Research Article

Pippard Relations Close to the Melting Point in the Premelting Region of Hexadecane

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We examine here the validity of the Pippard relations close to the melting point in the premelting region of hexadecane. For this verification, we analyze the observed data for the thermal expansivity α_p obtained for various pressures at constant temperatures of 302 and 325 K in this system. By calculating the isothermal compressibility κ_T and the specific heat C_p in the same pressure region of the premelting region of hexadecane, we obtain that C_p varies linearly with α_p and also that α_p varies linearly with κ_T for this system. This indicates that some molecular organic compounds, such as solid hexadecane studied here, can exhibit λ -phase transitions prior to melting which are expected to verify the Pippard relations.

1. Introduction

Phase behaviour of pure n-alkanes is important for industrial and scientific applications. The controlled precipitation of solid phases of these mixtures is widely applied in pharmaceutical, cosmetic, and food industries as a separation process, as also pointed out previously [1]. Those paraffin waxes are also used in latent thermal energy storage applications, and additionally for cool storage applications in regard to the phase transition processes a binary mixture of tetradecane and hexadecane is widely used [2].

In the literature, various sources of experimental data have been reported in regard to the thermodynamic properties of hexadecane. Some recent experimental reports are the following: T - X phase diagrams [1], entropy changes with molality at constant temperature [3], an anomalous heat effect during colloidal phase transitions [4], determination of the melting temperature (6.8°C) and a corresponding heat of fusion (121 kJ/kg) for a mixture of tetradecane (40%) and hexadecane (60%) [2], and also the crystallization temperatures of two binary mixtures: the tetradecane + hexadecane and tetradecane + pentadecane system up to 100 MPa [1].

Solid hexadecane among long-chain paraffin solids exhibits considerable precursor effects [5]. It has been shown that there exists an orientational disorder around the long

axis of the molecule in solid hexadecane [6]. Experimentally, it has been demonstrated that this is a kinked chain-like disorder rather than a librational disorder [7, 8], as also indicated by Pruzan et al. [9]. This orientational disorder occurring in solid hexadecane gives rise to instability and melting of the solid phase. Instability and melting have been associated with a soft phonon of zero wave vector [10–13].

Solid hexadecane melts into the liquid phase as a second-order transition associated with a particular type of orientational disorder which depends on the symmetry [9]. As in many molecular organic compounds, solid hexadecane exhibits orientational disorder in a small range where the thermodynamic quantities such as the thermal expansivity α_p , isothermal compressibility κ_T , and the specific heat C_p show anomalous behaviour close to the melting point [5, 9].

The anomalous behaviour of α_p , κ_T , and C_p can be described by a power-law formula near the melting point in solid hexadecane. In the premelting region of hexadecane close to the melting point, we can assume that α_p , κ_T , and C_p exhibit similar critical behaviour associated with the same critical exponent. Buckingham and Fairbank [14] have indicated that C_p behaves like κ_T and α_p in the vicinity of the critical point. In the precursor zone of the solid hexadecane, C_p , α_p , and κ_T are expected to increase as approaching

the melting point. This increase in the thermodynamic quantities considered is similar to the critical behaviour of λ -phase transitions. Pippard has established a linear variation of the specific heat C_p with the thermal expansivity α_p in the vicinity of the λ -phase transition in NH_4Cl [15]. The Pippard relations have been tested for a variety of materials exhibiting λ -phase transitions.

In this study, we also examine the Pippard relations in the premelting region of hexadecane near the melting point. For this examination, we calculate the isothermal compressibility κ_T and the specific heat C_p from our analysis of the thermal expansivity α_p which was measured experimentally at various pressures near the melting point for constant temperatures of 302 and 325 K in solid hexadecane [9]. By obtaining the values of the critical exponent γ from our analysis, we calculate κ_T and C_p as functions of pressure in the premelting region of hexadecane. We then establish a linear variation of C_p with α_p (first Pippard relation) and also a linear variation of α_p with κ_T (second Pippard relation) close to the melting point in this molecular organic compound.

