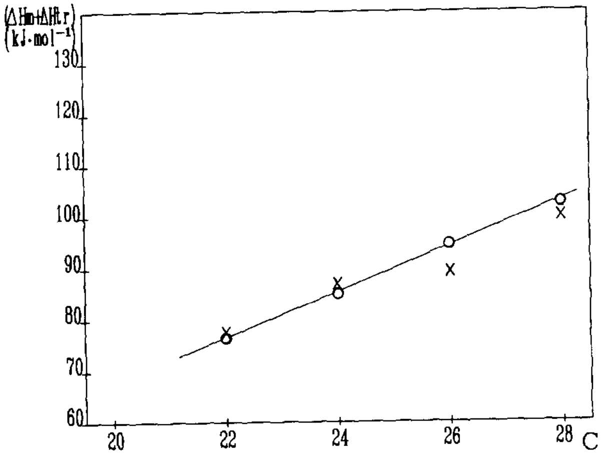

Fig. 3. The sum of the enthalpies of fusion and transition as a function of the number of chain carbon atoms (C); × our values; o, Schaerer et al. [16].

It is worth noting that the density of the monoclinic (C_{28}) form is lower ($\rho_M = 0.935$ g cm^{-3}) than the density of the triclinic form (C_{22}, C_{24}) ($\rho_T = 0.973$ g cm^{-3}) which constitutes an exception to the "law" of close packing [8].

Values of the temperature and enthalpy of transitions and fusions obtained through adiabatic calorimetry were reported by Schaerer et al. [16]. Their results for the temperature of transitions and fusions are 0.1–1.8 K higher than ours, but as to the sums of the enthalpy of fusion and transition ($\Delta H_m + \Delta H_{tr}$) the agreement is within 1%. However, our enthalpies of the phase transitions (except C_{22}) are smaller. Westrum and McCullough [20] pointed out that the enthalpy of fusion (ΔH_m) of the paraffins with an even number of carbon atoms from C_6 to C_{20} is almost linearly related to carbon number and the plot of the sum of the enthalpies of fusion and transition ($\Delta H_m + \Delta H_{tr}$) up to C_{28} is an extension of the ΔH_m curve. Our value of ($\Delta H_m + \Delta H_{tr}$) for hexacosane is 94.28 kJ mol^{-1}, higher than that of ref. 16 but very close to the value 94.12 kJ mol^{-1} obtained by Andon and Martin [17] and is closer to the straight line for ($\Delta H_m + \Delta H_{tr}$) against carbon number of paraffins C_{22}–C_{28} (see Fig. 3). Higher values than ours for the sum of the enthalpies of fusion and transition for C_{22} and C_{24} were obtained by Atkinson and Richardson [5] who studied the phase behaviour of *n*-alkanes by adiabatic calorimetry. From their measurements they calculated the Gibbs energy of fusion as a function of temperature and fitted the results to a cubic equation in temperature. From this equation, values of enthalpy of phase transition at the melting point of 94.0 kJ mol^{-1} for C_{26} and 100.0 kJ mol^{-1} for C_{28} were obtained. These may be compared with the sum of the enthalpies of fusion and transition (94.28 kJ mol^{-1} and 100.18 kJ mol^{-1}, respectively) from the present work.

In conclusion it must be emphasized that only so-called conditioning of samples, i.e. three to five runs, made the identification and interpretation of peaks possible.

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