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## Liquid Crystals

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## A study of the nematic-smectic A-smectic C point in a binary liquid-crystalline mixture by adiabatic scanning calorimetry

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An adiabatic scanning calorimetric technique has been used to investigate the nematic-smectic A-smectic C (NAC) multicritical point in mixtures of 4-*n*-pentyl-oxyphenyl-4'-*n*-octyloxybenzoate and 4-*n*-hexyloxyphenyl-4'-*n*-octyloxybenzoate. The NC transitions are weakly first order and the latent heat becomes zero at or very near the NAC point. Near the NAC point no thermal feature associated with the NA transitions could be observed. The heat capacity anomalies along the second order AC transition line and along the first order NC line indicate the presence of a tricritical point at or very near the NAC multicritical point. No thermal indications for a biaxial nematic phase were observed.

### 1. Introduction

When a liquid-crystalline compound which has an NA and an AC transition is mixed with another one which has a direct NC transition, a phase diagram with an NAC multicritical point where the NA, AC and NC phase transition lines merge is obtained. This NAC point has been the subject of extensive theoretical and experimental studies during the past decade. However, the nature of this multicritical point is still not clearly established.

The many theoretical approaches to describe various aspects of the multicritical behaviour fall into two categories, a basic difference being the number of order parameters in the model. The first class, introduced by Chen and Lubensky [1], is based on a single infinite dimensional order parameter for the smectic density wave. In a mean field analysis of their model these authors predicted that the NAC point should be a ( $d = 3, n = 2, m = 2$ ) Lifshitz point. The second class of models involves two order parameters, one for the smectic density modulations and another for the smectic C tilt angle of the director with respect to the normal to the smectic layers [2-6]. On the basis of their dislocation loop theory, Grinstein and Toner [5] have shown that in this case the NAC point is, in fact, a decoupled tetracritical point and that in the immediate vicinity of the NAC point a biaxial nematic (N') phase should intervene between the nematic phase and the smectic C phase. This type of phase diagram near the NAC multicritical point is also consistent with the Chen-Lubensky model when fluctuations are included [7].

Since the first discovery [8, 9] of NAC multicritical points in 1977, several systems have been studied experimentally. What seems to be best established by now is the phenomenological observation of a universal topology of the phase diagram near the NAC point [10, 11]. No indication for a biaxial N' phase has been found so far, but

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it seems possible to describe the shape of the NA, NC and AC transition lines by means of power law expressions with the same universal exponents for all systems. The exact type of power laws (and the values of the exponents) as well as the slopes of the phase transition lines at the NAC point are still a matter of debate, because alternative approaches seem to be consistent with the existing experimental data [12]. Several techniques have been used to study the multicritical NAC behaviour extensively in the binary system of heptyl- and octyloxyphenyl-phenylthiolbenzoate ( $\bar{7}S5 + \bar{8}S5$ ) [8, 13–16]. Unfortunately this system seems to have an unusually small multicritical region [10, 16], and the results obtained were not very conclusive. More recently the binary system of 4-*n*-heptyloxy-4'-*n*-pentyloxyphenylthiolbenzoate ( $\bar{7}S5$ ) and 4-*n*-octyloxy-4'-cyanobiphenyl (8OCB), which has a much larger multicritical region, has also been investigated in quite some detail. Light scattering [17] and X-ray scattering [18, 19] results for the  $\bar{7}S5 + 8OCB$  multicritical point are best described by a Lifshitz point model [1]. However, the relationship between the bend elastic constant, as obtained from Fréedericksz deformation measurements [20], and the smectic correlation lengths, derived from X-ray scattering, is not described by the existing theories. The bend elastic results also raise questions about the interpretation of the light-scattering data [20]. High resolution heat capacity results [21] with an A.C. calorimetric technique for the NC transition in  $\bar{7}S5 + 8OCB$  indicate the presence of a classical tricritical point along the smectic C transition line at (or very close to) the NAC point. This is in qualitative agreement with adiabatic calorimetric results by Anisimov *et al.* [22] for the binary system 4-*n*-hexyloxyphenyl-4'-*n*-octyloxybenzoate ( $\bar{6}O\bar{8}$ ) and 4-*n*-hexyloxyphenyl-4'-*n*-decyloxybenzoate ( $\bar{6}O\bar{10}$ ).

