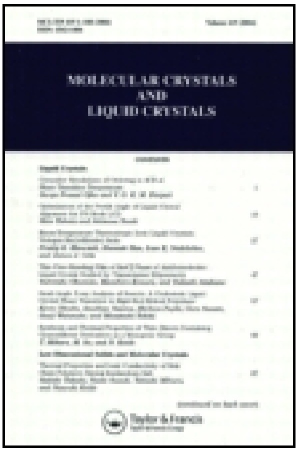

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Analysis of the Specific Heat in the Supercooled Solid Phase of Liquid Crystals

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The specific heat C_p is analyzed using the experimental data at various temperatures in the solid phase of cholesteryl myristate according to a power-law formula for the rapidly and slowly cooled solid in the stability limit. We also analyze the temperature dependence of the C_p using the experimental data for the supercooled solid phase of p-azoxyanisole in the stability limit and the stability temperatures are determined for both cholesteryl myristate and p-azoxyanisole.

Our results show that the method of analysis given here is adequate to describe the observed behaviour of the C_p at low temperatures in the solid phase.

Keywords Liquid crystals; specific heat; supercooled solid

1. Introduction

The liquid crystals of p-azoxyanisole (PAA), anisaldazine (AAD) and cholesteryl myristate (CM) exhibit mesophases between solid and the isotropic liquid. PAA and AAD exhibit a single mesophase of the nematic type and CM forms both smectic and cholesteric type mesophases [1]. Phase sequence observed for PAA, AAD and CM are as follows:

P-Azoxyanisole

$$\text{Solid} \overset{117.6°\text{C}}{\longleftrightarrow} \text{Nematic} \overset{133.9°\text{C}}{\longleftrightarrow} \text{Isotropic}$$

Anisaldazine

$$\text{Solid} \overset{168.9°\text{C}}{\longleftrightarrow} \text{Nematic} \overset{180.5°\text{C}}{\longleftrightarrow} \text{Isotropic}$$

Cholesteryl Myristate

$$\text{Solid} \overset{73.6°\text{C}}{\longleftrightarrow} \text{Smetic} \overset{79.7°\text{C}}{\longleftrightarrow} \text{Cholesteric} \overset{85.5°\text{C}}{\longleftrightarrow} \text{Isotropic}$$

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In these liquid crystalline materials, the solid phase has crystal-like order and the isotropic liquid phase has liquid-like disorder [1]. Their measurements on the specific heat (C_p) using the differential scanning calorimetric (dsc) technique have shown the crystalline solid, the mesophase and the isotropic liquid, and also supercooled phases at low temperatures [1].

Various physical properties of those liquid crystals which are in the same family, have been studied close to phase transitions using different experimental techniques and the theoretical models suggested, as given in the literature. Among the experimental studies, measurements of specific volume [2], the specific heat [1] as stated above, the thermal expansion [3], ultrasonic wave velocities [4], the Raman scattering [5] and neutron diffraction [6] for PAA have been reported. The effect of disorder on the nematic to isotropic liquid phase transition [7] and an experimental study on confined geometries [8] for PAA have also been reported. Recently, the elastic constants of the nematic liquid crystal PAA have been measured [9].

In order to explain some physical properties of PAA close to the phase transitions, the Maier-Saupe model [2] was developed many years ago. Some other model studies [10–12] have been reported for PAA, as we have reviewed in our earlier study [13]. We have also established the Pippard relations close to the phase transitions in PAA [14] and, we have calculated the temperature dependence of the thermal expansion and of the C_p near the nematic-isotropic [13] and the solid-nematic [15] transitions in this liquid crystal.

