Analysis of the specific heat of p-azoxyanisole (PAA) near the phase transitions

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The analysis of the experimental data for the specific heat C_p at various temperatures is given here near the nematic-isotropic liquid ($T_{NI} = 133.9°C$) and the solid-nematic ($T_{SN} = 117.6°C$) transitions in p-azoxyanisole (PAA). The analysis of the specific heat C_p is performed according to a simple power-law formula and a renormalisation-group expression. The values of the critical exponent α are extracted above and below the transition temperatures of T_{NI} and T_{SN} for this liquid crystalline material. Our exponent values are compared with the predictions of a three-dimensional Ising model and XY model for liquid crystals. Using the specific heat C_p, the temperature dependence of the enthalpy H and the entropy S is calculated in the nematic phase ($T > T_{SN}$) of p-azoxyanisole.

Keywords: specific heat; phase transitions; PAA

1. Introduction

PAA (p-azoxyanisole) is a mesophase system which undergoes successive phase transitions from the isotropic liquid to the nematic at $T_{NI} = 133.9°C$ and from the nematic to the solid phase at $T_{SN} = 117.6°C$, as the temperature decreases.

Various physical properties of p-azoxyanisole have been studied. The temperature dependence of the volume V near the nematic-isotropic liquid (NI) transition was measured and the thermal expansivity α_p was calculated for PAA by Maier-Saupe [1]. The specific heat C_p has also been measured at various temperatures close to the nematic-isotropic liquid (NI) and solid-nematic (SN) phase transitions in this liquid crystalline material [2]. Close to both NI and SN transitions, by keeping the temperature fixed at 413 K, the thermal expansivity α_p has been measured as a function of pressure for PAA [3]. Some other experimental techniques have also been used to study the crystal, nematic and isotropic liquid phases. The measurements of Raman [4,5], neutron diffraction [6,7], X-rays [8], ultrasonic [9], dielectric constant [10,11], magnetic susceptibility [11], elastic constants [12] and differential scanning calorimetry (DSC) [13] have been reported, as we have also reviewed in our recent study [14]. Using a molecular theory, the phase diagram of the nematic-isotropic liquid transition has been calculated [15]. We have also calculated the temperature dependence of the thermal expansivity α_p and the specific heat C_p near

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the nematic-isotropic liquid (NI) phase transition in PAA in our recent work [14]. In our earlier study [16] we have established the Pippard relations for the nematic-isotropic liquid (NI) and the crystal-nematic (CN) phase transitions in PAA.

In this study we analyse the experimental specific heat C_p data close to the NI and SN phase transitions in PAA according to a simple power-law formula, as we have analysed the C_p data for anisaldazine previously [17]. We also analyse the C_p data by the renormalisation-group expression. The temperature dependence of the enthalpy and entropy is calculated from the specific heat in the nematic phase ($T > T_{SN}$) for PAA. Below, our analysis of the specific heat C_p for PAA is given in Section 2. The experimental C_p data [2] is used for our analysis. In this section, calculation of the enthalpy and the entropy is also given. Sections 3 and 4 give a discussion of our results and conclusions, respectively.

2. Calculations and results

We analysed the specific heat C_p using the power-law formulae for the nematic-isotropic liquid (NI) and solid-nematic (SN) phase transitions in PAA. This analysis was performed using a simple power-law formula and also a renormalisation-group expression with a corrections to scaling term. From the analysis of the specific heat C_p, we then calculated the enthalpy H and the entropy S as a function of temperature in the nematic phase for $T < T_{NI}$ and for $T > T_{SN}$ in PAA.

2.1. *Analysis of the specific heat C_p*

We analysed the specific heat C_p using a power-law formula,

$$C_p = A\varepsilon^{-\alpha}, \tag{1}$$

where α is the critical exponent for the specific heat and A is the amplitude. The reduced temperature represents $\varepsilon = |T - T_{NI}|/T_{NI}$ and $\varepsilon = |T - T_{SN}|/T_{SN}$ for the isotropic liquid-nematic ($T_{NI} = 133.9°C$) and solid-nematic ($T_{SN} = 117.6°C$) phase transitions in PAA. The experimental C_p data [2] was used for our analysis. Table 1 gives the values of α and A within the interval of the reduced temperature ε above and below $T_{NI}(T_{SN})$ for PAA. We plot in a log-log scale C_p against ε according to the expression:

$$\log C_p = \log A - \alpha \log \varepsilon \tag{2}$$

for both NI and SN transitions. Figures 1 and 2 give our plots above and below T_{NI}, respectively. $\log C_p$ is plotted against $\log \varepsilon$ in Figures 3 and 4 above and below T_{SN}, respectively, for PAA.