In this paper we present the results of an adiabatic scanning calorimetric investigation of the NAC point in mixtures of 4-*n*-pentyloxyphenyl-4'-*n*-octyloxybenzoate ( $\bar{5}O\bar{8}$ ) and 4-*n*-hexyloxyphenyl-4'-*n*-octyloxybenzoate ( $\bar{6}O\bar{8}$ ), which are compounds of the same homologous series as used by Anisimov *et al.* [22].

## 2. Experimental

The measurements were carried out with an adiabatic scanning calorimeter similar to that described earlier [23, 24]. The present calorimeter is a reduced three-stage version of the four-stage one used previously for phase transition studies in liquid crystals [23, 25]. In the present case the whole calorimeter was submerged in a water thermostat, and for its most exterior stage 3 we obtained a temperature stability (of the order of 10 mK) comparable with that for stage 3 in the four-stage calorimeter. The electronics for the new calorimeter is, however, quite different. Instead of using high-resolution A.C. bridges and proportional power amplifiers, for the new system a scanning digital multimeter set-up and programmable power sources, connected with a microcomputer were used. The readings of the temperature sensors (via the digital voltmeter system) as well as the heat supplied to the heaters of the different stages (via the programmable power sources) were controlled by means of a program on the microcomputer [26]. The present sample holder (stage 1) was made of tantalum and has a maximum sample volume of about 5 cm<sup>3</sup>. Stirring the sample is achieved in a way similar to that described previously [23, 24]. Heating as well as cooling runs at very slow scanning rates, typically of the order of 30 mK h<sup>-1</sup>, were carried out. With a constant heating (cooling) power,  $P$ , applied to the sample, the experimental curve of temperature versus time,  $T(t)$ , results directly in the enthalpy of the sample [23]:

$$H(T) = H(T_s) - P(t - t_s), \quad (1)$$

where the index  $s$  refers to the starting conditions of the run. The heat capacity  $C_p(T)$  is given by

$$C_p = P/\dot{T}. \quad (2)$$

$\dot{T}$  can be obtained by numerical differentiation from the direct experimental data for  $T(t)$ . It is also possible to obtain values for latent heats when they are present for a given phase transition. If a first order transition occurs at  $T_1$  between  $T_s$  and  $T$ , the temperature will be essentially constant for a time interval  $\Delta t = \Delta H_L(T_1)/P$ , with  $\Delta H_L$  the latent heat. For mixtures the transitions are not expected to take place at a single temperature  $T_1$  but over a finite temperature range  $\Delta T = T_f - T_i$ .

The pure compounds  $\bar{5}O\bar{8}$  and  $\bar{6}O\bar{8}$  were synthesized for us by Ofichem (Gieten, The Netherlands), and were used without further purification. All the transition temperatures for the different phase transitions, as observed under the polarizing microscope, differed by less than  $0.5^\circ\text{C}$  from the values published by Demus *et al.* [27].

### 3. Results and discussion

Above its melting temperature (at  $58^\circ\text{C}$ ), pure  $\bar{5}O\bar{8}$  changes with increasing temperature from a smectic C phase first into a narrow smectic A phase (between  $63$  and  $65^\circ\text{C}$ ), and then into a nematic phase with a  $20^\circ\text{C}$  width.  $\bar{6}O\bar{8}$  has its melting point at  $55^\circ\text{C}$  and changes at  $66^\circ\text{C}$  from its smectic C phase directly into the nematic phase. The clearing point for  $\bar{6}O\bar{8}$  is at  $89.5^\circ\text{C}$ . Before carrying out the calorimetric measurements a complete phase diagram of the binary system  $\bar{5}O\bar{8} + \bar{6}O\bar{8}$  was obtained by means of visual observations under a polarizing microscope equipped with a Mettler hot stage. The phase diagram obtained in this way is given in figure 1. The variable  $x$  is the weight fraction of  $\bar{6}O\bar{8}$  in the mixtures. A small smectic A region with an NAC point for  $x_{\text{NAC}} \approx 0.13$  and  $T_{\text{NAC}} \approx 62.8^\circ\text{C}$  has been observed.

