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The nematic–isotropic two phase region in mixtures of quasi-spherical solutes in alkylcyanobiphenyls: an E.S.R. study using tempone as probe

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The transitional behaviour of binary mixtures, each containing a non-mesomorphic quasi-spherical solute at a low mole fraction in a nematogenic solvent, has been investigated by E.S.R. spectroscopy using 4-oxo-2,2,6,6-tetramethyl-4-piperidinyl-1-oxy (tempone) as a spin probe. This approach makes use of the smaller coupling constant obtained for the spin probe in the orientationally ordered nematic phase relative to that obtained in the isotropic phase. The solutes included Et_4C (tetraethylmethane) and R_4Sn ($R = C_2H_5$, n-C_3H_7 and n-C_4H_9). The solvents were 4-*n*-pentyl-4′-cyanobiphenyl (5CB) 4-*n*-hexyl-4′-cyanobiphenyl (6CB) and 4-*n*-heptyl-4′-cyanobiphenyl (7CB). This fast approach compares favourably with other studies. In addition it provides the tempone spectral parameter, f, which is a relative measure of the fraction of the nematic phase at different temperatures within the two phase region.

1. Introduction

The addition of a non-rod-like solute impurity to a nematogenic solvent leads, with few exceptions [1, 2], to a depression of the nematic–isotropic transition temperature and the formation of a two phase region. The existence of a two phase region is consistent with the first order nature of the nematic–isotropic transition. From visual [3–7] and density [8, 9] studies the phase diagram shown in figure 1 is usually obtained for a non-mesomorphic–nematogenic solvent mixture at moderately low solute mole fractions x_2 ($0{\cdot}005 \approx x_2 \leqslant 0{\cdot}06$) where T^* ($= T/T_{NI}$) is the reduced temperature and T_{NI} is the nematic–isotropic transition temperature of the pure liquid-crystalline solvent. The moduli of the slopes of the nematic and isotropic boundary lines, β_N and β_I, respectively, reflect the ability of the solute to destabilize the nematic phase. These solute probe approaches have yielded [10] much useful information on the relationship between molecular structure and phase stability.

In this study the transitional behaviour of binary mixtures, each containing a non-mesomorphic solute at a low mole fraction in a nematogenic solvent, was investigated by E.S.R. spectroscopy using 4-oxo-2,2,6,6-tetramethyl-4-piperidinyl-1-oxy (tempone) as a spin probe. This approach depends on the knowledge that as a result of the existence of a liquid crystal potential, a smaller coupling constant is obtained for the spin probe in the orientationally ordered nematic phase than in the isotropic phase [11]. This creates a spectral doublet in the high and low field lines at temperatures within the two phase region. The use of very low concentrations of tempone (see §2) ensured that its effect on the nematic–isotropic transitions of the systems studied is negligible.

The solvents used in this study were 4-*n*-pentyl-4′-cyanobiphenyl (5CB), 4-*n*-hexyl-4′-cyanobiphenyl (6CB) and 4-*n*-heptyl-4′-cyanobiphenyl (7CB). The

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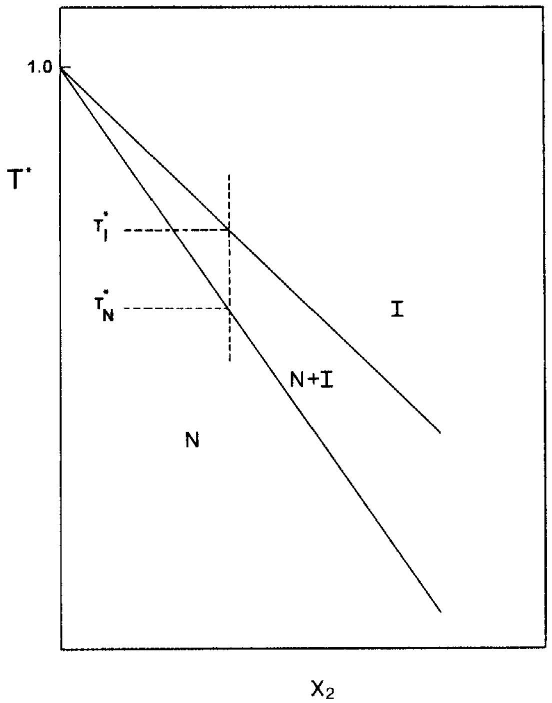


Figure 1. Typical reduced temperature, T^*, versus solute mole fraction, x_2, phase diagram for non-mesomorphic solute + nematogenic solvent mixtures at low x_2.

non-mesomorphic quasi-spherical solutes used were Et_4C (tetraethylmethane) and R_4Sn ($R = C_2H_5$, n-C_3H_7 and n-C_4H_9). The non-mesomorphic solute–nematogenic solvent mixtures investigated are listed in the table. Each mixture was studied at a single solute concentration, since an earlier study [8] established the virtual linearity of the nematic and isotropic boundary lines, at low x_2 values, in the phase diagram.

