Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

The heat capacity of the doubly reentrant mesogen: 4-cyanobenzoyloxy-4'-octylbenzoyloxy-*p*-phenylene

Gerald R. Van Hecke[a b]; Michio Sorai[a]
[a] Microcalorimetry Research Center, Faculty of Science, Osaka University, Toyonaka, Osaka, Japan [b] Department of Chemistry, Harvey Mudd College, Claremont, California, U.S.A.

To cite this Article Van Hecke, Gerald R. and Sorai, Michio(1992) 'The heat capacity of the doubly reentrant mesogen: 4-cyanobenzoyloxy-4'-octylbenzoyloxy-*p*-phenylene', Liquid Crystals, 12: 3, 503 — 513
To link to this Article: DOI: 10.1080/02678299208031063
URL: http://dx.doi.org/10.1080/02678299208031063

LIQUID CRYSTALS, 1992, VOL. 12, NO. 3, 503–513

The heat capacity of the doubly reentrant mesogen: 4-cyanobenzoyloxy-4′-octylbenzoyloxy-*p*-phenylene†‡

by GERALD R. VAN HECKE*§ and MICHIO SORAI

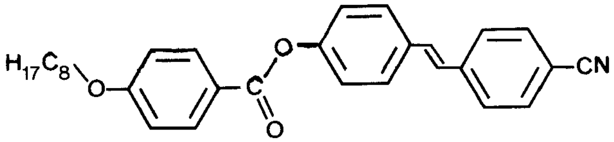
Microcalorimetry Research Center,
Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

(*Received 16 July 1991; accepted 19 February 1992*)

Heat capacity of a 20 g sample of the mesogen 4-cyanobenzoyloxy-4′-octylbenzoyloxy-*p*-phenylene was measured in the temperature range 380 to 510 K by adiabatic calorimetry. The C_p versus T data is interpreted in terms of thermodynamically equivalent S_{A1} and S_{Ad} phases whose Gibbs potential surface intersects the thermodynamically equivalent reentrant nematic and nematic Gibbs potential surface in such a way as to define the first order doubly reentrant phase sequence: S_{A1}–N–S_{Ad}–N. The data do not allow any precise estimates of transition enthalpies.

1. Introduction

Present day studies of reentrant phenomena in liquid crystals beyond those first reported by Cladis in 1975 [1] continue to expose new, challenging vistas for detailed investigation. One of these newer areas is the occurrence of multiple reentrancy, the first example of which was reported by Hardouin *et al.* [2] for the compound 4-octyloxybenzoyloxy-4′-cyanostilbene, T8.



This compound shows a thermotropic phase sequence of C–S_A–N–S_A–N–I implying reentrant behaviour for both the S_A and N phases. The lower temperature S_A phase is now called S_{A1} in light of its monolayer structure determined by X-ray diffraction studies. The higher temperature S_A phase is now called S_{Ad} and is generally believed to have a partial bilayer structure. However, for this compound the S_{A1} phase is metastable and obtained only through a monotropic phase transition. The first enantiotropic doubly reentrant compound was reported by Tinh and Destrade to be 4-cyanobenzoyloxy-4′-octylbenzoyloxy-*p*-phenylene, CBOBP [3]. The thermotropic phase sequence of CBOBP was the same as that of T8 except all the phase transitions were enantiotropic. Several studies of physical properties have been carried out on these

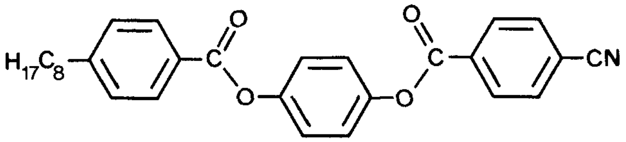
---

* Author for correspondence.

† Contribution No. 41 from the Microcalorimetry Research Center.

‡ Presented at the 13th International Liquid Crystal Conference, Vancouver, July 1990.

§ Permanent address: Department of Chemistry, Harvey Mudd College, Claremont, California 91711, U.S.A.



