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Thermal analysis of long-chain ketones and the extrapolated equilibrium melting for polyethylene

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Abstract

The thermodynamic quantities of fusion for long-chain symmetrical ketone homologues were studied by DSC measurements. The carbon numbers in the chain measured were from 23 to 63. A heat-flux-type DSC was used because of its relatively high sensitivity at slow scanning rates. In addition to these, the heat capacities of ketones in the solid and liquid states were measured, for which sapphire was used as a standard material.

Although the symmetrical ketones have almost the same crystal system and lattice constants as those of odd *n*-alkane crystals, known as model compounds for polyethylene, ketones have no high-temperature modifications.

In view of these points, the purpose of this paper is to examine the linearity of the entropies of fusion, $\Delta S_m(T_m^0)$ at the equilibrium melting temperature T_m^0 for $n = \text{infinity}$, calculated using the DSC data measured with ketones, also considering the contributions of another entropy term, $R \ln n$ as pointed out by Flory and Vrij in 1963. It is concluded that not only the heats of fusions, $\Delta H_m(T_m^0)$, but also $\Delta S_m(T_m^0)$ satisfactorily indicate a linearity. Furthermore, it seems reasonable to conclude that the validity of the term $R \ln n$ is not clearly shown in these analyzed results.

Keywords: Thermal analysis; Long-chain ketones; Polyethylene

1. Introduction

The melting of *n*-alkane homologues as model compounds of linear molecular crystals has been reported in order to obtain a comprehensive understanding of

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¹ Sadly passed away. Will be greatly missed.

polyethylene crystals [1–10]. An analysis based on the linearity of the heat of fusion and the entropy at the reference temperature was given by Broadhurst in 1962 [1,2]. The melting temperature equation from *n*-alkanes in the orthorhombic crystal structure up to the melting point was derived using the data from *n* = 44–100, where *n* represents the carbon number per molecule; the convergence temperature of 414.3 K was also introduced. Flory and Vrij [3] increased the data base by including extrapolated equilibrium melting points of *n*-alkanes from *n* = 11–100 with a low-temperature orthorhombic crystal structure, but no solid–solid transition before the final melting (1963). They also stated that a term $R \ln n$ should be included in the molar entropy of fusion; the limiting melting point T_m^0 for $n = \infty$, 418.5 K (± 1.0), was finally derived on considering this term.

However, Mandelkern et al. [9] and Ubbelohde [11] have pointed out that the entropy term for linear moleculars seems to be unclear, because of the occurrence of the premelting phenomenon. In long-chain linear *n*-alkane crystals, before the final melting, the high-temperature phase, not the rotator phase [12–14], has always appeared on the measurements using only pure samples. But the extent of the connection between the natural properties of high-temperature phases and the premelting phenomenon is still unknown, and the solution to these problems has not yet been obtained. Furthermore, high-temperature modifications with higher heat capacities make the evaluation of the total enthalpy change a little difficult [15].

Although a large number of studies have been made on the extrapolated equilibrium melting temperature for polyethylene by estimating the thermodynamic data of *n*-alkane homologues, only a few attempts have so far been made to investigate the linearity of the heats and entropies of fusion at T_m^0 . The linearity of the heats of fusion has already been confirmed by Atkinson and Richardson [5].

Symmetrical long-chain ketones have almost the same crystal group and lattice constants as odd *n*-alkane crystals, but generally melt without any transitions to high temperature phases [16–20].

In this report, in view of these points, the experimental results of the carbon number dependence of the melting thermodynamic quantities and the heat capacities, studied with the DSC method for the symmetrical ketones from *n* = 23–63, are reported and further discussed with respect to the extrapolated equilibrium melting of polyethylene, rather than the conventional method adopted by *n*-alkane homologues.

