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

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To cite this Article Cross, Collin W. and Fung, B. M.(1995) 'Tricritical points of smectic A to nematic phase transitions for binary liquid crystal mixtures containing cyanobiphenyls', Liquid Crystals, 19: 6, 863 — 869
To link to this Article: DOI: 10.1080/02678299508031110
URL: http://dx.doi.org/10.1080/02678299508031110

LIQUID CRYSTALS, 1995, VOL. 19, NO. 6, 863–869

Tricritical points of smectic A to nematic phase transitions for binary liquid crystal mixtures containing cyanobiphenyls

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(Received 6 October 1994; in final form 15 July 1995; accepted 1 August 1995)

The tricritical point of the smectic A (S_A) to nematic (N) phase transition in liquid crystals, at which the nature of the phase transition changes from first order to second order, is related to the change in the order parameter during the phase transition. In this study, ^{13}C NMR was used to determine the order parameters of four binary liquid crystal systems as a function of temperature and composition in order to investigate the tricritical behaviour of their S_A–N transition. The first system was mixture of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-pentylphenyl 4′-*n*-pentyloxybenzoate ($\bar{5}$O5), which have an injected smectic A phase. The tricritical point of this system has a McMillan ratio of 0·949 ± 0·008. The three other systems were binary mixtures of 4-*n*-alkyl-4′-cyanobiphenyls (*n*CB). At the tricritical point, the McMillan ratio is 0·986 ± 0·007 for the 5CB/10CB mixtures, and 0·985 ± 0·008 for the 8CB/9CB mixtures, but a tricritical point was not observed for the 9CB/10CB mixtures. The results are compared with those of previous investigations.

1. Introduction

Liquid crystals are widely known for their interesting phase behaviour. The nematic (N) phase only displays orientational ordering; the smectic A (S_A) phase displays both orientational and one-dimensional positional ordering. The S_A–N phase transition in liquid crystals has been studied extensively from both theoretical and experimental perspectives [1–18]. Phase transitions of this type are of interest because they often exhibit a tricritical point where the character of the transition changes from first order to second order.

The mean field theory was used by Kobayashi [1] and McMillan [2] independently to predict a tricritical point in the S_A–N transitions in the early 1970s. These were the first theories to predict such behaviour. Since that time, these theories have been merged and are now known as the Kobayashi–McMillan theory of the S_A–N phase transition. It predicts a tricritical point which is based upon the change of a dimensionless parameter obtained from the ratio of correlation lengths inside and perpendicular to the smectic layers.

A more fundamental approach used to describe the S_A–N phase transition is the de Gennes model [3]. This theory treats the phase transition by expanding the free energy density in terms of an orientational director terms, **n**, for nematic ordering, and a complex scalar field, Ψ, expressing both orientational ordering and a one-dimensional density wave perpendicular to the smectic layers. The de Gennes theory predicts a tricritical point which is related to the temperature range of the nematic phase. According to the de Gennes model, the change from first to second order is caused by coupling between the orientational order parameter in the nematic phase and the complex order parameter of the smectic A phase. A first order S_A–N phase transition occurs when the nematic phase is small, or the McMillan ratio ($M = T_{S_AN}/T_{NI}$) is close to 1, where T_{S_AN} is the S_A–N phase transition and T_{NI} is the nematic to isotropic phase transition temperature. In this case, orientational fluctuations in the nematic phase are large, thereby causing the order of the transition to depend upon the nematic order parameter only. For compounds with wider nematic ranges, $M = T_{S_AN}/T_{NI}$ is less than unity, and the ordering in the nematic phase is nearly saturated. This is believed to cause the formation of pretransitional smectic domains. In this case, the character of the transition is second order and only depends upon the purely translational part of the complex smectic order parameter.