In Figures 1–4 we represent with vertical lines the uncertainties in the specific heat C_p (in the log-log scale), which we determined when Equation (2) was fitted to the experimental data [2]. Uncertainties in the critical exponent α and in $\log A$, as given in Table 1, were used to determine the uncertainties in the specific heat values (Figures 1–4). In particular, in Figures 2 and 3, because of the data dispersion, the uncertainties in the specific heat C_p are much larger and the solid lines represent the best fits to the experimental data [2].

Table 1. Values of the critical exponent α for the specific heat C_p and the amplitude A within the interval of the reduced temperature ε according to the power-law formula (Equation (1)) for the nematic-isotropic ($T_{NI} = 133.9°C$) and nematic-solid ($T_{SN} = 117.6°C$) phase transitions in PAA. Uncertainties in α and $\log A$ are given from fitting Equation (1) to the experimental C_p data [2].

Phase transitions	$T(K)$	α	$\log A$	$\varepsilon = \lvert T - T_C \rvert / T_C$ $(T_C = T_{NI}, T_{SN})$
Nematic-isotropic	$T > T_{NI}$	0.85 ± 0.07	-1.604 ± 0.12	$1.57 \times 10^{-2} < \varepsilon < 3.08 \times 10^{-2}$
liquid (NI)	$T < T_{NI}$	0.04 ± 0.005	-0.354 ± 0.014	$1.34 \times 10^{-3} < \varepsilon < 5.68 \times 10^{-3}$
Nematic-solid	$T > T_{SN}$	-0.07 ± 0.01	-0.246 ± 0.016	$7.06 \times 10^{-2} < \varepsilon < 9.42 \times 10^{-2}$
(SN)	$T < T_{SN}$	0.09 ± 0.002	-0.518 ± 0.002	$3.17 \times 10^{-2} < \varepsilon < 2.48 \times 10^{-1}$

Figure 1. The specific heat C_p in a log-log scale as a function of the reduced temperature, $\varepsilon = \lvert T - T_{NI} \rvert / T_{NI}$, above T_{NI} for the nematic-isotropic liquid phase transition in PAA according to Equation (2). Uncertainties in C_p calculated from the uncertainties in α and $\log A$ (Table 1), are shown as vertical lines.

The critical specific heat associated with the nematic-isotropic liquid (NI) and solid-nematic (SN) phase transitions can also be described by the expression [18]

$$C_p = \begin{cases} At^{-\alpha}(1 + Dt^{\Delta}) + B, & \text{for } T > T_C \\ A't^{-\alpha'}(1 + D't^{\Delta}) + B', & \text{for } T < T_C \end{cases} \qquad (3)$$