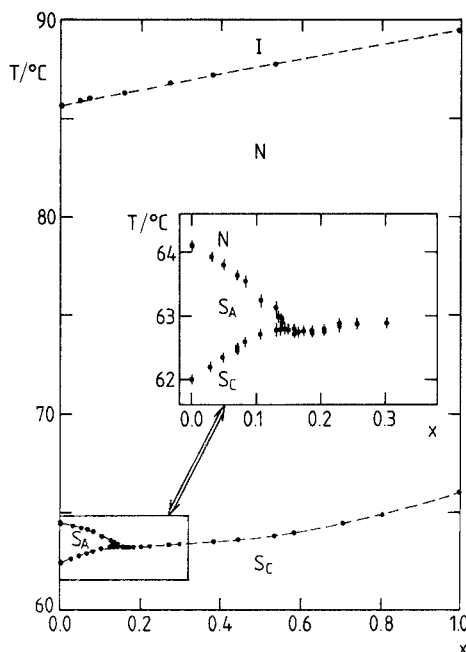


Figure 1. Phase diagram for the system  $\bar{5}O\bar{8}$  (left)– $\bar{6}O\bar{8}$  (right).  $x$  is the weight fraction of  $\bar{6}O\bar{8}$  in the mixtures.

Characteristics of the  $\bar{5}O\bar{8} + \bar{6}O\bar{8}$  samples investigated calorimetrically.

$x$ (wt fraction $\bar{6}O\bar{8}$ )	Transition	Transition temperature/ $^{\circ}C$	$\Delta H_L / J mol^{-1}$
0	N-A	63.912	< 0.5
0	A-C	62.400	< 0.5
0.1117	A-C	62.744	< 0.5
0.1308	A-C	62.748	< 0.5
0.1328	A-C	62.788	< 0.5
0.1331	N-C	62.742–62.752	$1.7 \pm 0.3$
0.1333	N-C	62.751–62.755	$1.8 \pm 0.3$
0.1346	N-C	62.758–62.768	$2.2 \pm 0.2$
0.1364	N-C	62.761–62.772	$3.5 \pm 0.2$
0.1417	N-C	62.763–62.778	$4.3 \pm 0.6$
0.1562	N-C	62.791–62.807	$8.5 \pm 1.5$
0.1666	N-C	62.803–62.821	$11.3 \pm 2.8$
0.2013	N-C	62.828–62.847	$25.0 \pm 4.3$
0.2629	N-C	62.864–62.885	$43.1 \pm 6.0$
1	N-C	65.148–65.164	$295.0 \pm 5.0$

In the table the principal characteristics are given for the different samples which were investigated calorimetrically. In addition to the two pure compounds, 12 different mixtures with compositions close to the composition of the NAC point were investigated.