Many studies of tricritical behaviour in liquid crystals have been performed calorimetrically [17]. Because the entropy and volume discontinuities are very small during the transition from one liquid crystalline phase to another, the results are sometimes ambiguous unless calorimeters with very high resolution are used. On the other hand, a study of the change in the order parameter during the phase transition gives direct information about the

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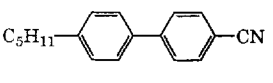
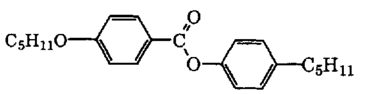
tricritical behaviour as predicted by the de Gennes model [11, 12, 18].

Cyanobiphenyl liquid crystals are of fundamental and practical interest because of their wide applications in twist nematic (TN) display devices. In order to investigate their tricritical phase behaviour, we have studied four binary systems which exhibit the S_A–N transition. Our investigations were performed by obtaining orientational information from ^{13}C NMR experiments. At the S_A–N transition point, the order parameter is discontinuous for first order phase transitions and continuous for second order phase transitions [11, 12, 18]. Thus, the tricritical points can be determined by plotting the magnitude of the discontinuity of the order parameter versus the McMillan ratio, *M*, or the mole fraction. The first system we studied was composed of mixtures of 4-*n*-pentyl-4′-cyanobiphenyl (5CB) and 4-*n*-pentylphenyl 4′-*n*-pentyloxybenzoate ($\bar{5}$O5). In this system, neither pure component displays a smectic phase, but their mixtures with appropriate compositions show an injected smectic A phase [6]. To our knowledge, the tricritical behaviour of an injected smectic A to nematic phase transition has not been reported. The purpose of this part of our work is an investigation of such behaviour. Three other binary mixtures of 4-*n*-alkyl-4′-cyanobiphenyls (*n*CBs, where *n* = the number of carbons in the alkyl chain), in which at least one compound has a smectic A phase, have also been studied. These systems were mixture of 5CB/10CB, 8CB/9CB, and 9CB/10CB. The results are compared with those of two previous reports on the 9CB/10CB system.



5CB



$\bar{5}$O5

2. Experimental

The determination of the orientational ordering was performed by carrying out ^{13}C NMR experiments. The method used was Separated Local Field Spectroscopy in combination with Variable Angle Spinning (SLF/VAS) [19, 20].

During a ^{13}C NMR experiment, measurement of C–H dipolar coupling constants for individual carbon atoms within a liquid crystal molecule allows the order parameters for various molecular segments to be obtained. In order to reduce dipolar couplings to measurable values, the sample is spun rapidly (approximately 1 kHz) near the magic angle (54° 44′). In this case, the director axis of the liquid crystal aligns along the spinning axis (for liquid crystals with a positive anisotropy of the magnetic susceptibility), and the dipolar coupling constants are reduced by a factor $(3\cos^2\beta - 1)/2$, where β is the angle formed between the spinning axis and the magnetic field. In the two-dimensional SLF experiment, an efficient homonuclear dipolar decoupling sequence known as BLEW-48 [21] is used to remove all proton–proton dipolar couplings during the evolution period, leaving only the carbon–proton couplings in the spectra. By applying the SLF/VAS procedure, all relevant order parameters can be calculated from the dipolar coupling constants given by the splitting between peaks in the first dimension. The 2D ^{13}C spectra of $\bar{5}$O5 at 75·43 MHz and 42·4°C are shown in figure 1. Since we are interested in the change of the order parameter during the phase transition, the C–H order parameters of the aliphatic chains were not studied because their changes are smaller than those of the aromatic core [19, 20].