compounds, primarily to report transition temperatures and X-ray diffraction structures. Miyajima and Chiba undertook a differential thermal anaylsis DTA study of CBOBP to characterize the enthalpy changes associated with the reentrant phase transitions [4]. They reported clear thermal events between the S_{A1}–N and S_{Ad}–N transitions but the transition N–S_{Ad} was very weak and almost not detectectable by DTA methods. Indekeu *et al.* [5] proposed a theoretical model for reentrant transitions and studied T8 by AC calorimetry to confirm their model. However, as much as the number and temperatures of reentrant phase transitions are of interest so too are the natures of those transitions. Here nature refers to whether the transition is first or second order. As mentioned the CBOBP reentrant transitions here involve S_A to N transitions. Ever since the pioneering work of McMillan [6], considerable debate has existed over whether S_A–N phase transitions are first or second order and when or how they change from one order to the other. Of course McMillan's theory pertains to the classic smectic A phase. The structures of the phases related by reentrant phenomena appear to be subtly different and the question of the first or second order nature of the S_A–N transition remains moot. The DTA experiment is a dynamic, only quasi-thermal equilibrium experiment that sometimes obscures the true nature of phase transitions. Just as DTA is a dynamic technique, so is AC calorimetry. The pertinence of this observation is that the answer to the question of first or second order behaviour can depend on the magnitude of the thermal relaxation times associated with the transition of interest. If the thermal relaxation time of the phase transition is not in concert with the time constant of the AC calorimetric measurement, the observation of a first order phase transition by AC calorimetry can be missed or obscured. While many workers suggest the reentrant S_A–N transitions are second order, it is fair to investigate such transitions from a first order viewpoint. Since in many ways adiabatic calorimetry is the final arbiter of thermodynamic puzzles, we undertook an adiabatic calorimetric study to better understand the thermodynamics of the phase transitions in CBOBP and report here the results of our preliminary study.

2. Experimental

2.1. *Synthesis*

The compound of interest CBOBP was prepared following the general outlines in the literature [3, 4]. The crude CBOBP was separated from the reaction products by column chromatography on 60–200 mesh silica gel (30 cm column, 2 cm I.D.) with about 1 l of benzene eluant per 2·5 g of crude CBOBP. Some care is necessary in the chromatographic separation since an impurity, suspected to be un-reacted 4-octylbenzoic acid, elutes out quite closely to the CBOBP. Final purification was through recrystallization from absolute ethanol. Since this was a large scale synthesis, yielding finally more than 20 g of CBOBP, recrystallization was done in smaller batches and it may be worth noting that 7·5 g of CBOBP required almost 1100 ml of ethanol for recrystallization. Purity checks by NMR and HPLC found no impurities to the detection limit of the instruments, implying a sample purity of $\geq$99·5 per cent.

2.2. *Thermal analysis*

Preliminary thermal investigations were made using a home-made differential thermal analysis (DTA) apparatus and a Shimadzu Corp DT-30 differential scanning calorimeter (DSC).

2.3. *Heat capacity measurements*

Heat capacities in the range 380 K to 510 K were measured with an adiabatic calorimeter [7]. The calorimeter cell was made of gold-plated copper and had an inner volume of 30 cm^3. The temperature of this cell was measured with a platinum resistance thermometer (Chino Works, Ltd., Model R800-0) whose temperature scale had been calibrated on the basis of the IPTS-68. The calorimeter cell was loaded with a repeated load-melt technique, i.e. under a helium gas-freeze and under a helium gas-load cycle of sample addition. The amount of sample used was 20·2779 g with a buoyancy correction assuming a density of 1·1 g cm^3. A small amount of helium gas (400 Torr) was sealed in the cell to aid in-heat transfer. For the compound CBOBP, we took the molecular weight to be 455·5536 g mol^{-1}.

3. Results

The results from one heating run from 380 K to 510 K are reported and discussed here. Figure 1 presents the experimental C_p versus T data in the range of the mesophase temperatures. The units of C_p are J K^{-1} mol^{-1} and were obtained using the molecular weight and sample size given previously.