The enthalpy results for pure  $\bar{5}O\bar{8}$  did not reveal any discontinuous latent heat increase at the smectic C to smectic A or at the smectic A to nematic phase transitions. Both these transitions are within our experimental resolution ( $\Delta H_L < 0.5 J mol^{-1}$ ), purely continuous second order transitions. The second order nature of the AC transition in  $\bar{5}O\bar{8}$  is consistent with the results for AC transitions in other (non-chiral) compounds [28–30]. An NA transition can be first order or second order, depending on the width of the nematic range. First order transitions are observed only for  $T_{NA}/T_{NI}$  ratios larger than the tricritical value. For all comparable systems which have been investigated in sufficient detail, the tricritical  $T_{NA}/T_{NI}$  ratio was found to be larger than 0.98 [31–33]. For  $\bar{5}O\bar{8}$  we have  $T_{NA}/T_{NI} = 0.944$ , and the observed second order nature of the NA transition is thus consistent with expectations on the basis of the results for other systems. The heat capacity results obtained via equation (1) revealed only a small (about 5 per cent) anomalous increase at the NA transition. This is also in agreement with the results for systems with wide nematic ranges [31]. The usual mean field heat capacity anomaly [28–30] was also obtained for the AC transition of  $\bar{5}O\bar{8}$  where it was very mean field like. At the transition  $C_p$  (per mol) in the smectic C phase was only  $11R$  larger than its  $122R$  value in the smectic A phase ( $R$  is the universal gas constant). The NC transition of  $\bar{6}O\bar{8}$  was found to be a first order one with a rather large latent heat of  $\Delta H_L = 295 J mol^{-1}$ . This first order character is expected theoretically [34, 35], and is in agreement with results for other systems [8, 16]. Here also a small mean field heat capacity anomaly was observed with a maximum value for the smectic C phase (at the transition) about  $12R$  above the nematic background value of about  $138R$ .

First order transitions were also observed for a series of nine mixtures with weight fractions  $x$  larger than  $x_{NAC}$ . In figure 2 the relevant parts of the enthalpy curves for these nine mixtures are compared. Note that for display reasons a large linear

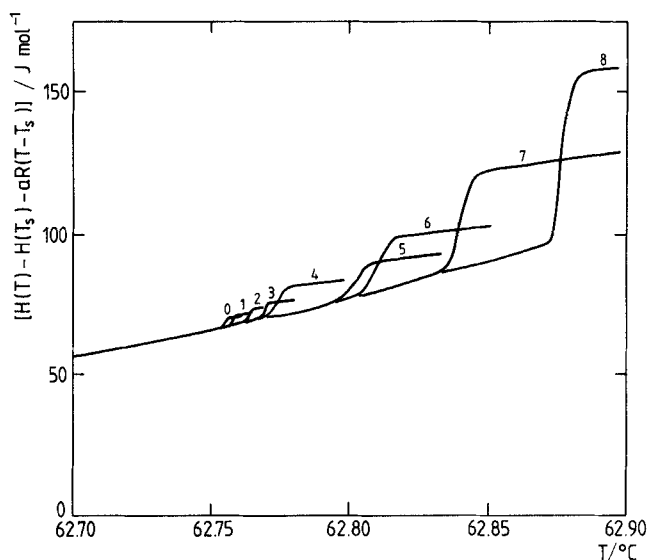


Figure 2. Temperature dependence of the enthalpy for several mixtures with NC transitions. 0,  $x = 0.1331$ ; 1,  $x = 0.1333$ ; 2,  $x = 0.1346$ ; 3,  $x = 0.1364$ ; 4,  $x = 0.1417$ ; 5,  $x = 0.1562$ ; 6,  $x = 0.1666$ ; 7,  $x = 0.2013$ ; 8,  $x = 0.2629$ . Note that for clarity a large linear background  $C_p^\circ(T - T_s)$ , with  $C_p^\circ = aR$ , has been subtracted from the experimental data.