The chemical shift of a particular carbon atom in a liquid crystal molecule oriented in a magnetic field is related to the order parameters by

$$\delta_{LC} = \delta_{iso} + \sum_{\alpha,\beta} S_{\alpha\beta}\sigma_{\alpha\beta} \qquad (1)$$

where δ_{iso} is the chemical shift of the liquid crystal in the isotropic phase, $S_{\alpha\beta}$ is the ordering tensor in a molecular coordinate system and $\delta_{\alpha\beta}$ is the chemical shift tensor in the same coordinate system. Because it is generally not easy to measure the chemical shift tensor of complicated molecules, it is not convenient to use this equation for the determination of order parameters from chemical shift data. It has been shown, however, that changes in the order parameter with temperature are related to the chemical shift data in a semi-empirical way [22]. Because of the effective D_2 symmetry of the phenyl rings in a liquid crystal molecule, the ordering matrix is diagonal and

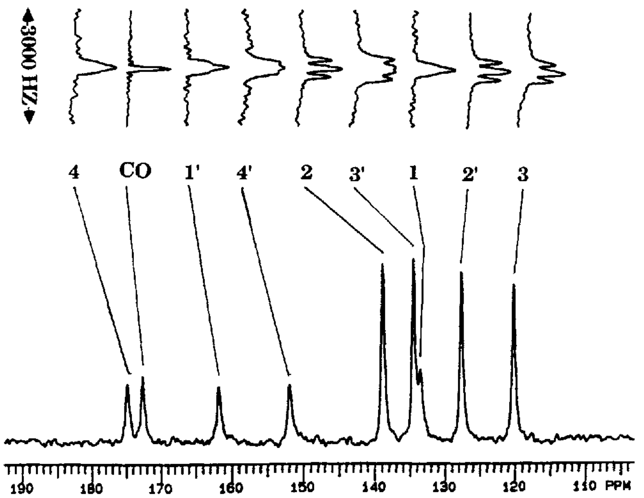


Figure 1. 2D SLF/VAS ^{13}C NMR spectra of $\bar{5}$O5 at 75·43 MHz and 42·4°C (aromatic range only). Spectra in the ω1 dimension are shown on top, and the first spectrum in the ω2 dimension is shown at the bottom.

traceless. Equation (1) is therefore reduced to

$$\delta_{\mathrm{LC}} = \delta_{\mathrm{iso}} + \tfrac{2}{3}S_{zz}\Delta\sigma + \tfrac{1}{3}(S_{xx} - S_{yy})(\sigma_{xx} - \sigma_{yy}) \qquad (2)$$

where $\Delta\sigma$ is the chemical shift anisotropy and is given by:

$$\Delta\sigma = [\sigma_{zz} - \tfrac{1}{2}(\sigma_{yy} + \sigma_{xx})]. \qquad (3)$$

In these equations the z axis is defined as the C_2 axis of the ring, the x axis is defined as the in-plane axis perpendicular to z, while the y axis is perpendicular to both these axes. Because the value of $(S_{xx} - S_{yy})$ is typically less than 10 per cent of S_{zz} and its temperature dependence is small compared to that of S_{zz}, equation (2) can be rewritten as

$$\Delta\delta = a \cdot S + b \qquad (4)$$

where $\Delta\delta = \delta_{\mathrm{LC}} - \delta_{\mathrm{iso}}$, $a \approx 2\Delta\sigma/3, b = \text{constant}$, and the subscript z is dropped from S_{zz}. This equation shows that the chemical shift anisotropy for a carbon atom in the phenyl rings of a liquid crystal molecule is a linear function of the order parameter. By plotting the value of $\Delta\sigma$ against the order parameter S obtained at the same temperature from two-dimensional SLF experiments, it is possible to compute the coefficients a and b by fitting the data to equation (4). After the coefficients a and b are obtained, order parameters can be easily calculated at any temperature from the ^{13}C chemical shifts determined from simple one-dimensional experiments. Because the chemical shifts can be measured accurately in experiments without applying VAS, this method is very useful for the study of order parameters as a function of temperature. In our work, the SLF/VAS experiments were performed on a Varian XL-300 spectrometer at 75·43 MHz, and the chemical shifts were measured with samples spinning slowly about an axis parallel to a 11·7 T magnetic field in a Varian VXR-500S spectrometer, at a ^{13}C resonance frequency of 125·72 MHz.