2. Experimental

2.1. Materials

The sapphire disk supplied by Rigaku Denki Co. was used as the reference material for the measurements of heat capacities. The symmetrical ketones used were 12-tricosanone, 13-pentacosanone, 14-heptacosanone, 15-nonacosanone, 16-hentriacontanone, 17-tritriacontanone, 18-pentatriacontanone, 20-nonatriacontanone, 22-tritetracontanone, 26-henpentacontanone and 32-trihexacontanone, abbreviated respectively as K23, K25, K27, K29, K31, K33, K35, K39, K43, K51 and K63, where

the numeral denotes the number of carbon atoms in the molecule. They were synthesized through a ketene dimerization reaction from the corresponding carboxylic acid chlorides, which were free from other homologues [21]. The *n*-alkanes are also abbreviated as *C_n*, where *n* represents the number of carbon atoms in the molecule.

The ketones measured were finally purified by recrystallization and elution through a silica gel column. The sample purity was determined with a Shimadzu capillary gas chromatograph GC-14A, equipped with a column of CBP1-M25-025. The purities are listed in Table 1.

2.2. Measurements

The DSC measurements were performed on a Rigaku DSC 8240B. The data acquisition and analysis were made with a Rigaku TAS-100 and a personal computer. The standard operational conditions for the melting point were: heating rate 0.5 K min^{-1} in a flow of dry nitrogen, with a sample size of $1.000 \pm 0.005 \text{ mg}$, for the bulk (BK) crystallized from the melt with a cooling rate of 1 K h^{-1} and for solution-grown crystals (SG) grown from suitable dilute solutions.

The standard operational conditions for the heat capacities of K31, K39, K51 and K63 solution-grown crystals were a heating rate of 1 K min^{-1} and a sample size of about 5.3–6.2 mg. The sapphire disk used as a standard material weighed 29.15 mg, and measurements were made on samples in a standard aluminum pan covered with a lid. As we reported before [15], it is important to note the thermal contact of the sapphire disk with the aluminum pan. The thermal fluctuation in this sapphire measurement was minimal, so it may be no problem in our experimental analysis. Correction for the aluminum pan was not made in these experimental results.

The X-ray diffraction measurement was made with a Rigaku Geiger flex 2027 with Ni-filtered $\text{CuK}\alpha$ radiation at room temperature. The textures measured were piled up solution-grown crystals; this is called a single crystal mat.

Table 1
Purity of symmetrical ketone homologues determined by gas chromatography with a capillary column

Samples	Purity %
12-Tricosanone (K23)	100.0
13-Pentacosanone (K25)	100.0
14-Heptacosanone (K27)	99.7
15-Nonacosanone (K29)	99.6
16-Hentriacontanone (K31)	99.9
17-Tritriacontanone (K33)	98.0
18-Pentatriacontanone (K35)	99.7
20-Nonatriacontanone (K39)	99.8
22-Tritetracontanone (K43)	99.1
26-Henpentacontanone (K51)	99.3
32-Trihexacontanone (K63)	98.4

3. Experimental results

3.1. Long period of K_n

The chain length dependence of the long spacings (nm) of K_n ($n = 23, 31, 39, 63$) crystals are shown in Fig. 1. Using the least squares method

$$l = 0.1297n + 0.130 \quad (1)$$

where l is the long spacing of solution-grown K_n crystals. The C–C bond length in a methylene chain gave 0.1297 nm, which is in good agreement with the X-ray data of 0.1280 nm reported by Saville and Shearer [16]. For the orthorhombic-type odd C_n crystals, stable at room temperature, the length of the crystal axes, although a little larger than the literature value of 0.1270 nm reported by Broadhurst [2], are almost identical for the K_n and C_n crystals.

3.2. Thermodynamic quantities of ketones

As has been reported before [20], the DSC curve for C39 solution-grown crystal undergoes a weak A' solid–solid transition and clearly shows the B and C transitions; it does not indicate the hexagonal transition before the melt. This experimental result is in complete disagreement with Broadhurst's compilation for the thermodynamics and structural data on n -alkanes [2]. Moreover, the DSC curve for K39 undergoes no solid–solid transition, except for a single melting peak [20].