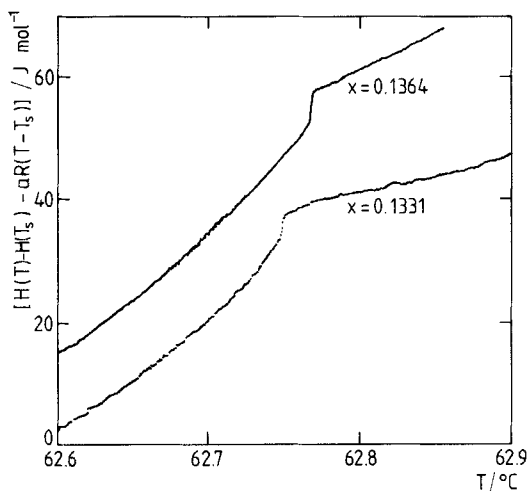


Figure 3. Detailed plot of the enthalpy near the NC transition in two mixtures of  $5O8$  and  $6O8$  with compositions close to the NAC point. Note that for clarity a large linear background  $aR(T - T_s)$  has been subtracted from the direct data.

background  $C_p^\circ(T - T_s)$ , with  $C_p^\circ = aR$ , has been subtracted from the data, where  $a$  is an arbitrary constant. Both the starting temperature  $T_s$  and the coefficient  $a$  have been chosen differently for each mixture in order to arrive at a common enthalpy curve for the smectic C phase of all the mixtures. No shifts have been introduced along the temperature axis. Figure 3 gives a more detailed view for two mixtures with compositions close to the  $x_{NAC}$ . From figure 2 it can be concluded that there is a

substantial decrease of the latent heat on approaching the NAC point along the NC line. Values for  $\Delta H_L$  for these mixtures are also included in the table. Even the largest enthalpy jump in figure 2 is almost an order of magnitude smaller than the value for pure  $\bar{6}O\bar{8}$ . The smallest value (for  $x = 0.1331$ ) measured close to the NAC point is less than  $2 \text{ J mol}^{-1}$  and more than two orders of magnitude smaller than the value for  $\bar{6}O\bar{8}$ .

The mixtures with  $x = 0.1328$  and  $x = 0.1308$ , which are very close to that with  $x = 0.1331$ , did not show an enthalpy discontinuity within our experimental resolution ( $\Delta H_L < 0.5 \text{ J mol}^{-1}$ ). This can be seen in the top part of figure 4 for  $x = 0.1328$  and of figure 5 for  $x = 0.1308$ , where the critical part of the enthalpy curves are given. In the lower part of these figures, the heat capacity is displayed, the small dots are derived from equation (2). The open circles were obtained by running the calorimeter in a pulsed mode [24]. In that case a known amount of heat  $\Delta Q$  was supplied to the sample and the corresponding temperature rise  $\Delta T$  was measured, resulting in  $C_p = \Delta Q/\Delta T$ . The  $C_p$  behaviour in figures 4 and 5 is typically AC like [28–30], and much sharper than that observed for the AC transition of pure  $\bar{5}O\bar{8}$ . A similar result, but with a smaller  $C_p$  peak, was obtained for the mixture  $x = 0.1117$ .