3. Results and discussion

The constants a and b for the cyanobiphenyls were taken from reference [22] and used to calculate the order parameters as a function of temperature. For $\bar{5}$O5, the core order parameter S was determined from 2D SLF/VAS experiments at five different temperatures. These data were then correlated with the chemical shifts to calculate the constants a and b as explained above.

The chemical shift data were collected as a function of temperature for each of the binary systems with different mole fractions. Near the S_A–N transition temperature, data sets were collected in 0·10°C increments, which were the limiting resolution of the temperature control unit of the Varian VXR-500S spectrometer. Fewer points were accumulated in other temperature ranges. The order parameter for each aromatic carbon atom was then calculated from the chemical shift measurements by the use of equation (4). The core order parameter was plotted versus temperatature to determine the change (ΔS) at the phase transition. Because the core order parameter can be

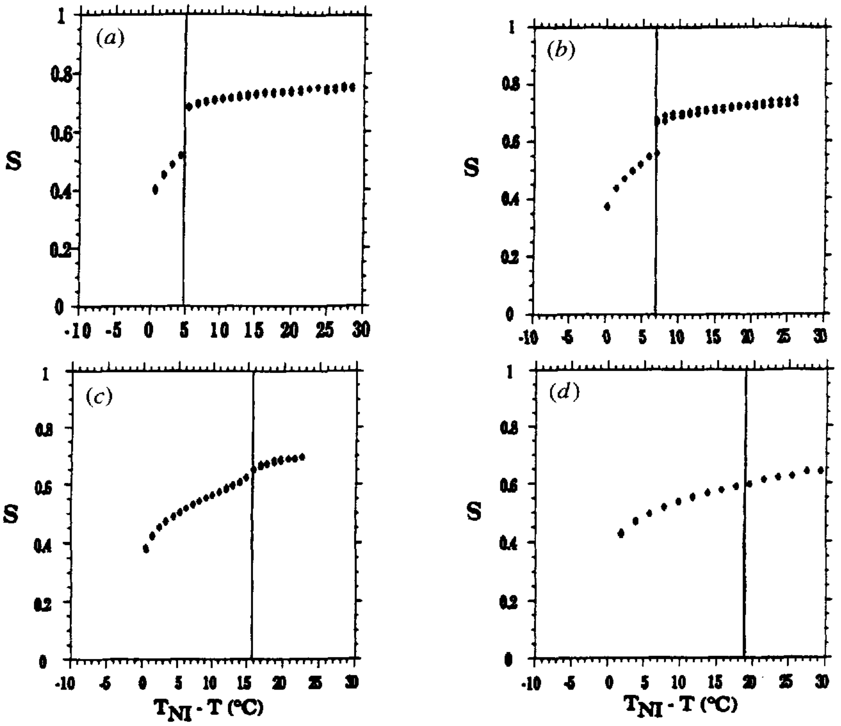


Figure 2. Plots showing the dependence of the order parameters for the two rings in $\bar{5}$O5 on temperature. ◆, ring with alkoxy chain, ◇, ring with alkyl chain. The mol fraction of $\bar{5}$O5 was (*a*) 0·521, (*b*) 0·473, (*c*) 0·363, (*d*) 0·262.