Thermodynamic quantities of the two kinds of K_n crystals measured are summarized in Table 2. The experimental error in T_m is within $\pm 0.01\%$ and for $\Delta H_m(T_m)$,

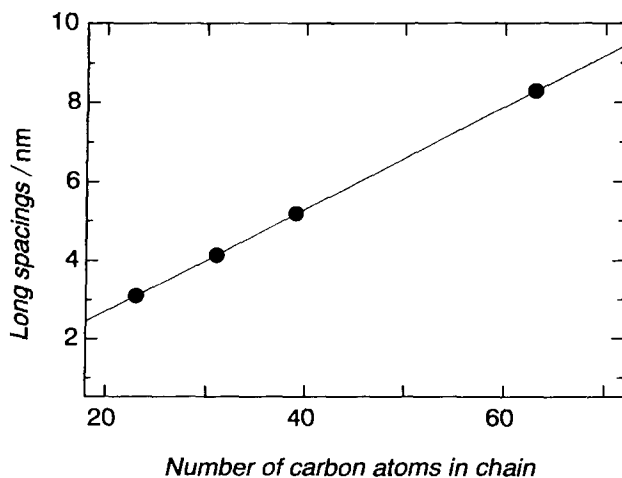


Fig. 1. Long spacings (nm) for symmetrical ketones (K23, K31, K39 and K63) crystallized from suitable dilute solutions, as a function of n , the carbon number in the chain. Data fit by the least squares methods as $l = 0.1297n + 0.130$.

Table 2

Thermodynamic quantities for bulk and solution-grown crystals of symmetrical ketones measured by DSC

K_n	Crystal	T_m/K	$\Delta H_m/kJ\ mol^{-1}$	$\Delta S_m/J\ K^{-1}\ mol^{-1}$
K23	BK	340.9	86.8	254.5
	SG	341.0	88.8	260.3
K25	BK	345.3	97.0	280.8
	SG	—	—	—
K27	BK	349.0	106.0	303.7
	SG	349.0	107.5	308.0
K29	BK	352.1	110.5	313.8
	SG	—	—	—
K31	BK	355.6	123.9	348.5
	SG	356.4	119.9	336.3
K33	BK	358.5	132.1	368.5
	SG	—	—	—
K35	BK	361.6	139.6	386.0
	SG	361.0	140.4	388.9
K39	BK	365.0	157.1	430.4
	SG	365.6	154.2	421.7
K43	BK	—	—	—
	SG	367.3	165.9	451.5
K51	BK	371.3	190.9	514.2
	SG	373.4	201.8	540.3
K63	BK	379.9	251.0	660.8
	SG	379.7	256.6	675.9

within $\pm 1.0\%$. The melting points and chain length relationship for K_n (open circles) and C_n (solid circles) crystals are shown at the same time in Fig. 2. The data plotted are bulk crystals for $n = 23$ – 39 and solution-grown crystals for $n = 43$ – 63 , respectively. The data for C_n are adopted from the previous work by Takamizawa and coworkers [8,10]. T_m is obtained as the extrapolated onset temperature. The values of T_m get closer with increasing n , and will gradually meet at $n = \text{infinity}$. These function relationships will be discussed later.

The calorimetric data of $\Delta H_m(T_m)$ and $\Delta S_m(T_m)$ for the K_n and C_n data previously reported [8,10] are plotted as a function of n in Figs. 3 and 4. In both measurements, the experimental values for K_n are a little larger than those of C_n . These differentials may be introduced by the existence of dipole–dipole moments at the center of the K_n molecules, i.e. there is an additional heat of fusion required to break up the dipole layers [16,19,22]. Differentials may be rather larger for entropies of fusion, than for conformations of the liquid state.

The experimental results for the heat capacities, C_p , of the solid and liquid state of solution-grown K_n crystals, for K31 (solid triangles), K39 (open triangles), K51 (squares) and K63 (circles) are shown in Fig. 5. Each C_p curve for the solid state was derived from their 2nd-order master curve fit to the four kinds of K_n experimental data, and for the liquid-state linear equation fit to the data. The extrapolated equilibrium