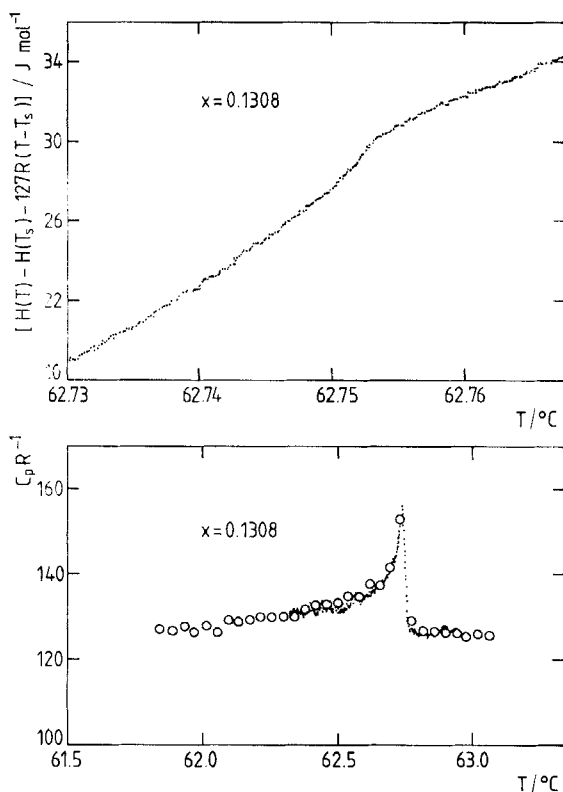


Figure 4. Temperature dependence of the enthalpy and the heat capacity for a mixture with a composition very close to the NAC composition. Note that for clarity a large linear background  $121R(T - T_s)$  has been subtracted from the direct enthalpy data. The dots in the  $C_p/R$  plot were calculated from the enthalpy with equation (2). The open circles are  $C_p/R$  data obtained by running the calorimeter in a step-by-step mode.

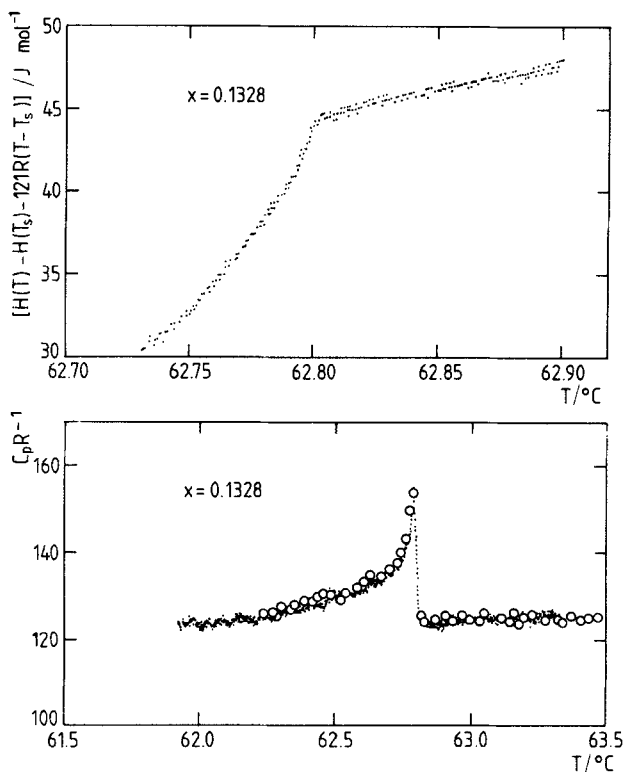


Figure 5. Temperature dependence of the enthalpy and the heat capacity for a mixture with a composition very close to the NAC composition. Note that for clarity a large linear background  $121R(T - T_s)$  has been subtracted from the direct enthalpy data. The dots in the  $C_p/R$  plot were calculated from the enthalpy data with equation (2). The open circles are  $C_p/R$  data obtained by running the calorimeter in a step-by-step mode.

Under the polarizing microscope both an AC and an NA transition (about  $0.4^\circ\text{C}$  above the AC one) could be observed for the mixture with  $x = 0.1117$ . Unfortunately the NA transition did not result in a heat capacity anomaly above the experimental resolution (about 2 per cent). The absence of any NA thermal feature close to the NAC point is an unfortunate but common result, and is related to the increased curvature of the NA line near the NAC point [16, 22, 36]. For the mixtures with  $x = 0.1308$  and  $x = 0.1328$  no clear evidence for a smectic A phase was found. However, from an extrapolation of the NA and AC lines we did not expect a width larger than  $0.2^\circ\text{C}$ , which was the resolution limit of our microscope observations. In fact, it could not be excluded that a smectic A phase, over such a small temperature range, is also present for the mixtures with  $x = 0.1331$  and  $x = 0.1333$ , which show first order transitions. From this we can conclude that it is very likely but not entirely certain that the NC latent heat becomes zero exactly at the NAC point.