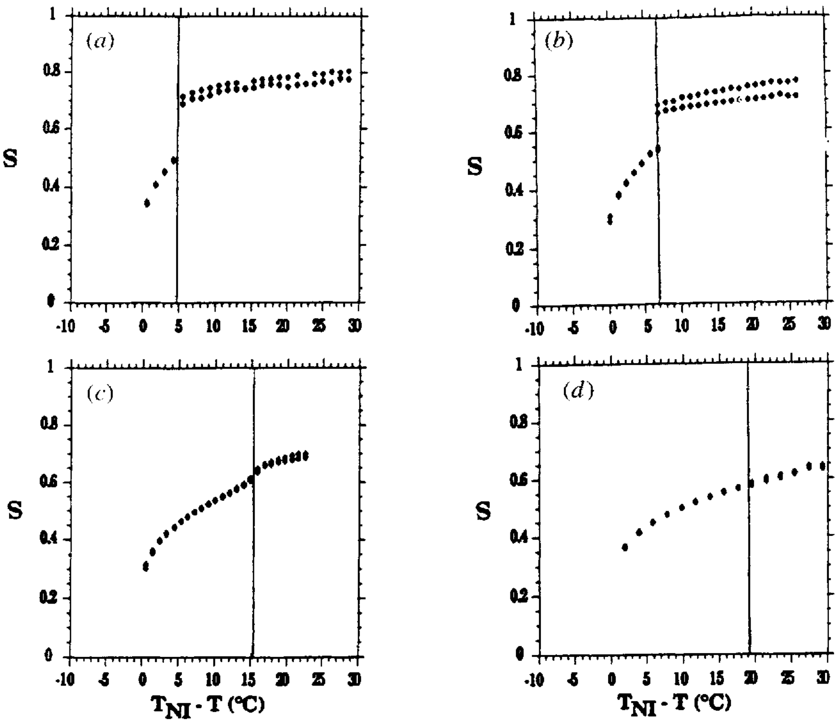


Figure 3. Plots showing the dependence of the order parameters for the two rings in 5CB on temperature. ◆, ring with alkyl chain, ◇, ring with cyano group. The mol fraction of $\bar{5}$O5 was (*a*) 0·521, (*b*) 0·473, (*c*) 0·363, (*d*) 0·262.

calculated from any carbon signal in the phenyl rings, the 1 and 1′ carbons from rings one and two, respectively, were chosen for both $\bar{5}$O5 and 5CB.

The core order parameter for $\bar{5}$O5 is plotted against temperature in figure 2 for several mol fractions of the $\bar{5}$O5/5CB system, and the corresponding plots for 5CB are given in figure 3. At the S_A–N transition temperature, the order parameter changes from discontinuous to continuous as the mole fraction of $\bar{5}$O5 increases. This can clearly be seen in the results for both compounds. Because the plot for each mixture contains data from both rings, an average values for ΔS was used. Figure 4 shows a plot of ΔS versus the McMillan ratio ($M_{TCP} = T_{SN}/T_{NI}$) as computed from both $\bar{5}$O5 and 5CB. When the segment on the right side of each plot is extrapolated to $\Delta S = 0$, values of $M_{TCP} = 0{\cdot}948 \pm 0{\cdot}008$ and $0{\cdot}950 \pm 0{\cdot}007$ are obtained for $\bar{5}$O5 and 5CB, respectively. These values are the same within experimental error, indicating an internal consistency for the method. They are comparable with the value of $M_{TCP} = 0{\cdot}959 \pm 0{\cdot}005$ for the *n*O.*m* system [11, 12]. On the other hand, the theoretical McMillan ratio predicted from mean field calculations [1, 2] is $M_{TCP} = 0{\cdot}87$, which is lower than the experimental value of almost all systems studied [4, 5, 7, 9–18]. The present results indicate that the injected smectic A phase behaves normally like an ordinary smectic A phase, which is not surprising. In the injected smectic A region of the $\bar{5}$O5/5CB system, our results show that the tricritical point occurs at a mol fraction of $0{\cdot}358 \pm 0{\cdot}005$ of $\bar{5}$O5. In comparison, a previous study suggested that the $\bar{5}$O5/5CB system might display tricritical phase behaviour at 0·45 mol fraction of $\bar{5}$O5 [6], but no definitive evaluation was given.