In Section 2, we review the method and conditions about experimental study of Pruzan et al. [9]. In Section 3, our calculations and results are presented. In Sections 4 and 5, we present our discussion and conclusions, respectively.

2. Review of the Experimental Technique

Using a P - V - T method, the thermal expansivity α_p was observed by Pruzan et al. [9] at various pressures close to the melting point. Using a high-pressure calorimetric method, the heat of compression was measured. The measurement of heat, in open-system conditions, was conducted, which flows out of (into) the sample when it is compressed (decompressed) isothermally [9]. The thermal expansivity α_p was then determined according to the first Maxwell equation:

$$\alpha_p = -V^{-1} \left(\frac{\partial S}{\partial T} \right)_P, \quad (1)$$

where V and S are the molar volume and entropy of the sample, respectively. This technique was referred to as the piezothermal method [9]. For the measurements, the pressure steps were about 20 MPa far from the melting point and they were 0.1–10 MPa close to the melting point [9]. For their measurements, Pruzan et al. [9] reported that their observations were made over different times, sometimes greater than 72 h, during which no change could be observed in the expansivity variation against pressure for hexadecane.

3. Calculations and Results

Near the melting point of solid hexadecane, the thermodynamic quantities such as the thermal expansivity α_p , isothermal compressibility κ_T , and the specific heat C_p can exhibit critical behaviour. This critical behaviour of the thermal expansivity can be expressed as

$$\alpha_p = A(P - P_m)^{-\gamma}, \quad (2)$$

where γ is the critical exponent for α_p and A is the amplitude. Here, P_m denotes the melting pressure of solid hexadecane, which is close to the critical point [5]. Using the thermodynamic relation near the melting point:

$$\frac{\alpha_p}{\kappa_T} = \left(\frac{dP_m}{dT} \right), \quad (3)$$

the isothermal compressibility κ_T can be expressed as a function of pressure

$$\kappa_T = \frac{A(P - P_m)^{-\gamma}}{(dP_m/dT)} \quad (4)$$

by means of (2).

We can also obtain the pressure dependence of the specific heat C_p using the thermodynamic relation near the melting point as follows:

$$C_p = TV\alpha_p \left(\frac{dP_m}{dT} \right). \quad (5)$$

In (5), the volume V is a function of pressure, which can be obtained as

$$V_T(P) = V_m \exp \left[\frac{A}{1 - \gamma} \frac{1}{(dP_m/dT)} (P - P_m)^{1-\gamma} \right], \quad (6)$$

where V_m denotes the melting volume of solid hexadecane. Equation (6) can be derived easily using the definition of the isothermal compressibility $\kappa_T = -(1/V)/(\partial V/\partial P)_T$. Thus, the pressure dependence of the molar volume $V_T(P)$ has been derived here, as given by (6), in the case when the isothermal compressibility κ_T is a function of pressure according to (4). We note here that when the isothermal compressibility κ_T is a function of the molar volume V , the pressure dependence of the molar volume $V_T(P)$ can also be derived. But, its functional form should not be the same as (6) since the volume dependence of the isothermal compressibility κ_T changes the pressure dependence of the molar volume in the premelting region close to the melting point of solid hexadecane. Finally, by means of (5), the pressure dependence of the specific heat C_p can be written as a power-law formula:

$$C_p = ATV \left(\frac{dP_m}{dT} \right) (P - P_m)^{-\gamma}. \quad (7)$$

In the vicinity of the melting point of solid hexadecane, the specific heat C_p can be related to the thermal expansivity α_p linearly, according to the first Pippard relation:

$$C_p = TV \left(\frac{dP_m}{dT} \right) \alpha_p + T \left(\frac{dS}{dT} \right)_m. \quad (8)$$

Similarly, the thermal expansivity α_p can be related linearly with the isothermal compressibility κ_T by the relation in the vicinity of the melting point:

$$\alpha_p = \left(\frac{dP_m}{dT} \right) \kappa_T + \frac{1}{V} \left(\frac{dV}{dT} \right)_m \quad (9)$$

according to the second Pippard relation. Thus, linear plots of C_p against α_p (8) and α_p against κ_T (9) can be obtained near the melting point in solid hexadecane. From those linear plots, (8) and (9), we can extract the values of the slope dP_m/dT numerically for solid hexadecane close to the melting point.