In figure 6 the latent heat values for the NC transitions are plotted as a function of  $x$ , the weight fraction of  $\vec{O}8$  in the mixtures. The inset gives an expansion of the region near the NAC point. The solid line is a linear fit to the  $\Delta H_L$  results and accounts for the data quite well. This linear behaviour is in accord with theoretical expectations formulated by Swift [37]. In the inset of figure 6 we have also indicated the position and the upper limit for a possible latent heat for two mixtures ( $x = 0.1328$  and



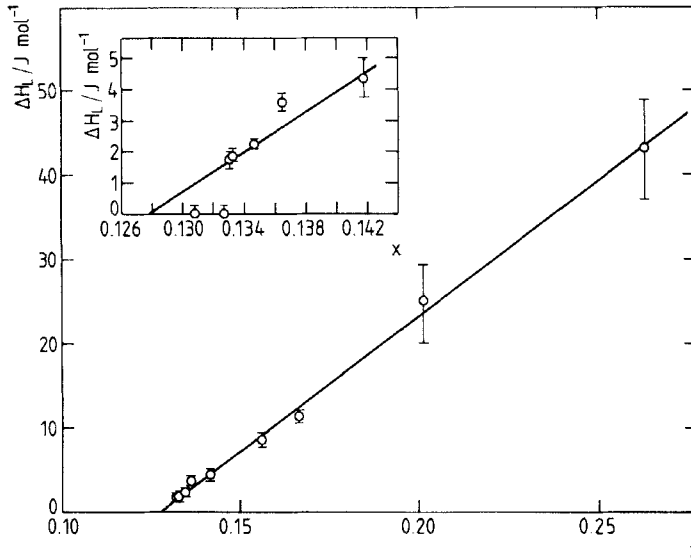


Figure 6. NC latent heats as a function of composition near the NAC point. The inset gives an expansion of the NAC region.

$x = 0.1308$ ) close to the NAC point, which were observed experimentally as second order (AC) transitions (see figures 4 and 5). It is clearly seen that the upper limits are lower than the extrapolated straight line. We have to conclude therefore that  $\Delta H_L$  must have a non-linear concentration dependence in a narrow range above  $x = 0.1328$ . Such non-linear behaviour was observed by Anisimov *et al.* [22] for  $\bar{6}O\bar{1}0\text{-}\bar{6}O\bar{8}$  and by Brisbin *et al.* [10] for  $\bar{7}S\bar{5}\text{-}\bar{8}S\bar{5}$  in a range close to the NAC point. In our case the non-linear range seems to be extremely small, and almost inaccessible.

The heat capacity variations for the second order AC transitions are usually described quite well by a Landau free energy expansion up to sixth order in the tilt order parameter [38]. Starting with a free energy expression

$$G = G_0 + a\varepsilon\phi^2 + b\phi^4 + c\phi^6, \quad (3)$$

with  $\varepsilon = (T_c - T)/T_c$  and  $\phi$  the tilt order parameter, we arrive at

$$C_p/R = C_p^o/R \quad \text{for } T > T_c, \quad (4)$$

$$C_p/R = C_p^o/R + A \frac{T}{T_c} \left( \frac{T_m - T_c}{T_m - T} \right)^{1/2} \quad \text{for } T > T_c, \quad (5)$$

where  $A \equiv a^2/(2bRT_c)$ ,  $T_m \equiv T_c + (b^2/3ac)$ , and  $C_p^o$  is the background heat capacity arising from the regular part  $G_0$ . For a continuous transition, as observed for the AC transitions, we must have  $b \geq 0$  and  $a, c > 0$ . If  $b = 0$  a tricritical point is observed and a diverging  $C_p$  is predicted below  $T_c$  with a critical exponent of 1/2. If  $b > 0$ , there is an ordinary second order transition that might be close to a tricritical point for small  $b$ . In the analysis of second order AC transitions it has become common to use a characterizing parameter  $\varepsilon_0$ , related to the parameters in equations (3) and (5) by

$$\begin{aligned} \varepsilon_0 &\equiv 3(T_m - T_c)/T_c \\ &= b^2/ac. \end{aligned} \quad (6)$$