For pure *n*CB systems, single compounds with $n \geqslant 8$ exhibit a smectic A phase. In two previous investigations of the behaviour of the S_A–N phase transition, it was reported that 9CB/10CB mixtures exhibit a tricritical point at 0·01 mol fraction of 9CB [4, 5]. However, when we measured the order parameters of these mixtures, it was found that they were all discontinuous at the S_A–N phase transition, corresponding to first order behaviour. To illustrate this point, the ^{13}C NMR spectra of pure 9CB at several temperatures are shown in figure 5. The coexistence of the smectic A and the nematic phases were observed during the phase transition because of the nature of the system as well as a small temperature gradient due to radiofrequency heating during the NMR experiments. The coexistence of separately resolved peaks means that the chemical shift anisotropy, and hence the order parameter, is different in the nematic and smectic A phases at the transition temperature, and is therefore discontinuous. This evidence shows that the S_A–N transition is clearly first order for pure 9CB. Because pure 9CB exhibits a first order phase transition and 10CB does not have a nematic phase, it is reasonable to expect that any mixture of these two compounds would also undergo first order phase transitions.

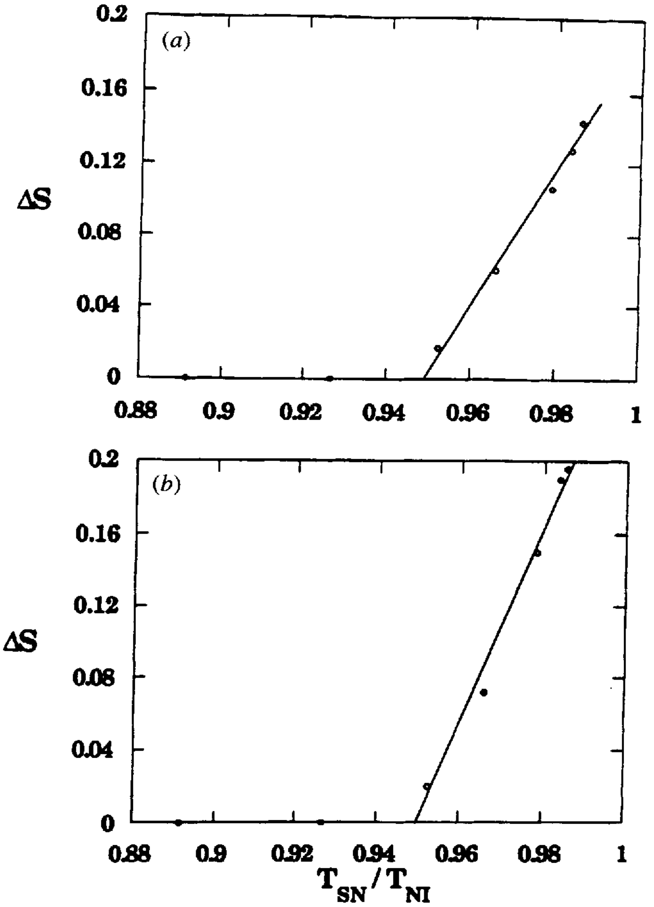


Figure 4. Plots of ΔS versus the McMillan ratio for $\bar{5}$O5/5CB mixtures. (*a*) Data for $\bar{5}$O5, (*b*) data for 5CB.