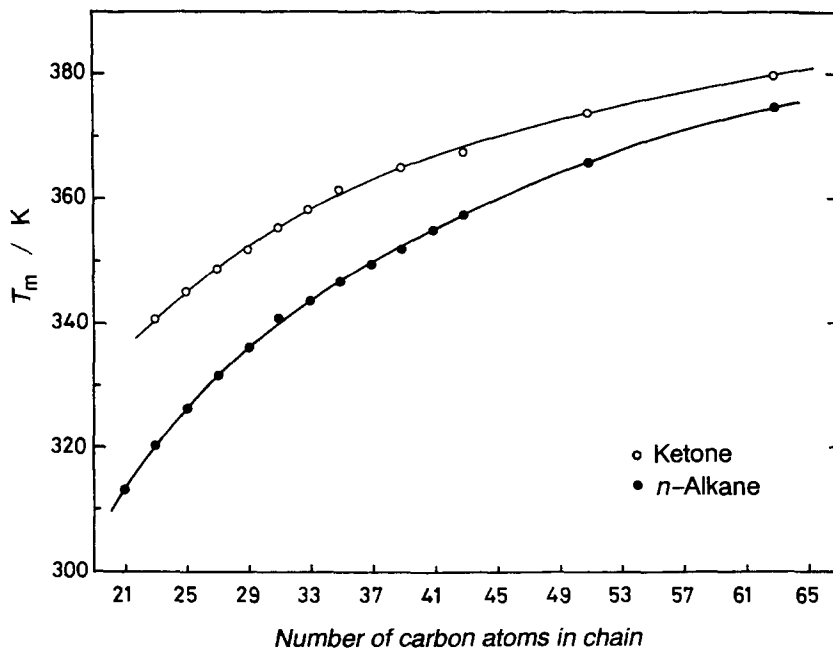


Fig. 2. Experimental results of the melting points for symmetrical ketones (○) as a function of n , as well as n -alkane data (●) previously reported by Takamizawa and coworkers [8,10].

melting temperature T_m^0 for $n = \infty$, represented by the vertical broken line, is assumed to be 414.3 K.

4. Discussion

4.1. Heats of fusion and entropy at T_m^0 for polyethylene

The heat capacity differentials $\Delta C_p(T_m^0)$ at the transition from solid to liquid is written as

$$\Delta C_p(T_m^0) = C_{p,l}(T_m^0) - C_{p,c}(T_m^0), \quad (2)$$

where $C_{p,l}(T_m^0)$ is the heat capacity of the liquid state at T_m^0 , and $C_{p,c}(T_m^0)$ that of the crystal state at T_m^0 . As shown in Fig. 5 by the vertical broken line, both are calculated from the extrapolated cross point of each experimental result. $\Delta C_p(T_m^0)$ values obtained are plotted as a function of n , and values of $\Delta C_p(T_m^0)$ for the other kinds of n are estimated from the least-squares fitting line in Fig. 6. Before the entropy term, we first consider the linearity of the heats of fusion. The heat of fusion at the melting point T_m , $\Delta H_m(T_m)$, is written as