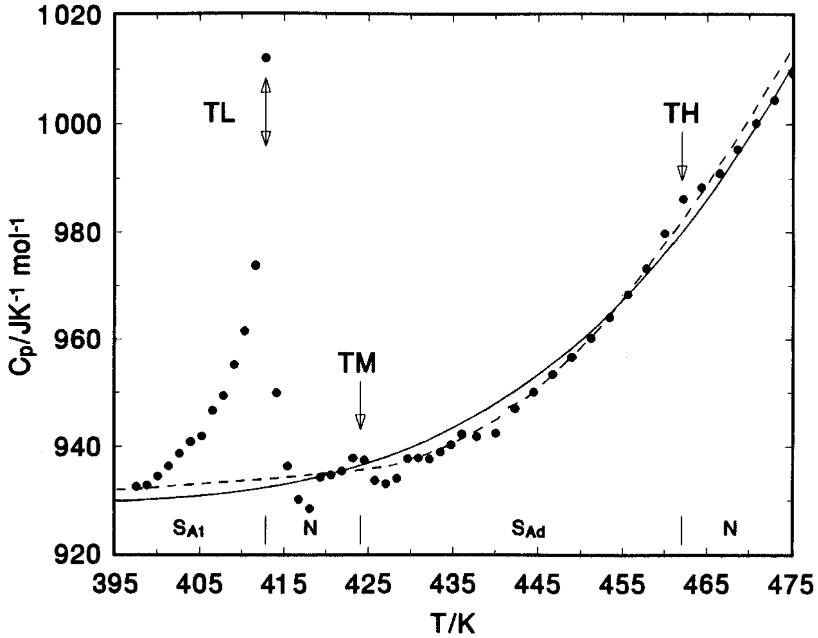


Figure 1. Constant pressure heat capacity versus temperature for the substance 4-cyanobenzoyloxy-4′-octylbenzoyloxy-*p*-phenylene CBOBP as measured by adiabatic calorimetry. The literature transition temperatures are marked approximately by the arrows. The lines are estimates for the heat capacities of the smectic A and nematic phases; Experimental C_p; ---, smectic A; —, nematic.

Table 1. Transition temperatures (in Kelvins) for the doubly reentrant mesogens T8† and CBOBP‡.

Compound	C		S_A		N		S_A		N		I
T8 [2]	●	367	●	370	●	412	●	520	●	556	●
				367·41 [11]	●	410·52 [11]					
CBOBP [3]	●	398	●	415	●	430	●	459	●	511	●
CBOBP heating [4]	●	398	●	416	●	430	●	456	●	510	●
CBOBP cooling	●	392	●	414	●	428	●	459	●	509	●
CBOBP this work	●	397	●	413	●	425	●	463			●

† 4-Octyloxybenzoyloxy-4′-cyanostilbene.
‡ 4-Cyanobenzoyloxy-4′-octylbenzoyloxy-*p*-phenylene.

Literature values for the mesogenic phase transitions are presented in table 1 and are marked approximately by the arrows in figure 1. These heat capacity results clearly show the presence of the S_{A1}(413 K)–N transition and suggest the presence of the N(425 K)–S_{Ad} and S_{Ad}(463 K)–N transitions as well. The data does not give any strong indication of latent heats for these latter two transitions, but as this data is preliminary, neither does it rule out the existence of latent heats. The discussion below is made assuming all the reentrant phase transitions are characterized by intersecting Gibbs chemical potential curves, that is, first order phase transitions.

4. Discussion

4.1. *Qualitative*

The discussion presented here is strictly phenomenological thermodynamics. Nothing is invoked save the fundamental laws. The lines drawn in the figures are polynomial fits to guide the eye, though they were constructed to be thermodynamically consistent with each other. The thermodynamic analysis presented here will interpret these heat capacity results within the framework of two critical assumptions:

(i) the reentrant smectic phases S_{A1} and S_{Ad} are thermodynamically the same phase as are reentrant nematic and nematic phases.

(ii) the reentrant phase transitions are characterized by intersecting Gibbs chemical potential curves, that is, first order phase transitions.

How can the assertion of the thermodynamic equivalence of the smectic A and nematic phases be made, that is, how can S_{A1} and S_{Ad} be thermodynamically equivalent when their microscopic structures determined by X-ray diffraction are different? Since the only difference between the S_{A1} and S_{Ad} phases seems to be a slightly altered layer spacing, it could be that the difference between these phases could be explained by a significant temperature dependent thermal expansion coefficient and that the nematic phase just happens to intervene as the more stable phase in the region of greatest thermal expansion. A particularly interesting measurement would be the density as a function of temperature for CBOBP. Taking the view that the nematic phase does nothing unusual in terms of its heat capacity as a function of temperature, strongly suggests that the phenomenon of reentrancy lies in the subtle changes in the smectic A structures that are reflected macroscopically in the subtle heat capacity differences. In fact, the nematic phase is a reasonable intermediate phase between the layers of S_{A1} and the partially interdigitated layers of S_{Ad}. Looking at figure 1, the rate of change of $C_{pS_{Ad}}$

with temperature appears to be more pronounced than that of $C_{pS_{A1}}$, suggesting the molecular arrangements and motions in the partially interdigitated S_{Ad} phase are likely to be more extensive than in the monolayer S_{A1} phase which is not inconsistent with simple thermal effects. This might also imply that the viscosity of the S_{Ad} phase is less viscous than the S_{A1}.