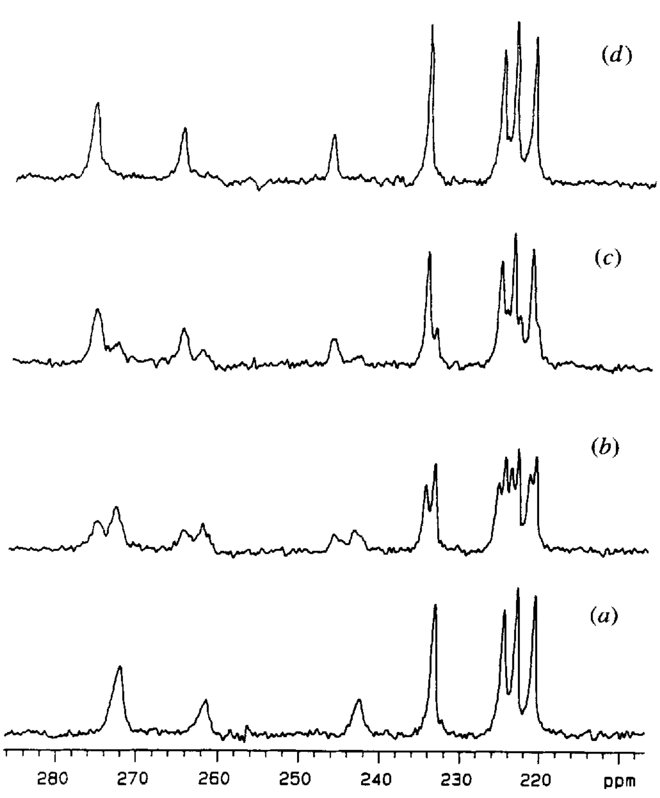


Figure 5. 125·7 MHz ^{13}C NMR spectra of the aromatic region of 9CB taken around the S$_A$–N phase transition. (*a*) 48·2°C, (*b*) 48·1°C, (*c*) 48·0°C, (*d*) 47·9°C. The coexistence of the nematic and smectic A phases can clearly be seen in spectra (*b*) and (*c*).

Because of the discrepancy between the present results and the previous ones [4, 5], we proceeded to examine whether there might be tricritical behaviour for 8CB/9CB mixtures. This is because 8CB has a nematic range (33·5–40·5°C, data from the manufacturer, E. Merck) much wider than that of 9CB (48·0–49·5°C), and its order parameter is continuous at the S$_A$–N phase transition [23]. However, these mixtures have considerably smaller values of ΔS compared with the $\bar{5}$O5/5CB system. Near the S$_A$–N transition it is not always straightforward to discern whether the order parameter is discontinuous or merely showing an inflection point. In order to help make the analysis less subjective, the first derivatives of these curves were computed numerically. Curves showing a strong delta function at the transition temperature were considered to be discontinuous, whereas curves only showing a weak λ shape were considered to be continuous. By applying this criterion, it was possible to determine ΔS for all mixtures we studied [23]. The plot of ΔS versus mol fraction for the 8CB/9CB system is shown in figure 6. Because of the smaller values of ΔS, the data are more scattered than those in figure 4. Nevertheless, it is clear that ΔS decreases as the mol fraction of 8CB increases (see figure 6). By fitting the data for $\Delta S > 0$ to a straight line and extrapolating the line to $\Delta S = 0$, the tricritical point was found to occur at a mol fraction of 0·46 ± 0·02 of 9CB, corresponding to a McMillan ratio of $M_{TCP} = 0{\cdot}985 \pm 0{\cdot}008$.

To ascertain the reliability of this result, we studied another *n*CB binary system. Because 5CB has a nematic

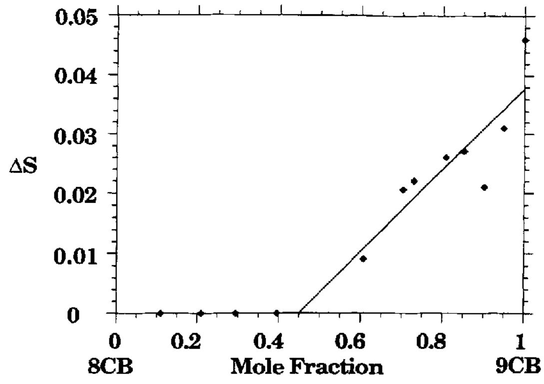


Figure 6. Plot of ΔS against mol fraction for the 8CB/9CB system.

