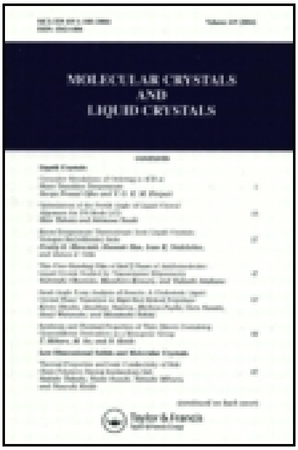

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

High Resolution Volumetric Studies. Smectic-A-Smectic-C Transition in 4-n-Pentylphenylthiol-4′-n-Decyloxybenzoate (10S5)

Andrzej żywociński [a] & Stefan A. Wieczorek [a]

[a] Institute of Physical Chemistry, Polish Academy of Sciences, 01-224, Warsaw, Poland

To cite this article: Andrzej żywociński & Stefan A. Wieczorek (1987): High Resolution Volumetric Studies. Smectic-A-Smectic-C Transition in 4-n-Pentylphenylthiol-4′-n-Decyloxybenzoate (10S5), Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 151:1, 399-410

To link to this article: http://dx.doi.org/10.1080/00268948708075346

Mol. Cryst. Liq. Cryst., 1987, Vol. 151, pp. 399-410
Photocopying permitted by license only

Printed in the United States of America

HIGH RESOLUTION VOLUMETRIC STUDIES. SMECTIC-A - SMECTIC-C TRANSITION IN 4-n-PENTYLPHENYL-THIOL-4'-n-DECYLOXYBENZOATE ($\overline{10}S5$)

ANDRZEJ ŻYWOCIŃSKI and STEFAN A. WIECZOREK
Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warsaw, Poland

Abstract High resolution measurements of molar volume V(T) and isothermal compressibility coefficient were made on pure $\overline{10}S5$. The molar-volume variations show a classical second order smectic-A - smectic-C transition. These data are very well described by a mean-field Landau model. The isobaric thermal-expansion coefficient has been calculated. The data of the compressibility at the SmA-SmC transition do not show any singularity.

INTRODUCTION

The compound 4-(n-pentyl)phenylthiol-4'-(n-decyloxy)benzoate ($\overline{10}S5$) studied here belongs to the same homologous series as 4-(n-pentyl)phenylthiol-4'-(n-octyloxy)benzoate ($\overline{8}S5$), studied by us previously.[1,2] Both these compounds exhibit the smectic-C (SmC) to smectic-A (SmA) phase transition followed by the smectic-A to nematic (N) phase transition. The SmC-SmA transition has been studied extensively and the nature of the transition has been discussed (Birgeneau et al.[3] and references therein). In the majority of cases the mean-field model proposed by Huang and Viner[4] is more adequate than the critical behavior model proposed by de Gennes.[5]

The transition in all compounds studied is second order; however, Huang[6] suggests a possibility of a first order. Recently, Huang and Lien[7] have collected experimental heat capacity data from which the mean-field parameters can be determined and discuss the effect of the SmA temperature range on the behavior of the SmC-SmA transition. This effect is characterized by a dependence of mean-field parameters on the size of SmA temperature range represented by $r = 1 - T_{AC}/T_{NA}$.

From our precise molar-volume data we were able to calculate one important dimensionless parameter, t_o. In this paper we report the results of V(T) and $\beta_T(T)$ data for $\overline{10}$S5, the compound with rather large size of the SmA temperature range. In conclusion the comparison with results for $\bar{8}$S5[1] is given.