In characterizing phase transitions, it is customary to argue that the absence of a latent heat is prima-facie evidence for a non-first order phase transition. This is, however, an incomplete argument for it is possible for a system to undergo a first order phase change without exhibiting a latent heat. Consider entropy plotted versus temperature in the region of a phase transition. Normal first order phase transitions exhibit vertical transitions and allow for super-cooling. This is consistent with crossing Gibbs potential curves shown in figure 2 (*a*). Figure 2 (*c*) shows what would be expected for a true second order transition, one with no latent heat and no super-cooling

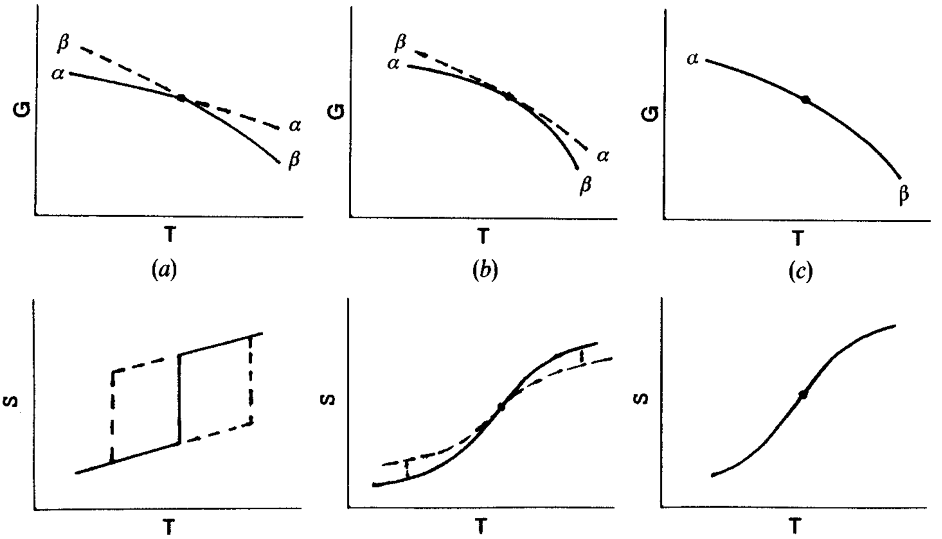


Figure 2. Idealized Gibbs potential and enthalpy curves drawn for various types of phase transitions. (*a*) First order phase transition with latent heat and super-cooling. (*b*) First order phase transition without latent heat but with super-cooling. (*c*) Second order phase transition without latent heat and without super-cooling.

Table 2. Possible combinations of phase transition orders (1st or 2nd) and latent heats ($\neq 0$, or $=0$).

	Phase transition			
Case	S_{A1}–N	N–S_{Ad}	S_{Ad}–N	Comments
1	1st, $\neq 0$	1st, $\neq 0$	1st, $\neq 0$	Gibbs potentials cross
2	1st, $\neq 0$	1st, $\neq 0$	1st, $=0$	Gibbs potentials cross as well as meet tangentially
3	1st, $=0$	1st, $=0$	1st, $=0$	Gibbs potentials meet tangentially
4	1st, $\neq 0$	2nd, $=0$	2nd, $=0$	Gibbs potentials cross as well as merge
5	2nd, $=0$	2nd, $=0$	2nd, $=0$	Gibbs potentials merge

resulting from a merging of the Gibbs potential curves. Suppose however the Gibbs potential curves intersected in such a manner as to be tangent to each other at the point of intersection. This is illustrated in figure 2 (*b*). For such a case no latent heat would be observed but super-cooling could still be observed. Examples of first order phase transitions without latent heats are known [8]. The point of this argument is that the simple lack of a latent heat is insufficient evidence to demand the absence of a first order phase transition. Indeed the DTA work of Miyajima and Chiba [4] reported in table 1 suggests the occurrence of super-cooling and thus the existence of first order transitions.

While we believe our interpretation to be a good one, it is just one possibility. Table 2 presents various combinations of first and second order transitions that could be invoked to explain the C_p data. Possibilities other than the case we present here will be discussed in a future communication.

Figures 3, 4 and 5 and the lines drawn in figure 1, show our interpretion of the data in light of the two assumptions previously made. Again we reiterate the interpretation is straight macroscopic thermodynamics and not based on any macroscopic or microscopic model. For doubly reentrant behaviour, the isobaric Gibbs chemical potential curves, one for the smectic A phase and one for the nematic phase, would have to cross three times. Alternatively, the difference between the Gibbs chemical potentials of each phase would have three zeros, one at each equilibrium phase transition temperature, here called *TL*, *TM*, and *TH*. Figure 3 was drawn qualitatively showing