$$\Delta H_m(T_m) = H_l(T_m) - H_c(T_m) \quad (3)$$

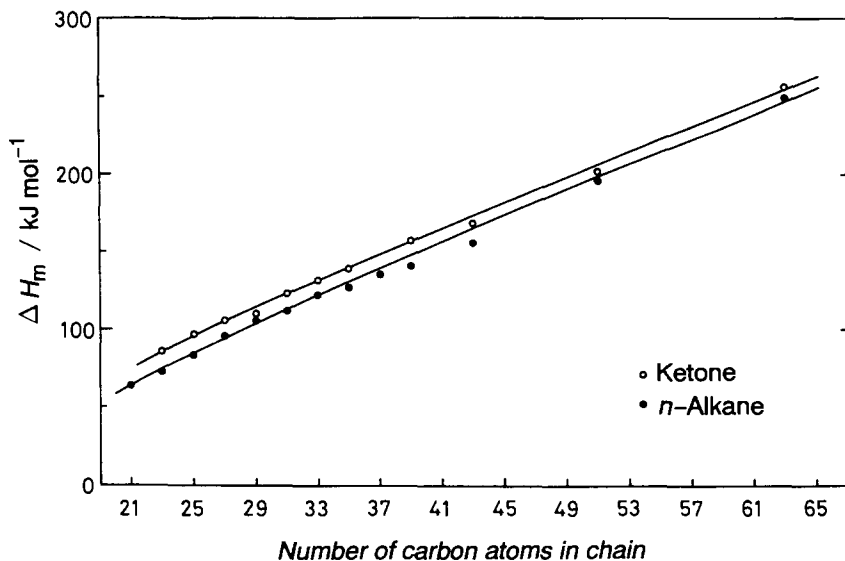


Fig. 3. Experimental results for the heat of fusion for symmetrical ketones (○) as a function of n , and for n -alkanes (●), reported by Takamizawa and coworkers [8,10].

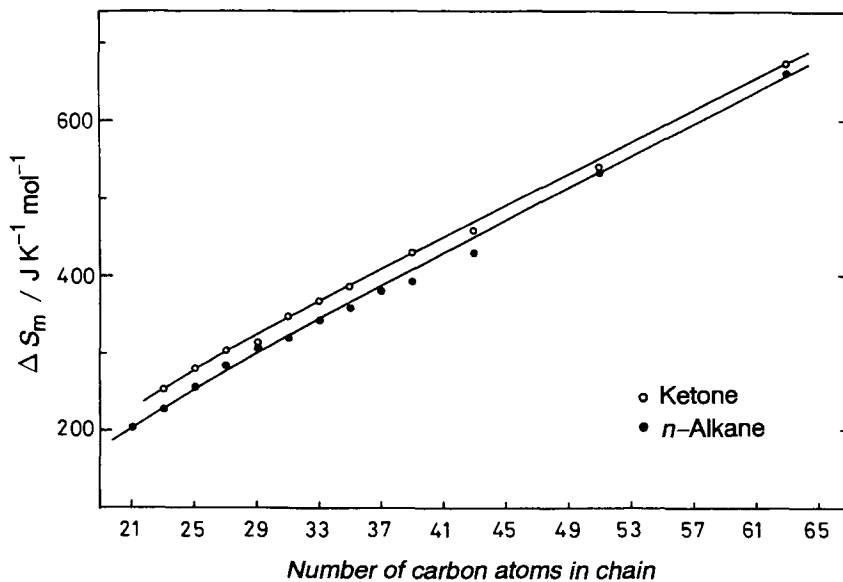


Fig. 4. Experimental results for the entropies of fusion of symmetrical ketones (○) as a function of n , and also for n -alkanes (●), reported by Takamizawa and coworkers [8, 10].

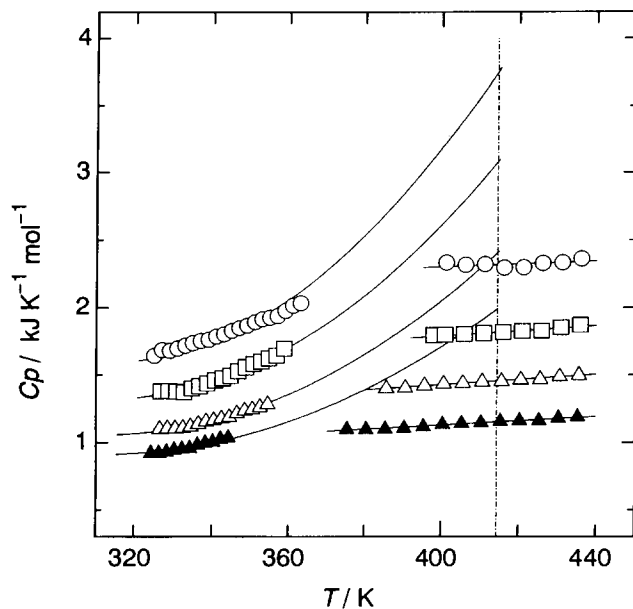


Fig. 5. The temperature dependence of experimental data plots of the heat capacities for K31 (▲), K39 (△), K51 (□) and K63 (○) in the solid and liquid states, respectively. The vertical broken line indicates the extrapolated equilibrium temperature, $T_m^0 = 414.3$ K.