where $t = \lvert T - T_C \rvert / T_C$, Dt^{Δ} is a corrections-to-scaling term in which $\Delta \approx 0.5$ and B is a nonsingular critical contribution, which was used to analyse the critical heat capacity of NH_4Br and $NH_4Br_xCl_{1-x}$ single crystals [19]. When $D = 0$, which was the constraint to analyse the C_p data [19], the above relation reduces to Equation (1) with
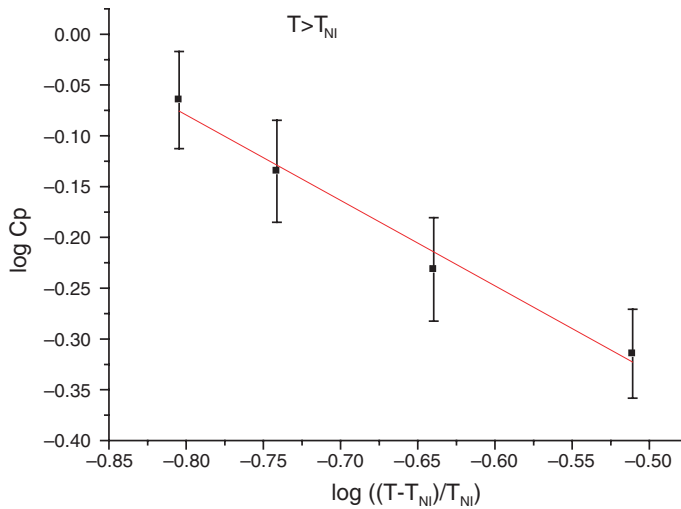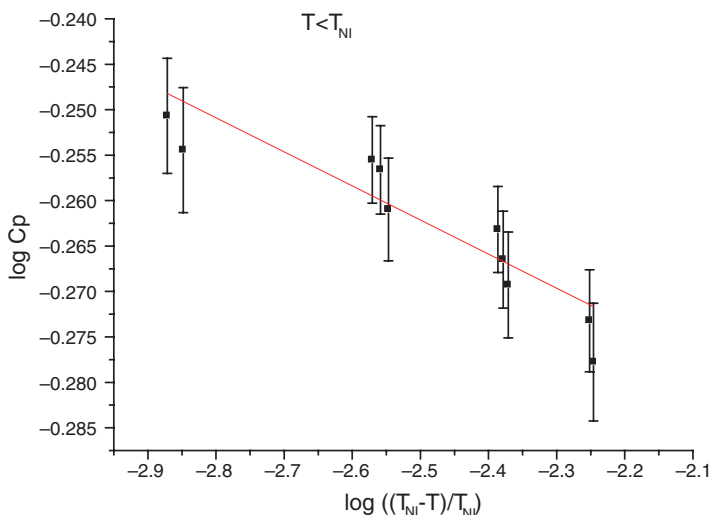
Figure 2. The specific heat C_p in a log-log scale as a function of the reduced temperature, $\varepsilon = |T - T_{NI}|/T_{NI}$, below T_{NI} for the nematic-isotropic liquid phase transition in PAA according to Equation (2). Uncertainties in C_p calculated from the uncertainties in α and log A (Table 1), are shown as vertical lines.
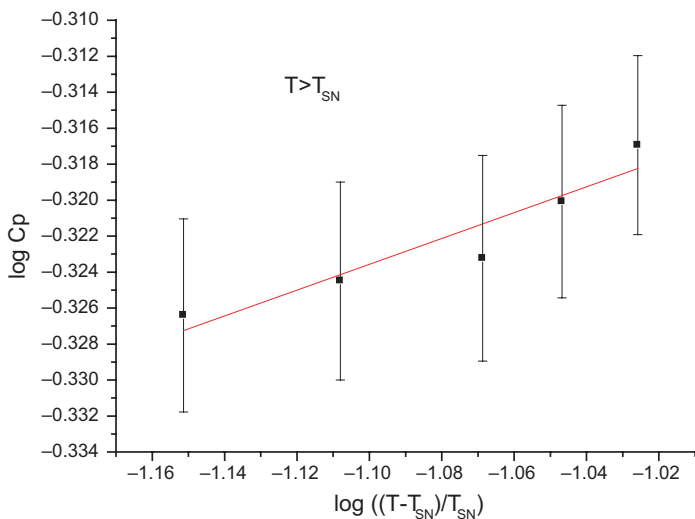
Figure 3. The specific heat C_p in a log-log scale as a function of the reduced temperature, $\varepsilon = |T - T_{SN}|/T_{SN}$, above T_{SN} for the solid-nematic phase transition in PAA according to Equation (2). Uncertainties in C_p calculated from the uncertainties in α and log A (Table 1), are shown as vertical lines.

the coefficient B. This renormalisation group expression Equation (3) including first-order corrections-to-scaling terms has also been used to analyse the specific heat data for a binary mixture of SCE9 and SCE10 close to a chiral-nematic-smectic-A-chiral-smectic-C point [20].