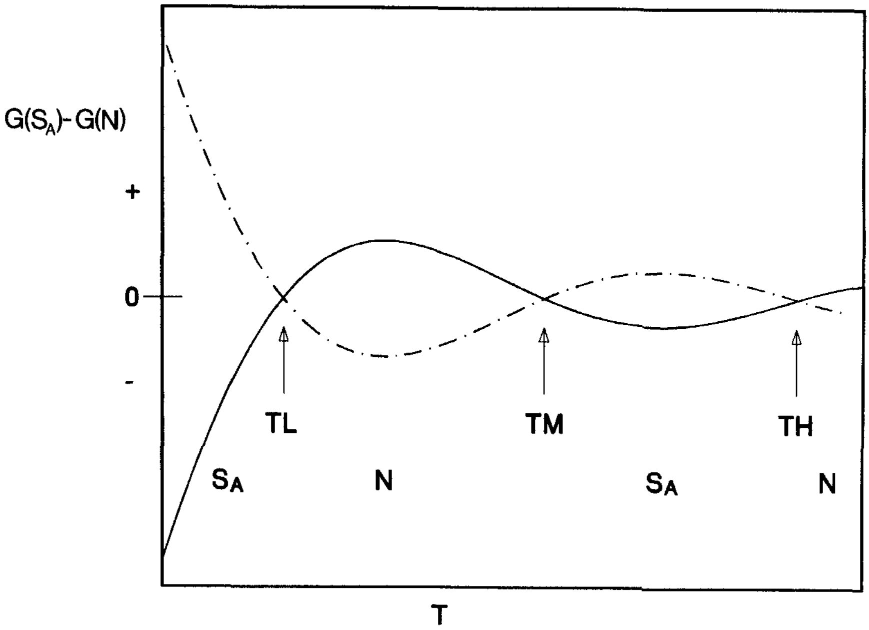


Figure 3. Suggested qualitative isobaric Gibbs chemical potential difference curves for the smectic A and nematic phases of 4-cyanobenzoyloxy-4′-octylbenzoyloxy-*p*-phenylene defining the reentrant phase transition temperatures. For $[G(S_A)-G(N)]<0$, S_A is the thermodynamically stable phase, and vice versa for $[G(S_A)-G(N)]>0$. The zeros of either curve (or their intersections) define the equilibrium phase transition temperatures, *TL*, *TM*, and *TH* (*L* for lowest, *M* for middle, *H* for highest). The stable phase sequence is doubly reentrant: S_A–N–S_A–N. ——, $G(S_A)-G(N)$; ·—, $G(N)-G(S_A)$.

how the entropy should vary with temperature in light of the two assumptions. Each continuous curve, one for each phase, was fit to a polynomial. Since

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \text{and} \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p \tag{1}$$

the entropy curve for each phase was integrated [9] to obtain the Gibbs chemical potentials and differentiated to obtain the heat capacity. The differences between $G(S_A)$ and $G(N)$ are plotted in figure 3 rather than $G(S_A)$ and $G(N)$ alone for increased sensitivity to the very slight changes in slope (entropy) implied by the entropy curves drawn in figure 4. Each difference is continuous because the potential of each phase is continuous as a necessary consequence of the first assumption. If S_{A1} and S_{Ad} were not thermodynamically the same phase, separate Gibbs potential curves would have to be drawn for each smectic A phase and CBOBP could not be called doubly reentrant. In such a case only the nematic phase would be reentrant since its Gibbs potential curve would cross the S_{Ad} curve twice (or the difference have only two zeros). Either S_{A1} and S_{Ad} are the same phase or the claim that the smectic A phase is reentrant [2] is misleading. The isobaric phase transition temperatures are, as a consequence of the second assumption, determined by the curve intersections, or zeros of the Gibbs chemical potential differences.

The purpose of this discussion is really embodied in figure 5 which illustrates how the heat capacity of the smectic A and nematic phases should appear and disappear with temperature subject to the condition that the thermodynamic stable phase be the