EXPERIMENTAL

Accurate measurements of volume versus temperature were carried out in dilatometer shown in Figure 1. The dilatometer D consists of a capillary C 0.3 mm in diameter and 37 cm long, connected with 9 cm^3 vessel surrounded by a pressure jacket PJ. At the bottom of the vessel and of the capillary about 2 cm^3 mercury is placed. The presence of mercury allows making measurements with both increasing and decreasing temperature. The volume of the dilatometer was determined during the calibration run with deionized and degassed water; the results of volume versus height of mercury in the

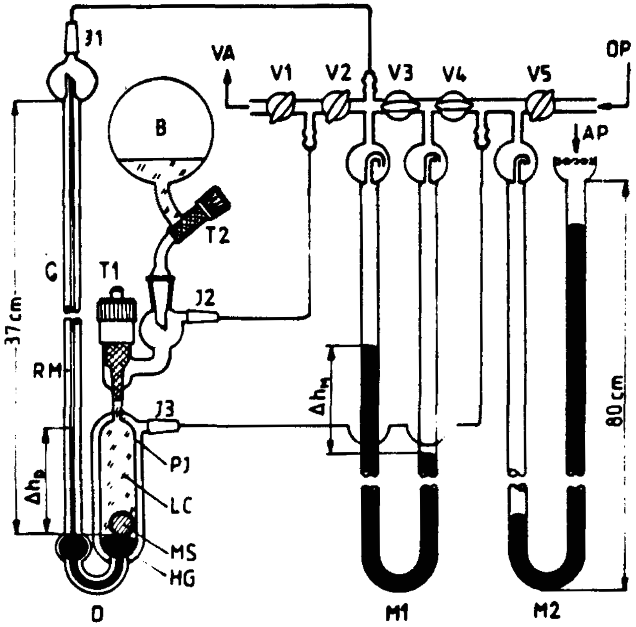

FIGURE 1. Schematic diagram of the apparatus: D, dilatometer; C, capillary; RM, reference mark; J1÷J3, taper joints; PJ, pressure jacket; LC, sample of liquid crystal; MS, magnetic stirrer; HG, mercury; T1, teflon needle tap; T2, teflon tap; B, bulb with degassed sample; M1, M2, mercury manometers; V1÷V5, valves; VA, vacuum; OP, overpressure; AP, atmospheric pressure.

capillary were correlated by a linear equation with the standard deviation $\sigma = 4\times10^{-6}$ cm^3. The calibration was made in the temperature range between 318 K and 357 K. However, the absolute volume of the dilatometer could differ in individual runs by less than 0.001 cm^3, owing to the use of a Teflon needle tap,T1.

The dilatometer is filled under vacuum with degassed sample; the sample of the liquid crystal warmed to the isotropic phase is flowing from the bulb B under the force of gravity through the open taps T1 and T2 into the dilatometer. The dilatometer is then placed in a 70 l water thermostat assuring a vigorous stirring and a stability of local temperature better than ±0.2 mK. The temperature was determined with a Tinsley 5187 SA platinum thermometer calibrated on IPTS-68 and continuously monitored with a HP 2801A quartz thermometer.

The measurements of V(T) were done under a constant pressure equal to 1.013 bar; this was assured by compensating the pressure of the mercury column in the capillary by means of an external manometer M1 connected to the end of the capillary (Figure 1, $\Delta h_D = \Delta h_M$). The small differences in pressure (within a few Torr) were corrected in calculations by using the compressibility of the sample, determined during the run. In the aim to determine the isothermal compressibility coefficient β_T the run under the pressure of about 2.0 bar was made. In this measurement the pressure expansion of the vessel of dilatometer was avoided by apply the equal pressure to the pressure jacket and to the sample of liquid crystal inside the dilatometer (the height of mercury in the capillary C was always taken in the consideration).

The sample of $\overline{10}$S5 was synthesized by"ZD Chemipan" and was further purified by us by a very slow crystallization from methanol. The transition temperatures are as follow $T_{AC} = 337.30$ K, $T_{NA} = 354.35 \div 354.38$ K and $T_{NI} = 359.62 \div 359.65$ K (for the first order transitions, the coexistence range is cited).