Figure 4. The specific heat C_p in a log-log scale as a function of the reduced temperature, $\varepsilon = |T - T_{SN}|/T_{SN}$, below T_{SN} for the solid-nematic phase transition in PAA according to Equation (2). Uncertainties in C_p calculated from the uncertainties in α and $\log A$ (Table 1), are shown as vertical lines.
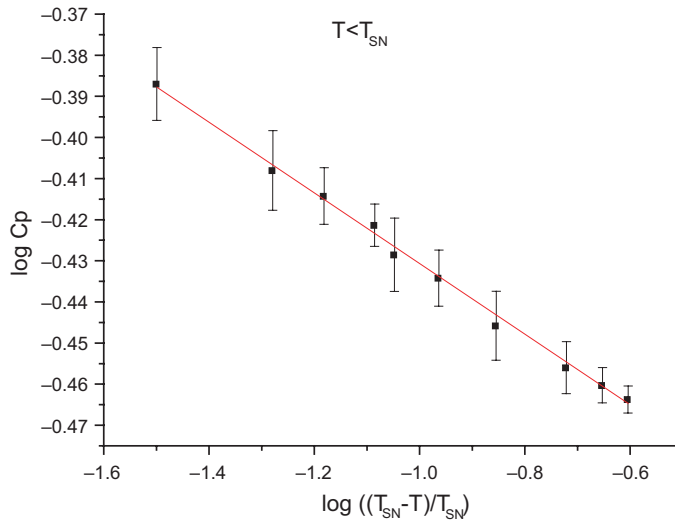
For the nematic-isotropic liquid (NI) transition in PAA, the temperature dependence of the specific heat can be expressed according to Equation (3) as

$$C_p = A \left| \frac{T - T_{NI}}{T_{NI}} \right|^{-\alpha} \left(1 + D \left| \frac{T - T_{NI}}{T_{NI}} \right|^{0.5} \right) + B. \tag{4}$$

Also, for the solid nematic (SN) transition in PAA, the temperature dependence of the specific heat C_p can be written as

$$C_p = A \left| \frac{T - T_{SN}}{T_{SN}} \right|^{-\alpha} \left(1 + D \left| \frac{T - T_{SN}}{T_{SN}} \right|^{0.5} \right) + B. \tag{5}$$

In this study, using the specific heat C_p data [2] at various temperatures for the NI and SN transitions of PAA ($T_{NI} = 133.9°C$ and $T_{SN} = 117.6°C$), the specific heat C_p was analysed according to Equations (4) and (5), respectively. From this nonlinear fitting, the values of the critical exponent α for C_p and, the parameters A, B and D are given within the temperature intervals ε in Table 2. Some parameters are given in the table with their uncertainties. Those without uncertainties were held constant and the remaining parameters were varied in Equations (4) and (5) during the fitting procedure.

2.2. Calculation of the enthalpy H

We calculated the temperature dependence of the enthalpy, H and the entropy, S in the nematic phase from the specific heat C_p for the solid-nematic (SN) phase transition in PAA. By defining $C_p = \partial H / \partial T$ and using the power-law formula for the

Table 2. Values of the critical exponent α for the specific heat C_p and the parameters A, B and D within the interval of the reduced temperature ε according to Equations (4) and (5) for the nematic-isotropic liquid (NI) and nematic-solid (SN) phase transitions, respectively, in PAA.

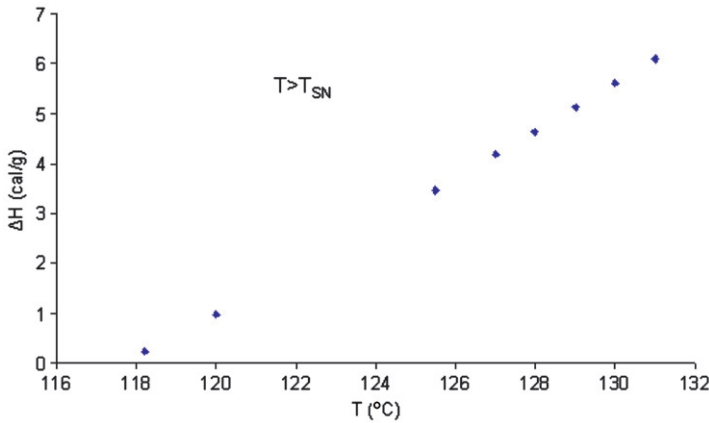| Phase transitions	$T(K)$	α	A (cal g^{-1}°C^{-1})	B (cal g^{-1}°C^{-1})	D	$\varepsilon = |T - T_{Cl}|/T_C$ $(T_C = T_{NI}, T_{SN})$
Nematic-isotropic liquid (NI)	$T > T_{NI}$	0.006	$(1.69 \pm 0.22) \times 10^2$	$(-1.74 \pm 0.23) \times 10^2$	0.067 ± 0.003	$9.0 \times 10^{-3} < \varepsilon < 4.6 \times 10^{-2}$
	$T < T_{NI}$	0.5	0.025 ± 0.013	-7.4×10^4	2.9×10^6	$2.2 \times 10^{-3} < \varepsilon < 4.4 \times 10^{-2}$
Nematic-solid (SN)	$T > T_{SN}$	-0.85 ± 0.02	-8.05×10^7	8.05×10^7	-1.13 ± 0.02	$5.1 \times 10^{-3} < \varepsilon < 9.4 \times 10^{-2}$
	$T < T_{SN}$	0.5 ± 0.01	-1.32×10^6	1.32×10^6	-1.02 ± 0.01	$2.2 \times 10^{-2} < \varepsilon < 2.5 \times 10^{-1}$