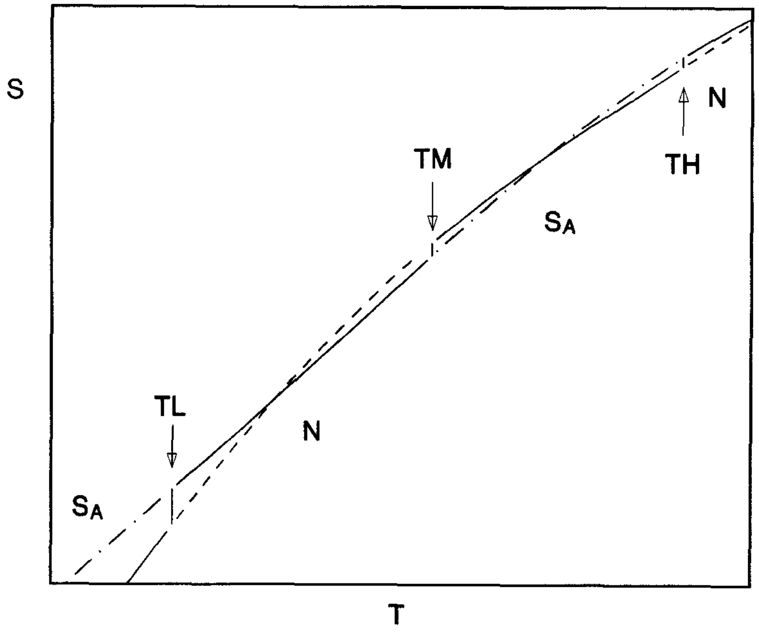


Figure 4. Entropy versus temperature first drawn qualitatively for a doubly reentrant system and then fitted to a polynomial fit is plotted. Phase transition temperatures are determined by the zeros of the Gibbs chemical potential differences shown in figure 3. The solid lines always note the stable phase which is seen to be S_A–N–S_A–N with increasing temperature. ·—·, Metastable nematic; —, Stable smectic A; —, stable nematic; - - -, Metastable smectic A.

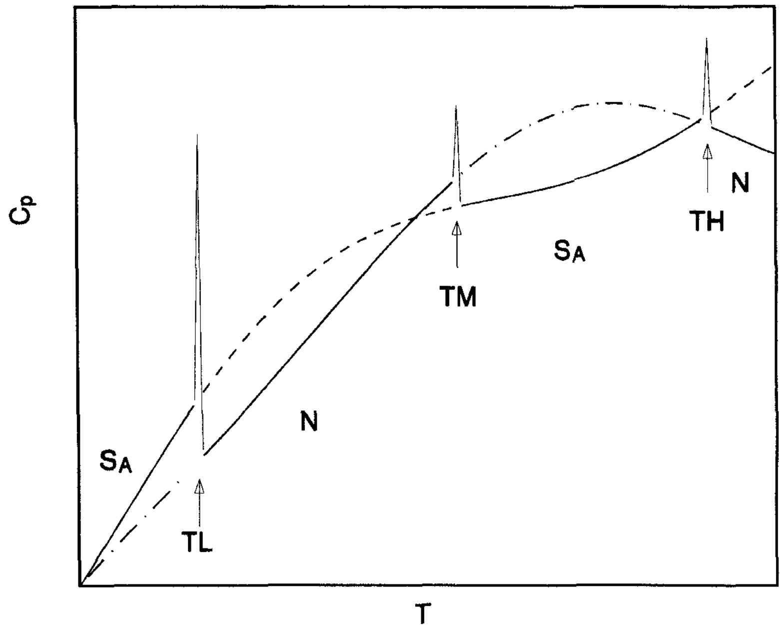


Figure 5. Heat capacity versus temperature curves, derived by differentiating the polynomial fit to the entropy versus temperature curves in figure 4, suggesting the sequence of stable and metastable regions and appearance of the expected experimental heat capacity curves for 4-cyanobenzoyloxy-4′-octylbenzoyloxy-*p*-phenylene. The solid lines always indicate the stable phase which is S_A–N–S_A–N as temperature increases. Phase stability or metastability is determined by the Gibbs chemical potential differences in figure 3. ·—·, Metastable nematic; —, stable smectic A; —, Stable nematic; – – –, Metastable smectic A.

one with the smallest Gibbs chemical potential. Specifically in figure 5, below *TL*, smectic A is the stable phase and its heat capacity rises to *TL*, then past *TL* falls to that of the nematic phase, and further, follows the heat capacity of the stable phases denoted by the solid line. The curves drawn in figures 3 and 5 are quantitative in that they are mathematically derived, via equations (1) from the polynomial fits to the entropy curves of figure 4. It is worthy to note, that while the suggested C_p anomaly at *TH* is extremely small, almost non-existent, it is still associated with an entropy discontinuity and crossing Gibbs chemical potential curves. This observation suggests caution when ascribing weak heat capacity changes to high order phase transitions. Though the heat capacity anomalies associated with the phase transitions are important, for this discussion it is more pertinent to note that the heat capacities of the smectic A and nematic phases are each individually continuous, stable in some temperature ranges, while metastable in others. The point here is that the experimental C_p curves should be interpretable, within the validity of the assumptions of this approach, by two continuous but intersecting C_p versus *T* curves.