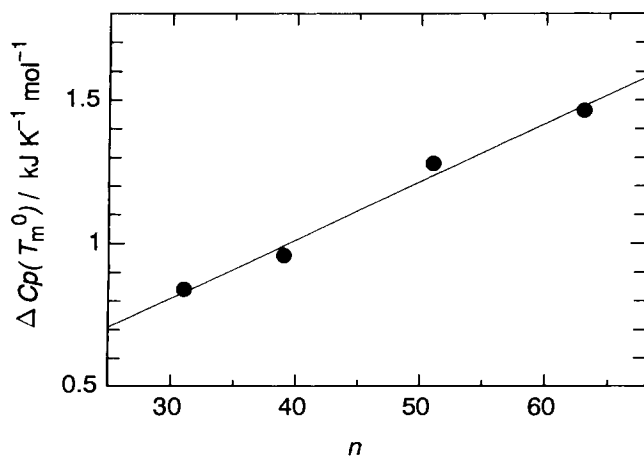


Fig. 6. The chain length dependence of the heat capacity changes from the liquid state to the solid state at the extrapolated equilibrium temperature, $T_m^0 = 414.3$ K, estimated from the experimental results in Fig. 5.

where $H_l(T_m)$ is heat of fusion at the liquid state, and $H_c(T_m)$ that of the crystal state.

Expanding around T_m^0 , we omit differential terms higher than second order. Eq. (3) is transformed as

$$\Delta H_m(T_m^0) = \Delta H_m(T_m) - \Delta T \Delta C_p(T_m^0) \quad (4)$$

where

$$\Delta H_m(T_m^0) = H_l(T_m^0) - H_c(T_m^0)$$

$$\Delta T = T_m - T_m^0$$

$$\Delta C_p(T_m^0) = C_{p,l}(T_m^0) - C_{p,c}(T_m^0)$$

Substituting the experimental data of $\Delta H_m(T_m)$, ΔT and $\Delta C_p(T_m^0)$ and $T_m^0 = 414.3$ K [1], the relationship of $\Delta H_m(T_m^0)$ per mole CH_2 and a fraction of n is plotted in Fig. 7. It seems reasonable to say that $\Delta H_m(T_m^0)$ is proportional to $1/n$, as reported by Atkinson and Richardson [5].

The intercept value of $\Delta H_m(T_m^0) = 4.20$ kJ mol^{-1} for $n = \text{infinity}$, calculated from the linear line is in agreement with the literature value $\Delta H_m(T_m^0) = 4.11$ kJ/mol^{-1} for the heat of fusion at T_m^0 for polyethylene [23].

Using the same method as discussed above, $\Delta S_m(T_m^0)$ was expanded as

$$\Delta S_m(T_m^0) = \Delta S_m(T_m) - \left\{ \Delta C_p(T_m^0)/T_m^0 - \Delta H_m(T_m^0)/(T_m^0)^2 \right\} \Delta T \quad (5)$$

The $1/n$ dependence of $\Delta S_m(T_m^0)/n$ calculated from Eq. (5) is plotted as open circles in Fig. 8; the solid circles represent the values of $[\Delta S_m(T_m^0) - R \ln n]/n$, considering the entropy term $R \ln n$ as suggested by Flory and Vrij. This gave satisfactory linearity of $\Delta S_m(T_m^0)/n$, but the effect of $R \ln n$ was not clearly confirmed in these experimental results.

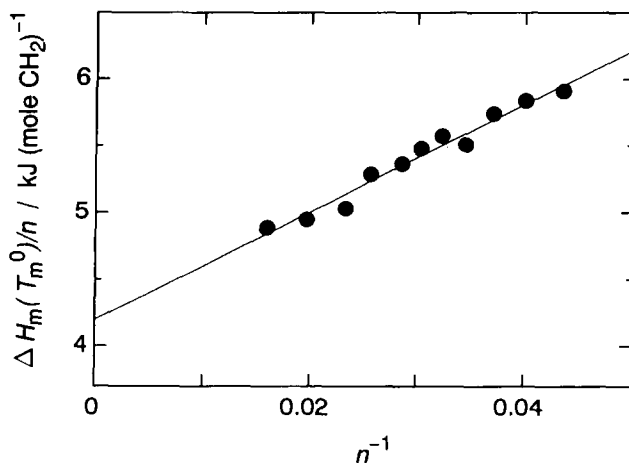


Fig. 7. Plots of Eq. (4) substituting the calorimetric data for ketones as a function of $1/n$.