We reanalyzed here the thermal expansivity α_p measured at various pressures in the premelting region close to the melting point for constant temperatures of 302 and 325 K in solid hexadecane due to Pruzan et al. who also analyzed their experimental data [9]. For our analysis, we followed the steps, as given below.

- (1) We used the power-law formula (2) in the logarithmic form obtained as

$$\ln \alpha_p = \ln A - \gamma \ln(P - P_m) \quad (10)$$

for the premelting region of hexadecane. We then extracted the values of the critical exponent γ as 2.06 ± 0.05 and 1.97 ± 0.04 with the values of the amplitude A for constant temperatures of 302 and 325 K, respectively, as given in Table 1. Similarly, from their analysis of the thermal expansivity α_p , Pruzan et al. [9] have obtained the value of the critical exponent as $\gamma_m = 1.9$ in the melting zone of hexadecane. Figure 1 gives the thermal expansion α_p plotted as a function of $P - P_L$ in a log-log scale for constant temperatures of 302 K and 325 K. Since we used for our analysis the experimental data in the melting zone, which was obtained in the range $P - P_L < 50$ MPa where P_L is the liquid or melting (P_m) pressure [9], we were able to describe the critical behaviour of the thermal expansivity α_p in the premelting region of hexadecane according to (10). On the other hand, $P - P_L > 50$ MPa corresponds to the precursor zone (solid phase) for hexadecane [9]. These pressure ranges have also been reported in the work of Pruzan et al. [9] as $P_1 - P_L = 140$ MPa and $P_2 - P_L = 60$ MPa, where P_1 represents the beginning of the precursor range and P_2 is the pressure for a change of regime, which is closer to the critical pressure P_C for the solid hexadecane.

- (2) Using those values of γ and A which we obtained (Table 1), we then calculated the isothermal compressibility κ_T as a function of pressure according to (4) where we used the experimental value of $dP_m/dT = 10$ MPa/K [9].
- (3) The next step was to calculate the pressure dependence of the volume $V_T(P)$ in the premelting region of hexadecane near the melting point for constant temperatures of 302 and 325 K using (6). In this equation, the values of the melting volume V_m [16], as given in Table 1, were used with the experimental value of $dP_m/dT = 10$ MPa/K.
- (4) Finally, the pressure dependence of the specific heat C_p was calculated by (7) for the premelting region of hexadecane near the melting point for those constant

TABLE 1: Values of γ and A extracted (Figure 1) for α_p using the experimental data [9] and the V_m values for the solid hexadecane at temperatures indicated.

T (K)	γ	A (MPa) $^\gamma$ /K	$V_m \times 10^{-6}$ (m ³ /mol)
302	2.06 ± 0.05	1.9837	294.93 at 303 K
325	1.97 ± 0.04	1.3624	300.13 at 323 K

temperatures considered using $V_T(P)$ values (6) with the dP_m/dT value [5] given above.

Since we obtained the pressure dependence of the thermal expansivity α_p (2), isothermal compressibility κ_T (4), and the specific heat C_p (7) in the same pressure interval for constant temperatures of 302 and 325 K in the premelting region of hexadecane, we were then able to establish the Pippard relations ((8) and (9)) in this crystalline system. We plot the specific heat C_p against the thermal expansivity α_p in the premelting region of hexadecane near the melting point for constant temperatures of 302 K and 325 K in Figure 2.