4.2. *Quantitative*

For an isobaric phase equilibrium between the α and β phases of a pure substance,

$$\mu_\alpha(T,p)=\mu_\beta(T,p). \tag{2}$$

The Gibbs chemical potential as a function of temperature ultimately depends on the constant pressure heat capacity since

$$\left(\frac{\partial S_\alpha}{\partial T}\right)_\mathrm{p}=\frac{C_{\mathrm{p}\alpha}}{T}=-\left(\frac{\partial^2 2\mu_\alpha}{\partial T^2}\right)_\mathrm{p}. \tag{3}$$

Integrating for $\mu_\alpha(T)$ from a reference temperature T_i and entropy at T_i, $S(T_i)$ gives

$$\mu_\alpha(T)=\mu_\alpha(T_i)-\int_{T_i}^{T}\left[S_\alpha(T_i)+\int_{T_i}^{T}\left(\frac{C_{\mathrm{p}\alpha}(T)}{T}\right)dT\right]dT. \tag{4}$$

The difference between the Gibbs chemical potentials of two phases, α and β, as a function of temperature is given by

$$\Delta\mu(T)=-[S_\alpha(T_i)-S_\beta(T_i)](T-T_i)-\int_{T_i}^{T}\left[\int_{T_i}^{T}\left(\frac{C_{\mathrm{p}\alpha}(T)-C_{\mathrm{p}\beta}(T)}{T}\right)dT\right]dT, \tag{5}$$

where T_i is now an α–β transition temperature.

For each T such that $\Delta\mu(T)=0$, a phase equilibrium exists between the α and the β phases (T_i is such a temperature.) If the heat capacities of the α and β phases are negligibly different, the integral in equation (5) is zero. In such a case the Gibbs chemical potential curves for each phase would be straight lines with no possibility of crossing more than once to ensure reentrant behaviour. If at a minimum, the heat capacity were non-zero but constant, then the Gibbs chemical potential can curve and cross to exhibit reentrant behaviour. Thus the heat capacity term will dictate the type of any possible reentrant behaviour.

If the heat capacity difference $C_{\mathrm{p}\alpha}(T)-C_{\mathrm{p}\beta}(T)$ is a constant called ΔC_p, then equation (5) can be evaluated and the simplest reentrant behaviour is described by

$$\Delta\mu(T)=-\Delta S(TH)[T-TH]+\Delta C_\mathrm{p}\left[T-TH-T\ln\left(\frac{T}{TH}\right)\right], \tag{6}$$

where T_i of equation (6) has been called TH, the higher reentrant phase transition temperature. The second, lower transition temperature will be noted TL [10]. For equation (6) to have two roots, that is, two temperatures TH and TL such that $\Delta\mu(TH)=\Delta\mu(TL)=0$ and reentrant behaviour be observed, it can be shown that the following relationship between $\Delta S(TH)$, ΔC_p, TH, and TL must satisfy equation (7).

$$\frac{\Delta C_\mathrm{p}}{\Delta S(TH)}=\left(\frac{(TL/TH)-1}{[(TL/TH)-1-(TL/TH)\ln(TL/TH)]}\right). \tag{7}$$

Often TL, TH, and $\Delta S(TH)$ can be measured which means ΔC_p can be calculated from equation (7). For one component reentrant compounds, the usefulness of these relationships is limited. However, in binary mixtures, equation (7) is vital to any calculations of the complete phase diagram [11]. If any three of $\Delta S(TH)$, ΔC_p, TH, or TL are known, the fourth can be calculated.

If the heat capacity difference has at least a linear dependence on temperature defined in the following way

$$\left.\begin{aligned}C_{\mathrm{p}\alpha}(T)=c_\alpha+b_\alpha T \quad\text{and}\quad C_{\mathrm{p}\beta}(T)=c_\beta+b_\beta T,\\ \Delta C_\mathrm{p}(T)=C_{\mathrm{p}\alpha}(T)-C_{\mathrm{p}\beta}(T)=\Delta c+\Delta bT,\end{aligned}\right\} \tag{8}$$

carrying out the integration in equation (5) gives

$$\Delta\mu(T) = -\Delta S(TH)[T-TH] + \Delta c\left[T - TH - T\ln\left(\frac{T}{TH}\right)\right] - \frac{\Delta b}{2}(T-TH)^2. \quad (9)$$

Analysis of equation (9) shows that it is possible for the Gibbs chemical potential energy curves to cross three times at the three reentrant phase transition temperatures TL, TM, and TH. In fact the three zeros are illustrated in figure 3 and equation (9) (and equation (10)) could be used to fit the different curves. Thus the occurrence of a linear heat capacity difference is sufficient to thermodynamically describe doubly reentrant behaviour.