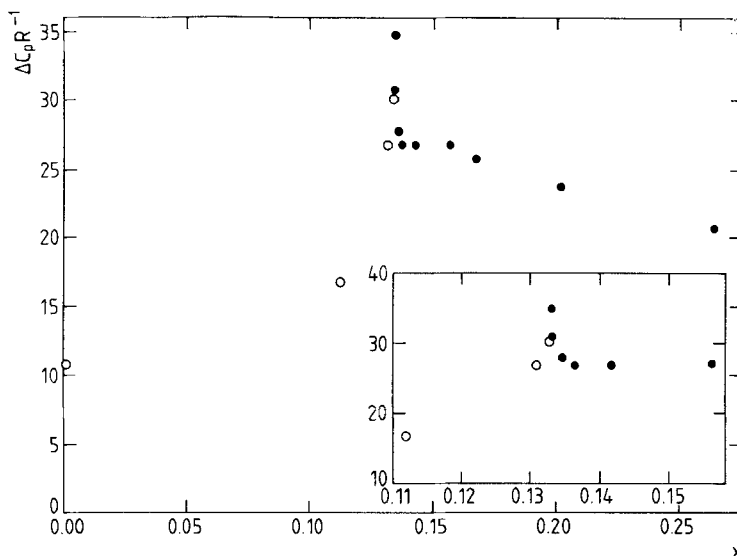


Figure 7. Heat capacity jumps near the NAC point. Open circles are for second order AC transitions and solid dots for first order NC transitions. The inset gives an expansion of the NAC region.

This characterizes the full width at half height ( $A/2$ ) of the mean field heat capacity anomaly. We have analysed our data for the second order AC transitions in terms of equations (5) and (6). Quite good fits could be obtained with these mean field expressions. The sharpening of the AC peaks on approaching the NAC point resulted in decreasing values of  $\varepsilon_0$ ; for example, for the mixture  $x = 0.1117$  a value of  $\varepsilon_0 \approx 1.6 \times 10^{-3}$  was obtained, whereas for  $x = 0.1308$  and  $x = 0.1328$  values two to three times smaller resulted from the fits. In figure 7 the heat capacity jump  $\Delta C_p/R$  at  $T_{AC}$  is given as a function of the composition  $x$  by the open circles. This quantity increases on approaching the NAC point. We observe therefore that the AC heat capacity anomaly increases (larger  $A$ ) and becomes sharper (smaller  $\varepsilon_0$ ) on approaching the NAC point. The same observations can be made for the heat capacity anomaly associated with the first order NC transitions. The  $\Delta C_p/R$  values for these transitions are indicated in figure 7 by means of solid circles. From both sides of the NAC point the heat capacity data indicate a decreasing value of  $|b|$ , suggesting the presence of a tricritical point at or near the NAC point.

#### 4. Summary and conclusions

In this paper we have presented new experimental data for the temperature dependence of the enthalpy and the heat capacity in several mixtures of the binary system  $\overline{5O\overline{8}}-\overline{6O\overline{8}}$  near its nematic-smectic A-smectic C multicritical point. AC and NA transitions are found to be second order, whereas the NC transitions are first order with a latent heat becoming zero at or very near the NAC point. The heat capacity anomalies along the AC line as well as along the NC line become larger and sharper on approaching the NAC point, indicating the presence of a tricritical point at or near the NAC point. This is in accord with thermal investigations of the NAC region of other systems [21, 22]. The NAC multicritical point seems to exhibit simultaneously the characteristics of a Lifshitz point and of a (mean field) tricritical

point. Whether a Lifshitz tricritical point [39] would be a possibility is not clear at the moment, and would probably require measurements much closer to an unambiguously located NAC point. This would be difficult and require very high concentration resolution for the binary system  $\overline{5}O\overline{8}-\overline{6}O\overline{8}$ . Finally, it should be pointed out that our data show no indication of a biaxial N' phase near the NAC point.

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