CM liquid crystalline exhibits smectic and cholesteric phases between the solid phase and the isotropic liquid, as the temperature increases. In the smectic phase, the molecules are arranged in layers with long axes approximately normal to the plane of the layers [1]. This structure of the smectic phase that occurs close to the cholesteric phase of CM is considered as the smectic A. This liquid crystalline material has also been studied extensively. As we have reviewed in our recent paper [16], CM has been studied experimentally by the ultrasonic [17], thermodynamic and viscometric [18] methods. Relaxation processes have been studied [19] and, the transition between the α -cholesteric and β-cholesteric phases for a binary mixture of cholesteryl chloride and CM has been investigated [20]. We have calculated T-X phase diagrams for binary mixtures of cholestanyl myristate- cholesteryl myristate (CM) and cholestanyl myristate- cholesteryl oleate by using the mean field theory in our recent study [16]. We have also analyzed the temperature dependence of the C_p for CM close to the cholesteric-isotropic liquid ($T_{CI} = 85.5°C$) and smectic-cholesteric ($T_{SC} = 79.7°C$) transitions, recently [21].

In this study, we analyze the C_p at low temperatures mainly focusing on the supercooled solids of CM and PAA. As we have analyzed the temperature dependence of the thermal expansion for PAA [14] and the specific heat C_p [15], the C_p for AAD [22] and for the CM [21], in this study we analyze the C_p at low temperatures for the supercooled solid phase of CM and PAA in the stability limit. Additionally, the analysis of C_p performed close to the smectic-solid transition is given here for the CM, both which have not been reported previously.

2. Analysis of the Specific Heat

The specific heat was analyzed close to the smectic-solid transition and, in the rapidly and slowly cooled samples for CM according to a power-law formula using the experimental data [1]. The analysis of the C_p was also performed in the supercooled

Table 1. Values of the critical exponent α for the C_p and the amplitude A in the temperature interval indicated close to the smectic A-solid phase transition of cholesteryl myristate (CM) according to a power-law formula (Eq. (1))

Transition	T_{SS} (°C)	α	A (cal/g.°C)	$\epsilon = \lvert T - T_{SS}\rvert / T_{SS}$
Smectic A-Solid	73.6	0.06	0.368	$1.2\times10^{-2} < \varepsilon < 2.0\times10^{-1}$
Smectic A-Solid		0.10	0.336	$6.5\times10^{-2} < \varepsilon < 3.0\times10^{-1}$

and stable solid phase for PAA using the experimental data [1] by a power-law formula.

2.1. *Cholesteryl Myristate (CM)*

Close to the smectic-solid ($T_{SS} = 73.6$°C) transition, the temperature dependence of the C_p can be expressed as

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

where $\varepsilon = (T_c - T)/T_c$ is the reduced temperature, ($T_c = T_{SS}$), α is the critical exponent for the C_p and A is the amplitude. The C_p was analyzed using the power-law expression (Eq. (1)) in the logarithmic form

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

for the two temperature intervals, with the values of α and A, as given in Table 1. The temperature range was divided into the two for our analysis to get a linear

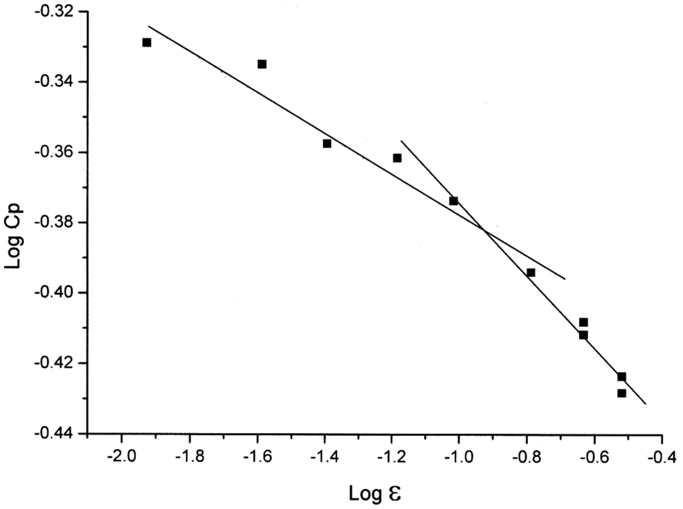

Figure 1. The specific heat C_p as a function of the reduced temperature ($\varepsilon = |T_c - T|/T_c$) in a log-log scale close to the smectic A-solid transition ($T_{SS} = 73.6$°C) for the cholesteryl myristate (CM) using the experimental data [1] analyzed according to Eq.(1) (see Table 1).