Figure 5. The enthalpy difference ($\Delta H = H - H_0$), calculated from Equation (7) as a function of temperature in the nematic phase ($T > T_{SN}$) of PAA ($T_{SN} = 117.6°C$).

specific heat (Equation (1)), the temperature dependence of the enthalpy H can be calculated from the integral expression:

$$H = \int_{T}^{T_C} A \left| \frac{T - T_C}{T_C} \right|^{-\alpha} dT + H_0, \tag{6}$$

where $T_C = T_{SN}$. From Equation (6), the temperature dependence of the enthalpy in the nematic phase of PAA for $T > T_{SN}$ can be calculated as

$$H = H_0 + \frac{A T_{SN}}{1 - \alpha} \left(\frac{T - T_{SN}}{T_{SN}} \right)^{1-\alpha}, \tag{7}$$

where H_0 denotes the enthalpy at the transition temperature T_{SN} when $\alpha < 1$. We calculated the temperature dependence of the enthalpy difference, $\Delta H = H - H_0$, in the nematic phase for $T > T_{SN}$ using our values of α, A (Table 1), $T_{SN} = 117.6°C$ and $H_0 = 28.1$ cal g^{-1} [2] according to Equation (7). Our calculated ΔH values are plotted as a function of temperature ($T > T_{SN}$) in Figure 5.

2.3. Calculation of the entropy S

We also calculated the temperature dependence of the entropy, S in the nematic phase above the solid-nematic (SN) phase transition in PAA. By defining $C_p = T(\partial S / \partial T)_P$, the entropy S can be calculated from the specific heat C_p at $T = T_C$ using the power-law formula Equation (1) according to the integral expression:

$$S = \int \frac{A}{T_C} \left(\frac{T - T_C}{T_C} \right)^{-\alpha} dT + S_0, \tag{8}$$

where $T_C = T_{SN}$. The entropy expression can be obtained above the solid-nematic transition ($T > T_{SN}$) from Equation (8), which gives:

$$S = S_0 + \frac{A}{1 - \alpha} \left(\frac{T - T_{SN}}{T_{SN}} \right)^{1-\alpha} \tag{9}$$

where S_0 denotes the entropy at $T = T_{SN}$ when $\alpha < 1$. As we performed for the calculation of the enthalpy H, we calculated the entropy difference, $\Delta S = S - S_0$, as a function of temperature by using the values of the critical exponent α and the amplitude A for $T > T_{SN}$ (Table 1) according to Equation (9), Figure 6 gives the entropy difference ΔS (entropy S with respect to the entropy value S_0 at the transition temperature) as a function of temperature in the nematic phase for $T > T_{SN}$ in PAA.