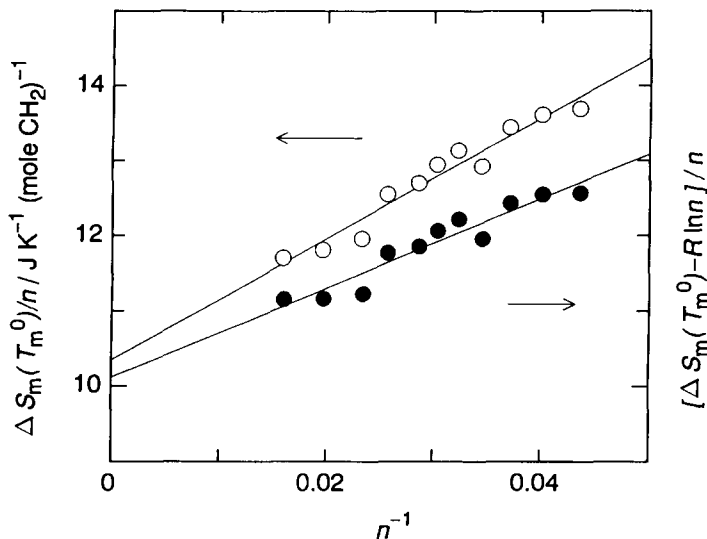


Fig. 8. Plots of Eq. (5) (○), substituting the calorimetric data of ketones as a function of $1/n$; “●” represent the values of $[\Delta S_m(T_m^0) - R \ln n]/n$, as indicated by Flory and Vrij in 1963.

The intercept value of $\Delta S_m(T_m^0)/n$ for $n = \infty$ is $10.35 \text{ J K}^{-1} \text{ mol}^{-1}$, and for $[\Delta S_m(T_m^0) - R \ln n]/n$, $10.12 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. They are in agreement with the literature value for polyethylene, $9.91 \text{ J K}^{-1} \text{ mol}^{-1}$ [23].

However, the value of T_m^0 obtained from $\Delta H_m(T_m^0)/\Delta S_m(T_m^0)$ is 405.7 K and for $\Delta H_m(T_m^0)/[\Delta S_m(T_m^0) - R \ln n]$, 414.9 K , respectively. Although Flory and Vrij discussed the entropy term, $R \ln n$, by using the carbon numbers in a chain longer than 11, these rather shorter chains were not measured in these experiments.

As has been mentioned before, it is not the main purpose of this work to obtain the convergent values themselves, but it is necessary to consider the validity of our calculations for the extrapolated equilibrium melting thermodynamic quantities. Our main interests are whether or not the linearity is clearly shown in $\Delta S_m(T_m^0)$, also taking the effect of $R \ln n$ into consideration. It is not clear how to evaluate the absolute values of $\Delta H_m(T_m^0)$ and $\Delta S_m(T_m^0)$ obtained from these calculations.

Finally, it seems reasonable to assume that ketone homologues are suitable model compounds for polyethylene. Ketones have some advantages over n -alkanes for use in theoretical analysis; the solution-grown n -alkane crystals clearly undergo solid transitions with high heat capacities, but for ketones it was easy to obtain precise heat capacity data, even in the solid state.

5. Conclusions

The thermodynamic quantities of fusion and the heat capacities for long-chain symmetrical ketones as a function of the carbon number in the chain were examined by

DSC measurements. From these experimental results, it is clear that ketones are simple to melt, for n from 23 to 63.

It is concluded that not only the linearity of $\Delta H_m(T_m^0)$ but also the linearity of $\Delta S_m(T_m^0)$ is demonstrated experimentally. It can be concluded however, that the contribution of the entropy term $R \ln n$, as pointed out by Flory and Vrij in 1963, is not clearly confirmed.

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