Table 2. Values of the critical exponent α and the amplitude A for the rapidly cooled solid phase of cholesteryl myristate (CM) in the stability limit according to a power-law formula (Eq. (3))

Phase	Stability temperature T_s (°C)	α	A (cal/g.°C)	Temperature interval (°C)
Rapidly cooled solid	-19.6	0.50 ± 0.02	2.98	$11.9 < T < 46.4$

variation of C_p with the temperature in the log-log scale according to Eq. (2). In Figure 1 we give our plot of the C_p as a function of the reduced temperature ε (in the log-log scale) for the temperature interval indicated.

In this study, we were particularly interested in the stability limit for the rapidly cooled and slowly cooled solid phases of CM. So, the experimental data for the C_p [1] was analyzed using the power-law formula for the stability limit [23]

$$C_p = A(T - T_S)^{-\alpha} \tag{3}$$

or in a log-log form

$$\log C_p = \log A - \alpha \log(T - T_s) \tag{4}$$

In Eq. (3), T_s is the stability temperature, $\alpha = 1/2$ is the critical exponent and A is the amplitude, as before. From our analysis, we determined the stability temperature as $T_s = -19.6$°C from the C_p data for the rapidly cooled solid [1] according to Eq. (3) ($\alpha = 1/2$). Table 2 gives the fitted parameters (Eq. (3)) in the temperature interval

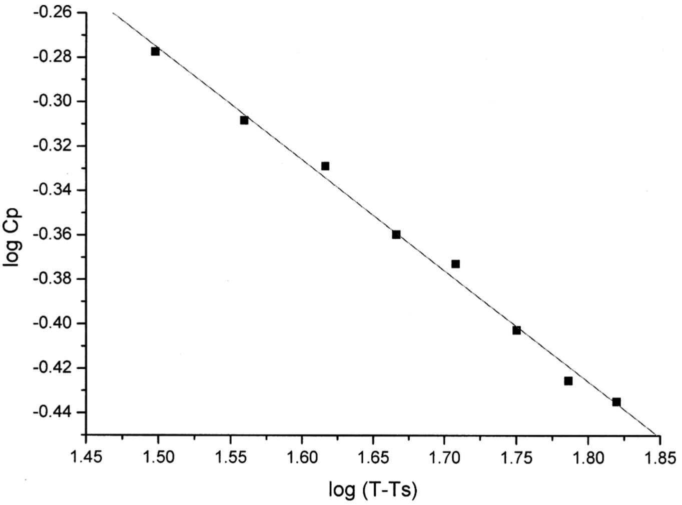

Figure 2. The specific heat C_p in a log-log scale as a function of the temperature with respect to the stability temperature T_s for the rapidly cooled solid phase of cholesteryl myristate (CM) using the experimental data [1] analyzed according to Eq. (3) (see Table 2).

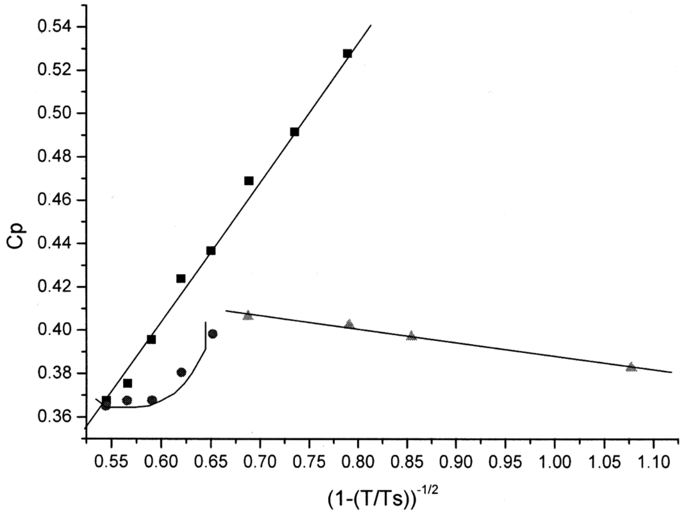

Figure 3. The specific heat C_p as a function of the reduced temperature with respect to the stability temperature T_s for the rapidly cooled solid phase (■ and ●) and for the slowly cooled solid phase (▲) of cholesteryl myristate (CM). The dashed lines represent the best fit to the experimental data [1] analyzed according to Eq. (3) (see Table 2).