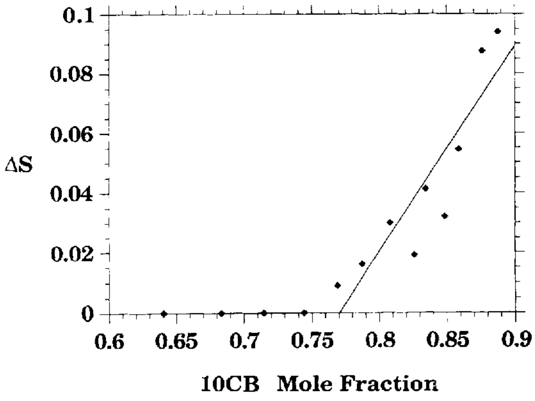


Figure 7. Plot of ΔS against mol fraction for the 5CB/10CB system.

range only, while 10CB has a smectic A range only, measurements were performed for 5CB/10CB mixtures. The similar structures of these two compounds make the nematic range of the system vary fairly linearly with mol fraction, thus providing an increasing nematic range with increasing 5CB content, which favours the tricritical behaviour. Indeed, our results (see figure 7) indicate the presence of a tricritical point in the 5CB/10CB system at a mol fraction of 0·77 ± 0·02 of 10CB. This corresponds to a McMillan ratio of $M_{\mathrm{TCP}} = 0{\cdot}986 \pm 0{\cdot}007$, which is essentially identical to the value of 0·985 ± 0·008 obtained for the 8CB/9CB system. These results are consistent with a previous observations that compounds in a homologous series show the same tricritical point [11, 12, 18]. Because the value of $M_{\mathrm{TCP}} = 0{\cdot}985$–$0{\cdot}986$ is less than the McMillan ratio $M = 0{\cdot}995$ for pure 9CB, and this ratio increases with the addition of 10CB, our results also support the conclusion that the 9CB/10CB mixtures do not show a tricritical point at any mol fraction.

4. Conclusions

We have investigated the phase behaviour of four binary mixtures of liquid crystals. The systems consisting of the $\bar{5}$O5/5CB mixtures as well as the 8CB/9CB and 5CB/10CB mixtures all display tricritical phase behaviour for the S_A–N transition. A previous investigation of the $\bar{5}$O5/5CB system, which exhibits an injected smectic A phase, gave only an estimation of the tricritical point at 0·45 mol fraction of $\bar{5}$O5 [6]. Our results gave a more definitive determination of the tricritical point, which occurs at a mol fraction of 0·358 ± 0·005 of $\bar{5}$O5. The corresponding McMillan ratio, $M_{\mathrm{TCP}} = 0{\cdot}948 \pm 0{\cdot}008$, is quite close to the value $M_{\mathrm{TCP}} = 0{\cdot}959 \pm 0{\cdot}005$ of the *n*O.*m* series, showing that there is nothing unusual for the injected smectic A phase. Our results for the *n*CB series do not agree with those of previous calorimetric studies, both of which reported a tricritical point very near the 9CB side of the 9CB/10CB phase diagram [4, 5]. However, we found that 9CB/10CB mixtures do not display tricritical behaviour, and determined that the tricritical point occurs in 8CB/9CB mixtures at a mol fraction of 0·46 ± 0·02 of 9CB, with $M_{\mathrm{TCP}} = 0{\cdot}985 \pm 0{\cdot}008$. The tricritical point for the 5CB/10CB system was measured to occur at 0·77 ± 0·02 mol fraction of 10CB, with $M_{\mathrm{TCP}} = 0{\cdot}986 \pm 0{\cdot}007$. The nearly identical values for these two systems give more validity to our measurements.

Because fluctuations of some physical properties occur near the S_A–N phase transition, uncertainties may be associated with measurements for some tricritical systems. On the other hand, chemical shifts are affected by orientational ordering but not sensitive to thermodynamic factors caused by changes in translational symmetry when a liquid crystal goes from a nematic phase to a layered smectic phase. Therefore, we feel that measurements of orientational ordering by the use of ^{13}C NMR are a reliable means for investigating the S_A–N tricritical behaviour of liquid crystals. In the case of the 9CB/10CB system, they probably give more dependable results than calorimetric studies.

This work was supported by the U.S. National Science Foundation under grant number DMR-9321114.

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