RESULTS AND DATA ANALYSIS

Molar-volume data

The molar-volume variations with temperature have been measured in the temperature range $334.65 \div 339.35$ K. In the immediate vicinity of the SmA-SmC transition the volume has been measured with a temperature steps about 10 mK. The results are presented in Figure 2 and show a typical cusp-like singularity with a strong pretransitional effect on the SmC side and with a straight line on the SmA side. A shape of this curve suggests that the power-law equations can not be applied in this case. Thus we have used the mean-field equations[1,4] derived from Landau model

$$V = \begin{cases} Bt + C, & T > T_{AC} \\ A'(1-3t/t_0)^{1/2} + B't + C', & T < T_{AC} \end{cases} \qquad (1)$$

where $t = T/T_{AC} - 1$ and t_0 is a crossover temperature. A meaning of parameter t_0 is explained in Figure 3. The parameter t_0 characterizes a difference between this transition and hypothetical tricritical behavior represented by extrapolated curve V(T) to the point $t = t_0/3$ at which dV/dT is infinite (dashed line in Figure 3).

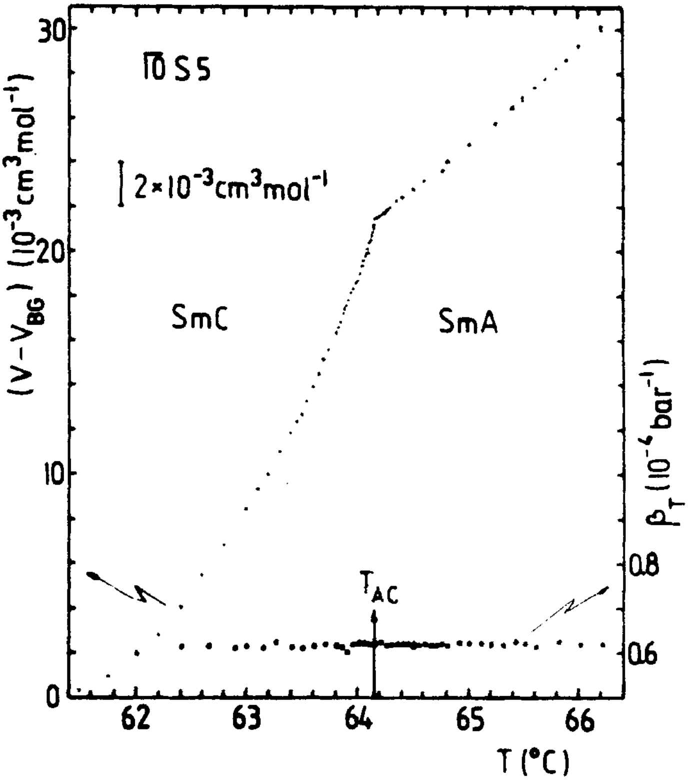

FIGURE 2. Molar volume near the SmA-SmC transition in $\overline{10}$S5 (upper curve), with a linear background $V_{BG} = a + bT$ subtracted, plotted against temperature: $a = 447.973\ cm^3mol^{-1}$, $b = 0.3738\ cm^3mol^{-1}(^oC)^{-1}$. Lower part shows isothermal compressibility coefficients $\beta_T(T)$.

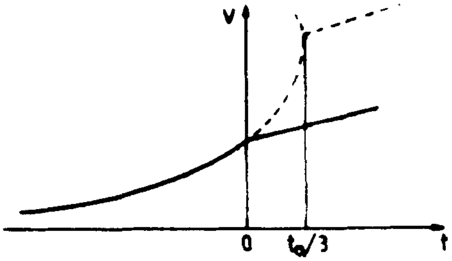

FIGURE 3. Meaning of the crossover temperature, t_o.