3. Discussion

The values of the critical exponent α, which were extracted from the specific heat C_p data for PAA [2], can describe the critical behaviour of this thermodynamic quantity close to the nematic-isotropic liquid (NI) and solid-nematic (SN) transitions. Apart from the exponent value of $\alpha = 0.85$ for $T > T_{NI}$, the exponent values of $\alpha = 0.04$ ($T < T_{NI}$), -0.07 ($T > T_{SN}$) and 0.09 ($T < T_{SN}$), which are all nearly equal to 0.1 describe similar critical behaviour of C_p as the NI and SN transitions of anisaldazine that has been obtained previously by us [17]. As we have indicated previously [17], this exponent value of nearly 0.1 is not expected from the mean field theory ($\alpha = \alpha' = 0$). Our negative exponent value of -0.07 for p-azoxyanisole (PAA) is not in disagreement with our earlier value of -0.02 for anisaldazine, both above the solid-nematic transition ($T > T_{SN}$). This is in agreement with the predicted value of -0.02 by the helium analogy and the inverted XY model for liquid crystals [18]. Those exponent values of 0.04 ($T < T_{NI}$), -0.07 ($T > T_{SN}$) and 0.09 ($T < T_{SN}$) can be compared with the value of $\alpha = 1/8$ predicted from a three-dimensional Ising model. Our value of $\alpha = -0.07$ for $T > T_{SN}$ can be renormalised according to the Fisher's renormalisation formula, $\alpha_R = -\alpha/(1 - \alpha)$, which gives the value of $\alpha_R = 0.06$. This α_R value is also close to the value of the three-dimensional Ising model. On the other hand, our value of $\alpha = 0.85$ for the nematic-isotropic liquid transition ($T > T_{NI}$) is much larger than the value of 0.04 ($T < T_{NI}$), the exponent values for the nematic-solid (SN) transition (Table 1). It is also much larger than our value of 0.05 ($T > T_{NI}$) for anisaldazine [17]. This may be due to the fact that the observed C_p drops rapidly just above $T_{NI} = 133.9°C$ for PAA and it does not vary considerably with the temperature in the isotropic liquid phase from 137 to 150°C [2]. This is not the case for the observed C_p of anisaldazine [17], which also drops rapidly just above $T_{NI} = 180.5°C$, but in the isotropic liquid phase it does depend on the temperature within the temperature interval up to about 200 K. Consequently, our exponent value of $\alpha = 0.85$ ($T > T_{NI}$) for PAA is too large to compare with the predictions of the models considered above. This large value of the critical exponent led us to investigate the mechanism of the nematic-isotropic liquid (NI) phase transition in PAA. Since both p-azoxyanisole and anisaldazine exhibit a single mesophase of the nematic type with the similar critical behaviour of the specific heat C_p, as measured experimentally [2], we expect a rather small α value for $T > T_{NI}$ in PAA, as we have obtained $\alpha = 0.005$ ($T > T_{NI}$) for anisaldazine [17] using the same analysis according to a power-law formula (Equation (1)). For this reason, we used the renormalisation-group expression (Equation (3)) and adopted it to analyse the observed C_p data [2] for the NI and SN transitions

in PAA. Since this renormalisation group-expression (Equation (3)) is appropriate to analyse a mean-field-like to tricritical cross-over behaviour ($\Delta \approx 0.5$), as applied to ammonium halides [19] and a binary mixture of SCE9 and SCE10 near the NAC* point [20], by analysing the C_p data for PAA, we initiate a mean-field-like to tricritical behaviour for this liquid crystal. From our analysis, we obtained $\alpha = 0.5$ for $T < T_{NI}$ and $T < T_{SN}$ (Table 2), as the mean-field-tricritical value. On the other hand, a small value of $\alpha = 0.006$ from our analysis for $T > T_{NI}$ can be compared with our previous value of 0.05 ($T > T_{NI}$) for anisaldazine [17]. This is based on the occurence of a mean field tricritical behaviour ($\alpha = 0.5$) below T_{NI} in the nematic phase of PAA.

Unexpected behaviour occurs above T_{SN} in the nematic phase with a large negative value of $\alpha = -0.85$ (Table 2) according to the renormalisation-group-analysis (Equation 3). This is also associated with the mean field tricritical behaviour ($\alpha = 0.5$) below T_{SN} (Table 2). This large negative value obtained from the renormalisation-group-expression cannot be compared with the value of -0.07 ($T > T_{SN}$) for PAA (Table 1) or -0.02 ($T > T_{SN}$) for anisaldazine [17]. This indicates that a mean field tricritical transition occurs below T_{NI} ($\alpha = 0.5$), which changes its character with the critical exponent value of $\alpha = 0.006$ above T_{NI} in PAA. On the other hand, the renormalisation-group-analysis does not give the expected critical behaviour above T_{SN} with the exponent value of -0.85 if one assumes a mean field tricritical transition ($\alpha = 0.5$) below T_{SN} (Table 2). So, the simple power-law formula (Equation (1)) describes adequately the solid-nematic transition with the α values, as given in Table 1.