We also examined the second Pippard relation (9) by α_p as a function of κ_T in the premelting region of hexadecane close to the melting point. Figure 3 gives our plot for constant temperatures of 302 and 325 K. From our plots of C_p against α_p (first Pippard relation) and α_p against κ_T (second Pippard relation), we extracted the value of the slope as $dP_m/dT = 10$ MPa/K. Since the experimental value of $dP_m/dT = 10$ MPa/K [5] was used as the initial value in (4) (step 2), (6) (step 3), and (7) (step 4) to calculate κ_T , $V_T(P)$, and C_p , respectively, as a function of pressure, we should expect the same slope value of 10 MPa/K from (8) as well.

4. Discussion

We examined here whether the specific heat C_p varies linearly with the thermal expansivity α_p (first Pippard relation) and also α_p varies linearly with the isothermal compressibility κ_T (second Pippard relation) in the vicinity of the melting point in the premelting region of hexadecane. As seen from our plots (Figures 2 and 3), we established the Pippard relations ((8) and (9)) with the slope $dP_m/dT = 10$ MPa/K which was extracted for this system. This indicates that those thermodynamic quantities, namely, C_p , α_p , and κ_T exhibit similar critical behaviour close to the melting point in the premelting region of hexadecane.

From our analysis of the measured thermal expansivity, we extracted the value of $\gamma = 2$ as the critical exponent for constant temperatures (302 K and 325 K), in the premelting region of hexadecane (Table 1). Our exponent value is very close to the value with the uncertainties (Table 1) of $\gamma = 1.9$ as obtained by Pruzan et al. [9]. They analyzed their experimental data according to the power-law relation (2) with the $P_m = P_C$. The critical pressure P_C at which α_p diverges due to the precursor transformation is always between P_2 and P_L [9]. For hexadecane, P_C is close to P_2 , as indicated previously. Within the pressure ranges $P_1 - P_L = 140$ MPa and $P_2 - P_L = 60$ MPa, Pruzan et al. [9] obtained the values of $\gamma_S = 0.5$ in the solid phase, $\gamma_P = 0.7$ in the precursor zone, and $\gamma_m = 1.9$ in the melting zone, where the pressure

FIGURE 1: α_p versus P in a log-log scale close to P_m in the premelting region of hexadecane for $T = 302$ and 325 K (10) when $P_m = P_L$ [9]. The experimental data [9] with the uncertainties extracted (error bars) are also given here.

FIGURE 2: C_p versus α_p at various P close to P_m for $T = 302$ and 325 K in the premelting region of hexadecane (8). Observed α_p values [9] are shown here.

range is greater than the melting pressure P_m . The exponent value of 1.9 or 2 from both analyses in the melting zone can be compared with an effective exponent greater than 1 for the critical behaviour of the thermal expansivity α_p due to surface melting model of Lipowsky and Speth [17, 18], as also pointed out previously [9]. It has been interpreted that the second regime (liquid phase) observed in molecular organic compounds might be ascribed to impurity effects for

FIGURE 3: α_p versus κ_T close to the premelting region of hexadecane at various P for P_m , $T = 302$ and 325 K (9). Observed α_p values [9] are shown here.

the critical exponents close to 2 [5]. Regarding the exponent value of 1.9 or 2, the melting zone can be shortened as the impurity decreases [19] close to the melting point in the premelting region of hexadecane. Our values of the critical exponent ($\gamma_m = 2$) for hexadecane can also be compared with those values for other organic compounds, which we obtained by Pruzan et al. [9]. Close to the melting point, they obtained the values of $\gamma_m = 2$ (cyclohexane), 1.8 (carbon tetrachloride), 1.6 (benzene), and 1.5 (butanediol), as given in Table 2 in [5]. Similarly, the γ_m values of 1.85 for hexamethylbenzene (HMB), 2 for paradichlorobenzene (PDCB), and the value of 1.7 for both paraoxydianisol (PAA, C–N transition) and heptyloxyazoxybenzene (HOAOB, C–S transition) compounds (Table 2 in [9]) can also be compared with our exponent value of $\gamma_m = 2$ for hexadecane or $\gamma_m = 1.9$ as obtained by Pruzan et al. [9]. The organic compounds indicated above have similar chemical structure (C–H– $\cdots$ bonds) within the close melting points and pressure ranges [9]. This shows that within the pressure ranges studied all those organic compounds exhibit similar divergence behaviour of the thermal expansion α_p near the melting point according to a power-law formula (2). Thus, our exponent value is within expectations in regard to the experimental results for various organic compounds stated above.