Eqs. (1) were fitted to the experimental V(T) data using a widely available nonlinear least-squares program.[8] The transition temperature T_{AC} was not a fitted parameter and was fixed at a value established during the preliminary fits as it was described earlier.[2] The parameters of Eqs. (1) obtained in fits along with the standard deviations are given in Table I. Three different temperature ranges were taken in the calculations and the results show that the parameters are stable to range shrinking. In all fits the standard deviations $\sigma < 1.2\times10^{-4}$ cm^{3}mol^{-1} were obtained.

The temperature dependence of thermal expansion coefficient $\alpha_p(T)$ has been calculated from the equations

$$\alpha_p(T) = \begin{cases} \dfrac{B}{V(T)T_{AC}}, & T > T_{AC} \\ \dfrac{1}{V(T)T_{AC}}\left[-\dfrac{3A'}{2t_o}(1-3t/t_o)^{-1/2} + B'\right], & T < T_{AC}. \end{cases} \qquad (2)$$

TABLE I **Parameter values obtained from the fitting of molar-volume data for 10S5 above and below the smectic-A to smectic-C transition with the Landau model, Eqs.(1). Transition temperature** T_{AC} = 337.303 K **was held fixed in all fits; σ - the standard deviation; $\alpha_p(T_{AC})$ calculated from** Eqs.(2); $V(T_{AC}^{+}) = C$ for $T > T_{AC}$ and $V(T_{AC}^{-}) = A' + C'$ **for** $T < T_{AC}$.

Fit $T > T_{AC}$	T_{max} [a] (K)	$10^3 t_{max}$	A (cm^3mol^{-1})	B (cm^3mol^{-1})	C (cm^3mol^{-1})		$10^4\sigma$ (cm^3mol^{-1})	$10^4\alpha_p(T_{AC}^{+})$ (K^{-1})	$V(T_{AC}^{+})$ (cm^3mol^{-1})
1	337.9525	1.926		127.46	471.9747		0.61	8.01	471.9747
2	338.6510	3.996		127.50	471.9747		0.77	8.01	471.9747
3	339.3526	6.076		127.51	471.9747		0.79	8.01	471.9747
$T < T_{AC}$	T_{min} [b]	$10^3 t_{min}$	A'	B'	C'	$10^3 t_o$	$10^4\sigma$	$10^4\alpha_p(T_{AC}^{-})$	$V(T_{AC}^{-})$
4	336.6527	-1.928	-0.0114	127.49	471.9859	4.8	0.97	8.23	471.9745
5	335.9522	-4.005	-0.0177	125.71	471.9922	4.4	1.06	8.25	471.9746
6	335.1538	-6.372	-0.0206	125.22	471.9952	4.9	1.18	8.26	471.9746

[a] T_{min} = 337.3123 K, $t_{min} = T_{min}/T_{AC} - 1 = 2.757\times10^{-4}$

[b] T_{max} = 337.3027 K, $t_{max} = T_{max}/T_{AC} - 1 = -0.889\times10^{-6}$

The curve $\alpha_p(T)$ calculated from Eqs. 2 is shown in Figure 4; calculated values $\alpha_p(T_{AC})$ are given in Table I.

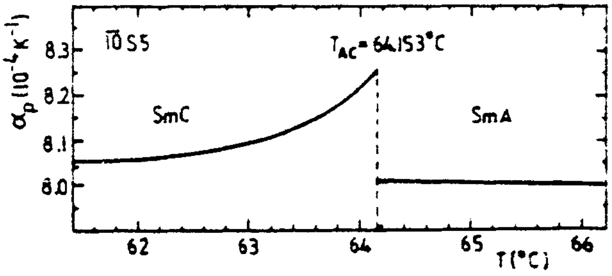

FIGURE 4. Calculated thermal expansion coefficient near the SmA-SmC transition in $\overline{10}$S5, plotted against temperature.

For comparison we have collected some results for $\overline{10}$S5 and for $\overline{8}$S5[1] in Table II. The values of t_o obtained from our volumetric measurements fit very well to a general tendency[7] of t_o changes with varying $r = 1 - T_{AC}/T_{NA}$.