indicated for the rapidly cooled CM. A plot of $\log C_p$ against $\log(T - T_s)$ is given in Figure 2 according to Eq. 4. We have also plotted C_p as a function of $(1 - T/T_s)^{-1/2}$ for the rapidly cooled solid (CM) in Figure 3. Furthermore, we analyzed the experimental C_p [1] for the slowly cooled solid (CM) according to Eq. 3 with the $\alpha = 1/2$ and we used the stability temperature as $T_s = -19.6°C$. For the two different temperature regions, C_p is plotted as a function of $(1 - T/T_s)^{-1/2}$ in Figure 3 for the slowly cooled solid. In this Figure, the dashed lines represent the curves fitted to the experimental data.

2.2. *P-Azoxyanisole (PAA)*

For PAA, we were in particular interested in the stability limit for the supercooled solid, as for the CM which was studied here. Using Eq. (3), the C_p data [1] was analyzed by taking the stability temperature as $T_s = 90°C$ for PAA in the solid phase and the fitted parameters were determined, as given in Table 3. Figure 4 gives a plot of C_p against $T - T_s$ in the log-log scale according to Eq. (4) for the supercooled solid phase of PAA. We also analyzed the C_p data for the solid phase of PAA through Eq. (3) with the $T_s = 90°C$. The fitted parameters α and A in the temperature interval

Table 3. Values of the critical exponent α and the amplitude A for the supercooled and solid phases of p-azoxyanisole (PAA) in the stability limit according to a power-law formula (Eq. (3))

Phase	T_s (°C)	α	A (cal/g.°C)	Temperature interval (°C)
Supercooled	90	−0.02	0.43	$11.8 < (T - Ts) < 26.3$
Solid		0.003	0.345	$0.23 < (T - Ts) < 5.38$

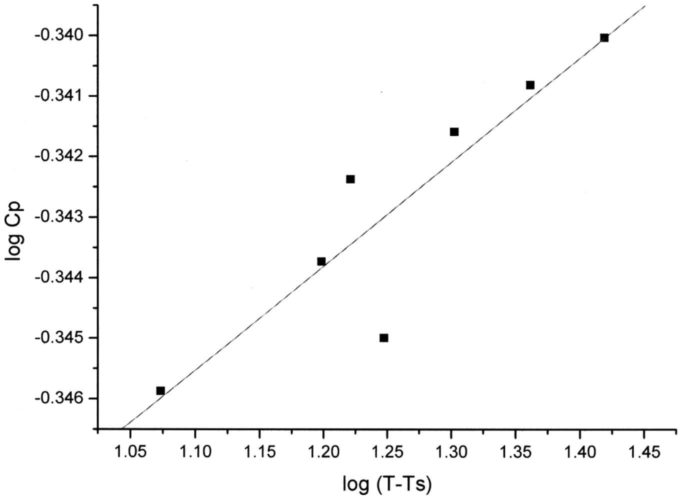

Figure 4. The specific heat C_p in a log-log scale as a function of the temperature with respect to the stability temperature T_s for the supercooled solid phase of p-azoxyanisole (PAA) using the experimental data [1] analyzed according to Eq. (3) (see Table 3).