Our γ values (Table 1) were used to calculate here the pressure dependence of volume $V_T(P)$ (6), isothermal compressibility κ_T (4), and the specific heat C_p (7), as indicated above. This calculation of C_p and κ_T then led us to plot C_p against α_p (Figure 2) and α_p against κ_T (Figure 3) with the zero values of the intercepts $T(dS/dT)_m$ and $(dV/dT)_m/V$, respectively, at the melting point in the premelting region of hexadecane. Those intercepts would have nonzero values

according to the Pippard relations ((8) and (9)) if the temperature dependences of the entropy and volume are known experimentally or their functional forms can be derived for solid hexadecane. Values of the critical exponent γ (Table 1) and also the slope dP/dT were extracted from one source of experimental data [9] for hexadecane in the melting region. Regarding the anomalous behavior of α_p , κ_T , and C_p close to the melting point in the premelting region of hexadecane, the other sources of the experimental data rather than the measurements of the thermal expansivity α_p due to Pruzan et al. [9] can be used to examine our relations given here. Some new experimental measurements of the α_p , κ_T , and C_p at various pressures for constant temperatures can be performed in the premelting region near the melting point for hexadecane. When this experimental data is available in the literature which can be obtained to high accuracy, our analysis can then be reconsidered to examine the Pippard relations given here.

Regarding the uncertainties in the measurements of the thermal expansivity α_p for hexadecane, it was pointed out [9] that the uncertainty in the α_p data depends on the respective uncertainties in the heat of compression (1 or 2%) and in the pressure step. It was also pointed out [9] that far from the transition lines, pressure steps around 20 MPa caused an uncertainty in α_p of about 5%. Close to the melting lines, within the pressure steps of 0.1–10 MPa, the uncertainty in α_p increased, whereas for the measurements of the molar volume V the uncertainty was considerably small ($\sim 0.3\%$) [9].

Using the experimental data [9], we extracted that the uncertainties in α_p are about 5% close to the melting point, which may be higher than this value, as pointed out by Pruzan et al. [9]. We represented the error bars in Figure 1 for $T = 302$ K and 325 K, as stated above. This gave us the uncertainties in the critical exponent γ for the thermal expansivity α_p , which changes from 1.9 to 2.1 (Figure 1).

On the basis of the volume measured or calculated as a function of temperature in the premelting region of hexadecane, the temperature dependence of the thermal expansivity α_p , isothermal compressibility κ_T , and the specific heat C_p can be obtained, and the Pippard relations ((8) and (9)) can also be established at various temperatures near the melting point for constant pressures in this system.

5. Conclusions

We studied here the Pippard relations (C_p versus α_p and α_p versus κ_T) close to the melting point in the premelting region of hexadecane. Linear variations of C_p with α_p (first Pippard relation) and α_p with κ_T (second Pippard relation) were both obtained at various pressures for constant temperatures of 302 K and 325 K in this system.

The Pippard relations can be also be applied to the solid hexadecane in the premelting region using the temperature dependence of C_p , α_p , and κ_T for constant pressures. They can be verified for some other molecular organic compounds near the melting point when the experimental data for the thermodynamics quantities is available.

Nomenclature

α_p :	Thermal expansivity
κ_T :	Isothermal compressibility
C_p :	Specific heat at constant pressure
S :	Entropy
V_T :	Volume at constant temperature
P_m :	Melting pressure
γ :	Critical exponent
A :	Amplitude
V_m :	Melting volume
P_L :	Liquid pressure
P_C :	Critical pressure
γ_s :	Critical exponent in the solid phase
γ_p :	Critical exponent in the precursor zone
γ_m :	Critical exponent in the melting zone.

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