TABLE II Parameters r, t_o, and $\Delta\alpha_p = \alpha_p(T_{AC}^-) - \alpha_p(T_{AC}^+)$ for two compounds with different size of SmA temperature range.

Compound	r	$10^3 t_o$	$10^4\Delta\alpha_p$ (K^{-1})
$\overline{10}$S5	0.048	4.4÷4.9	0.25
$\overline{8}$S5	0.023	1.3÷2.1	0.50

Isothermal compressibility

The isothermal compressibility of $\overline{1}$OS5 was measured as a function of temperature at constant pressure and the isothermal compressibility coefficient $\beta_T = -V^{-1}(dV/dp)_T$ was calculated. Results are shown in a lower part of Figure 2. There is no singularity in $\beta_T(T)$ on both sides of the transition temperature T_{AC}. The data show that β_T is independent of temperature in this rather narrow temperature range and is equal within experimental error for both SmC and SmA phases. For the SmA phase β_T remains constant up to 6 K above T_{AC}. Farther it increases slowly to about 0.788×10^{-4} bar^{-1} at temperature 353 K where a strong pretransitional effect of the first order SmA-N phase transition is observed[9] (maximum value β_T measured at the SmA-N transition is 5.7×10^{-4} bar^{-1}).

In the vicinity of the SmA-SmC transition mean values of β_T and their standard deviations were calculated. These values are $(0.616\pm0.004)\times10^{-4}$ bar^{-1} and $(0.620\pm0.002)\times10^{-4}$ bar^{-1} for SmC and SmA, respectively.

CONCLUSION

We have found that molar-volume variations near the SmA-SmC transition for $\overline{1}$OS5 are well described by the mean-field model. For this model we have found the crossover temperature t_o in the range from 4.4×10^{-3} to 4.9×10^{-3} for $r = 1-T_{AC}/T_{NA} = 0.048$. This value is consistent with results reported by Huang and Lien[6] and obtained from heat capacity measurements.

From our V(T) measurements we have estimated the jump of isobaric thermal-expansion coefficient at phase transition $\Delta\alpha_p(T_{AC}) = 0.25\times10^{-4}$ K^{-1}. Thus we conclude that SmA-SmC transition in $\overline{10}$S5 has a nature quite different from tricritical behavior.

Another interesting result has been obtained from compressibility measurements. It has been found that isothermal compressibility coefficient is independent of temperature in the vicinity of the SmA-SmC transition and is equal in both phases within experimental error less than 1%.

ACKNOWLEDGMENTS

We thank Professor J. Stecki for suggesting this work and for helpful discussions. This work was supported by the Polish Academy of Sciences Research Program No. 03.10.1.

REFERENCES

1. A. Żywociński and S.A. Wieczorek, Phys. Rev. A, 31, 479 (1985).
2. A. Żywociński, S. A. Wieczorek and J. Stecki, submitted for publication in Phys. Rev. A.
3. R. J. Birgeneau, C. W. Garland, A. R. Kortan, J. D. Litster, M. Meichle, B. M. Ocko, C. Rosenblatt, L. J. Yu, and J. Goodby, Phys. Rev. A, 27, 1251 (1983).
4. C. C. Huang and J. M. Viner, Phys. Rev. A, 25, 3385 (1982).
5. P. G. de Gennes, Physics of Liquid Crystals (Clarendon, Oxford, 1974).
6. C. C. Huang, Solid State Commun., 43, 883 (1982).

7. C. C. Huang and S. C. Lien, Phys. Rev. A, 31, 2621 (1985), and references cited therein.
8. P. R. Bevington, Data Reduction and Error Analysis for the Physical Sciences (McGrow-Hill, New York, 1969).
9. The first order smectic-A to nematic phase transition in 10S5 was also investigated and results will be given in subsequent paper.