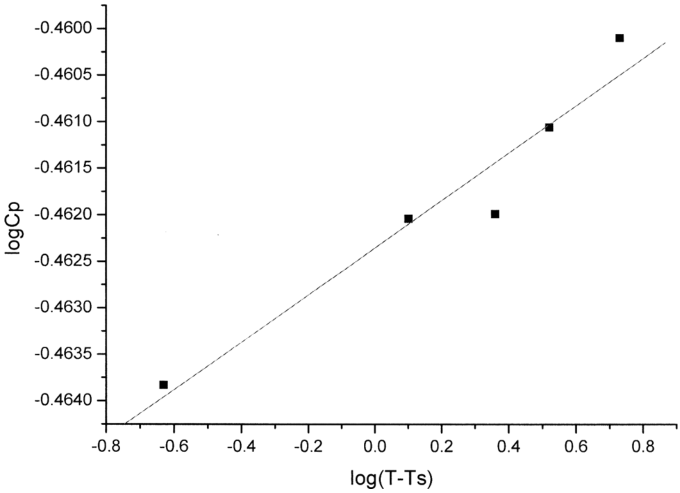

Figure 5. The specific heat C_p in a log-log scale as a function of the temperature with respect to the stability temperature T_s for the solid phase of p-azoxyanisole (PAA) using the experimental data [1] analyzed according to Eq. (3) (see Table 3).

studied, are given in Table 3 for the solid phase of PAA. Finally, Figure 5 gives our plot of $\log C_p$ against $\log(T - T_s)$ for the solid phase of this liquid crystal.

3. Discussion

The C_p data [1] was analyzed in a wide range of temperature (~70°C) for the smectic A-solid transition and, for the rapidly cooled and slowly cooled solid of CM. Close to the smectic A-solid ($T_{SS} = 73.6°C$) transition, the value of the critical exponent, $\alpha \cong 0.1$(Table 1), which we extracted from the analysis of the C_p (Fig. 1), indicates that this transition is of a second order. It is not a mean-field like ($\alpha = 0$), but it is rather of a λ-type transition, as we have also considered [21] for the cholesteric-isotropic liquid (CI) and for the smectic-cholesteric (SC) transitions, which was based on the experimental measurements [1]. For the rapidly and slowly cooled samples of CM, the exponent value becomes $\frac{1}{2}$ (Eq. 3) and the stability limit was reached at the stability temperature of $T_s = -19.6°C$ for this liquid crystalline material. For the stability temperature, the critical exponent α remains fixed within the experimental uncertainties (Table 2). As shown in Figure 3 for the rapidly cooled solid, C_p varies linearly with the $(1 - T/T_s)^{-1/2}$ in the temperature interval given. For slowly cooled solid, because of the kink that occurs around 25°C in the experimental C_p [1], almost linear variation of C_p with the $(1 - T/T_s)^{-1/2}$ in the reduced temperature interval of 0.54 to 0.62 changes towards a nonlinear behaviour at higher temperatures (Fig. 3). In the reduced temperature interval of 0.7 to about 1.1, C_p varies linearly with the $(1 - T/T_s)^{-1/2}$ for the slowly cooled solid, as shown in Figure 3. As observed experimentally [1], the C_p curves increasing in the solid phase and decreasing in the slowly cooled solid phase with decreasing temperature, construct a kink at around 25°C. This can be due to the fact that long-range ordering of the molecules is not completed in the solid phase or to some extent the molecules are still disordered (increasing C_p), whereas in the slowly cooled solid phase the molecules are more ordered (decreasing C_p), as the temperature decreases. Thus, the occurrence of the kink in C_p indicates a kind of transition from the solid phase with some disorder to the slowly cooled solid phase with the molecules oriented orderly, as stated above.

Similar analysis was performed for the supercooled solid phase and also solid phase of PAA, as plotted in Figures 4 and 5, respectively. Differently from the rapidly and slowly cooled solid phase of CM, supercooled solid phase of PAA has a negative critical exponent ($\alpha = -0.02$) in the temperature interval studied. For the solid phase, α is positive as given in Table 3. In the stability limit, the stability temperature was taken as $T_s = 90°C$ for PAA using the experimental C_p data [1].

In our analysis for the supercooled solid phase of PAA, we used the power-law formula (Eq. (3)) with the stability temperature T_s and the critical exponent of $\alpha = 1/2$, as stated above. However, our analysis gave us the values of -0.02 (supercooled solid phase) and ~ 0 (solid phase), as given in Table 3. The power-law formula (Eq. (3)) for the stability limit was appropriate for rapidly and slowly cooled solid of CM. But, it was obtained that Eq. 3 with the $\alpha = 1/2$ was not satisfactory for the supercooled solid phase of PAA. Thus, the power-law formula in the stability limit (Eq. (3)) that was applied to describe the supercooling and superheating in water [23], was also applied to rapidly and slowly cooled solid phases of CM successfully, as given here. However, it was found that Eq. (3) was inadequate for the PAA. In general, this power-law formula (Eq. (3)) can also be applied to some other systems which exhibit superheating and supercooling phases.