Detailed analysis of equation (9) will show that the three reentrant temperatures are related to heat capacity and entropy differences according to equation (10)

$$\frac{\Delta b}{\Delta S(TH)} = 2\left(\frac{(TH-TM)(TL-TH-TL\ln(TL/TH))-(TH-TL)(TM-TH-TM\ln(TM/TH))}{(TL-TH-TL\ln(TL/TH))(TM-TH)^2-(TM-TH-TM\ln(TM/TH))(TL-TH)^2}\right)$$

$$\frac{\Delta c}{\Delta S(TH)} = \left(\frac{(TH-TM)(TL-TH)^2-(TH-TL)(TM-TH)^2}{(TL-TH-TL\ln(TL/TH))(TM-TH)^2-(TM-TH-TM\ln(TM/TH))(TL-TH)^2}\right). \quad (10)$$

Here knowledge of any five of the parameters allows calculation of the sixth. Again the real usefulness of equations (9) and (10) is not realized until calculations on binary reentrant systems are undertaken.

5. Summary

To repeat and summarize the argument at this point: double (or single) reentrant behaviour is not possible if $C_{p\alpha}(T) = C_{p\alpha}(T)$. Moreover, the C_p of CBOBP can be interpreted in a manner consistent with previously mentioned analysis by noting the two lines drawn through the experimental points in figure 1, one for C_{pS_A} and one for C_{pN}. The behaviour of these lines follows that shown in the qualitative heat capacity–temperature plot of figure 5. While the fit of the C_p curves to the data is qualitative, the features expected in figure 5 do seem to appear in figure 1 and the suggestion that smectic A and nematic phases are thermodynamically equivalent cannot be ruled out by this preliminary evidence. Unfortunately the data does not allow any precise estimate of the transition enthalpies and entropies.

6. Conclusions

The thermodynamic analysis shows that singly reentrant behaviour only requires that $\Delta C_p = C_{p\alpha}(T) - C_{p\beta}(T)$ between the phases exhibiting the reentrant behaviour be a constant independent of temperature. Moreover, doubly reentrant behaviour only requires that $\Delta C_p = C_{p\alpha}(T) - C_{p\beta}(T)$ be linear in temperature. The C_p versus T data obtained for CBOBP for one heating run for 380 K to 510 K can be interpreted in terms of thermodynamically equivalent S_{A1} and S_{Ad} phases whose Gibbs potential surface intersects the thermodynamically equivalent reentrant nematic and nematic Gibbs potential surface in such a way as to define the first order doubly reentrant phase sequence: S_{A1}–N–S_{Ad}–N.

The authors thank K. A. Lawler for the dedicated synthesis of CBOBP in a quantity large enough to carry out the measurement. One of us (G.R.V.H.) wishes to thank Professors M. Sorai and H. Suga, and the members of the Microcalorimetry Research Center for their hospitality during this visit. Funds to help support this work from the Mabel and Arnold Beckman Research Fund of Harvey Mudd College are gratefully acknowledged.

References

[1] CLANDIS, P. E., 1975, *Phys. Rev. Lett.*, **35**, 48.
[2] HARDOUIN, F., SIGAUD, G., ACHARD, M. F., and GASPAROUX, H., 1979, *Physics Lett.* A, **71**, 347; 1979, *Solid St. Commun.*, **30**, 265.
[3] TINH, N. H., and DESTRADE, C., 1981, *Nouv. J. Chim.*, **5**, 337.
[4] MIYAJIMA, S., and CHIBA, T., 1985, *J. phys. Soc. Jap.*, **54**, 2793.
[5] INDEKEU, J. O., BERKER, A. N., CHIANG, C., and GARLAND, C. W., 1987, *Phys. Rev.* A., **35**, 1371.
[6] MCMILLAN, W. L., 1971, *Phys. Rev.* A., **4**, 1238.
[7] SORAI, M., KAJI, K., and KANEKO, Y., 1992, *J. chem. Thermodyn.*, **24**, 167.
[8] YOSHIKAWA, M., SORAI, M., and SEKI, S., 1983, *J. Phys. Chem. Solids*, **44**, 311.
[9] The constant of integration was set so that at $T = TL$, $G(S_A)$ and $G(N)$ equalled each other at a value that conveniently scaled the drawing.
[10] The choice of the higher reentrant temperature TH is arbitrary but practical in that for almost all reported reentrant compounds and binary systems, the higher temperature is the one experimentally observed, while TL often has to be inferred.
[11] VAN HECKE, G. R., 1985, *J. Phys. Chem.*, **89**, 2058.