Above the solid-nematic transition (T_{SN}) where the critical exponent was obtained as $\alpha = -0.07$, there occurs a supercooled region for PAA, as also occurs for anisaldazine experimentally [2]. The negative value of the critical exponent α for both liquid crystals just above T_{SN} may be due to the existence of this supercooled region where there is a jump discontinuity, as obtained experimentally [2]. This may be of interest to study, as pointed out previously for anisaldazine [17], also for PAA which require some detailed experimental measurements. The mechanism of the phase transition between solid and nematic phases in the supercooled region for both anisaldazine and p-azoxyanisole, can be different in comparison with the λ-type phase transition between nematic and isotropic liquid in these liquid crystals. This would then warrant a new approach to analyse the specific heat.

The temperature dependence of the enthalpy and the entropy in the nematic phase was also calculated from the specific heat C_p in this study. For this calculation, the values of α and A from our C_p analysis using the simple power-law formula (Equation (1)) were used. As seen in Figure 5, the enthalpy difference, $\Delta H = H - H_0$, increases as the temperature increases in the nematic phase ($T > T_{SN}$). This is consistent with the specific heat increasing as the T_{SN} is approached from the nematic phase, which was observed experimentally [2].

Similarly, we calculated the entropy difference, $\Delta S = S - S_0$, as plotted in Figure 6, from the specific heat C_p. As expected, the entropy difference, or entropy, increases as the temperature increases from the solid to the nematic phase ($T > T_{SN}$). As a measure of the disorderness, the entropy is much higher in the nematic phase than the solid phase in PAA. Thus, both the enthalpy difference ΔH and the entropy difference ΔS increase with increasing temperature (Figures 5 and 6).
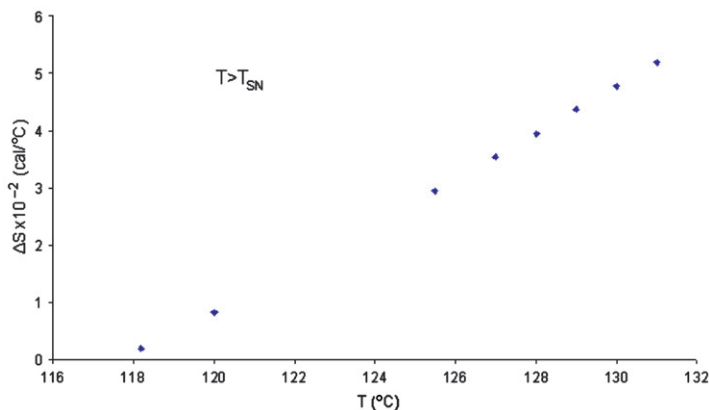
Figure 6. The entropy difference ($\Delta S = S - S_O$) calculated from Equation (9) in the nematic phase ($T > T_{SN}$) of PAA ($T_{SN} = 117.6°C$).

4. Conclusions

The critical behaviour of the specific heat C_p was studied here close to the nematic-isotropic liquid (NI) and solid-nematic (SN) phase transitions in PAA. This was done by analysing the experimental C_p data and the values of the critical exponent were determined above and below T_{NI} and T_{SN} for PAA. The C_p data was analysed by a simple power-law formula and the renormalisation-group expression. Our exponent values obtained from a simple power-law formula indicate that the specific heat C_p exhibits similar critical behaviour for $T < T_{NI}$ and $T < T_{SN}$, which can be described by a three-dimensional Ising model. For $T > T_{NI}$ our exponent value is much larger than those predicted by theoretical models. For $T > T_{SN}$ the negative exponent value is still close to the expected value of the helium analogy or XY model of liquid crystal, as in anisaldazine. It is indicated here that the negative value of the critical exponent for the specific heat C_p is due to the presence of the supercooled region between solid and nematic phases in p-azoxyanisole and also in anisaldazine. By analysing the experimental C_p data using the renormalisation-group expression, it was obtained that the critical exponent α is very close to zero (0.006) above T_{NI} on the basis of a mean-field tricritical behaviour ($\alpha = 0.5$) below T_{NI} for the nematic-isotropic liquid transition in PAA. This analysis gives a very large negative α value above T_{SN} accompanied with the $\alpha = 0.5$ value below T_{SN} for the solid-nematic phase transition in PAA.

Using the specific heat C_p the enthalpy H and the entropy S were calculated as a function of temperature in the nematic phase of PAA. They both increase as the temperature increases from the solid to the nematic phase ($T > T_{SN}$), as expected for PAA.

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