4. Conclusions

The specific heat C_p was analyzed at low temperatures close to the smectic A-solid transition and in particular, for the rapidly cooled and slowly cooled solid phases of CM. The temperature dependence of the C_p was also analyzed for the solid and supercooled solid phases of PAA.

It was found that a power-law formula in the stability limit, with the critical exponent $\frac{1}{2}$ was satisfactory for the CM, but it was inadequate for PAA. With some accurate measurements of the specific heat C_p for the supercooled solid phase of PAA, our method of analysis can be examined and, also it can be applied to some other liquid crystals exhibiting supercooling and superheating phases.

References

[1] Barrall, E. M., Porter, R. S., & Johnson, J. F. (1967). *J. Phys. Chem.*, *71*, 895.
[2] Maier, V. W., & Saupe, A. (1960). *Z. Naturforsch*, *15a*, 287.
[3] Pruzan, P.h., Liebenberg, D. H., & Mills, R. L. (1986). *J. Phys. Chem. Solids*, *47*, 949.
[4] Kapustin, A. P., & Bykova, N. T. (1966). *Sov. Phys. Crystallogr.*, *11*, 297.
[5] Bulkin, B. J., & Prochaska, F. T. (1971). *J. Chem. Phys.*, *54*, 635.
[6] Pynn, R. (1973). *J. Phys. Chem. Solids*, *34*, 735.
[7] Dadmun, M. D., & Muthukuvar, M. (1993). *J. Chem. Phys.*, *98*, 4850.
[8] Shao, Y., & Zerda, T. W. (1998). *J. Phys. Chem.*, *B 102*, 3387.
[9] Simoes, M., & Simeao, D. S. (2006). *Phys. Rev.*, *E73*, 062702.
[10] Zhang, Z., Zuckermann, M. J., & Mouritsen, O. G. (1993). *Mol. Phys.*, *80*, 1195.
[11] Williamson, D. C. (1998). *Mol. Phys.*, *95*, 319.
[12] Garcia-Sanchez, E., Martinez-Richa, A., Villeges-Gasca, J. A., Mendoza-Huizar, L. H., & Gil-Villegas, A. (2002). *J. Phys. Chem.*, *A 106*, 10342.
[13] Kilit, E., & Yurtseven, H. (2008). *J. Mol. Liq.*, *138*, 84.
[14] Kilit, E., & Yurtseven, H. (2007). *16th Conference on Liquid Crystals (CLC) Stare Jablonki, Poland, Conf. Proc.* 327–334.
[15] Kilit, E., & Yurtseven, H. (2010). *Phys. Chem. Liq.*, *48*, 450.
[16] Yurtseven, H., & Şen, S. (2009). *Ann. Acad, N. Y., Sci.*, *1161*, 416.
[17] George, A. K., & Padmini, A. R. K. L. (1981). *Mol. Cryst. Liq. Cryst.*, *65*, 217.
[18] Kishimoto, H., Iwasaki, T., & Yonese, M. (1986). *Chem. and Phar. Bull.*, *34*, 2698.
[19] Sabirov, L., Lerman, V., Turakulov, Y., & Semenov, D. (2001). *Mol. Cryst. Liq. Cryst.*, *366*, 1853.
[20] Schnur, J. M., & Martire, D. E. (1973). *Mol. Cryst. Liq. Cryst. 26*, 213.
[21] Yurtseven, H., & Kilit, E. (2009). *J. Optoelectronics and Adv. Mater., Symposia*, *1*, 597.
[22] Kilit, E., & Yurtseven, H. (2008). *J. Mol. Liq.*, *140*, 84.
[23] Speedy, R. J. (1982). *J. Phys. Chem.*, *86*, 3002.