The results of this study compare favourably with those from earlier visual [3, 4] and density [8, 9] investigations. This technique is faster than its predecessors and is therefore very promising for studies on non-mesomorphic solute–liquid-crystalline

Table 1. β_N and β_I values for mixtures of quasi-spherical solute in alkylcyanobiphenyl nematogenic solvents.

System no.	Solvent	Solute/mole fraction	β_N		β_I	
			This study	Other studies	This study	Other studies
1	5CB	Et_4C (0·0193)	0·78	0·73 [3, 9]	0·64	0·63 [3, 9]
2	5CB	Et_4Sn (0·0184)	0·78	0·86 [3]	0·70	0·72 [3]
3	5CB	Pr_4Sn (0·017)	1·10	1·12 [3]	1·02	0·91 [3]
4	5CB	Bu_4Sn (0·0100)	2·33	1·30 [3]	1·07	1·04 [3]
5	6CB	Pr_4SN (0·0135)	0·92	0·90†	0·63	0·74†
6	7CB	Et_4C (0·0195)	0·57	0·57 [8]	0·34	0·38 [8]
7	7CB	Pr_4Sn (0·0142)	0·77	0·68 [8]	0·54	0·48 [8]

† Unpublished results from density studies.

solvent interactions. In addition it provides the spectral parameter f [12] for the nitroxide spin probe, which is a relative measure of the fraction of the nematic phase, at different temperatures within the two phase region.

2. Experimental

The tetraalkyl (quasi-spherical) solutes each has a quoted purity of at least 98 per cent. Et_4C was obtained from Chemical Samples, tetraethyl tin (Et_4Sn) and tetrapropyl tin (Pr_4Sn) were obtained from K & K Rare and Fine Chemicals, and tetrabutyl tin (Bu_4Sn) was obtained from Aldrich. 5CB, 6CB and 7CB were obtained from B.D.H. Chemicals and, from the sharpness of their nematic–isotropic transition temperatures, they were assessed to be highly pure. All solutes and solvents were used without further purification. The nitroxide spin probe (tempone) was obtained from Molecular Probes, Junction City, Oregon. To a known mass of each of the pure liquid crystals several microlitres of one of the quasi-spherical solutes were added, using a Hamilton PB600-1 repeating dispenser. To each mixture an extremely small amount of tempone was added by touching the inner wall of the vial containing the mixture with the tip of a glass rod containing tempone on its surface. A sample of each mixture was then transferred to a Pyrex sample tube (3 mm i.d., 5 mm o.d.) adapted to 9 mm o.d. at the open end in order to fit into the quick-disconnect fitting (Seal structure, Sargent-Welch part No. S-76639-A, size 24/40) on the vacuum line manifold. The samples were degassed on a Pope vacuum line then sealed, using a gas torch, while they were immersed in liquid nitrogen.

E.S.R. spectra were taken over narrow temperature ranges, which included the two phase regions of the liquid crystal samples, with a Bruker ER 200D-SRC spectrometer operating at 9·11 GHz and interfaced with an Aspect 2000 data system. The temperature was controlled by a Bruker ER 4111 VT variable temperature unit. The spectra were recorded with a rapid scan unit using a scan time of 0·5 or 1 s over a 50 G scan range. The spectra recorded were those when the temperature was increasing from the nematic phase to the isotropic phase. The temperatures (stable to ±0·1°C) were read directly with an Omega digital thermometer equipped with an ultrafine copper–constantan thermocouple placed as close as possible to the sample tube without disturbing the cavity mode. The magnetic field sweep was calibrated with a Bruker ER 035 M N.M.R. gaussmeter with an accuracy of 2 mG. The frequency was measured using a Model 5342 A HP frequency counter. Both microwave power and modulation amplitude were verified to be at least five times below the onset of broadening. The scan speed and time constant were carefully chosen to ensure that no scanning artefacts were introduced.

3. Results and discussion

The spectra for tempone in the 7CB–Pr_4Sn mixture at several temperatures are given in figure 2. Similar spectra were obtained for the other systems studied. Figure 2 shows that the coupling constant for tempone in the orientationally ordered nematic phase, $(A_N)_N$, is, as expected [11], smaller than its coupling constant in the isotropic phase, $(A_N)_I$. Temperatures at which the nematic and isotropic phases coexist are therefore characterized by a doublet in both the high and low field lines. The temperature for the onset of the isotropic phase, T_N, on heating is that at which the doublet first appears. As the temperature rises and the fraction of the isotropic

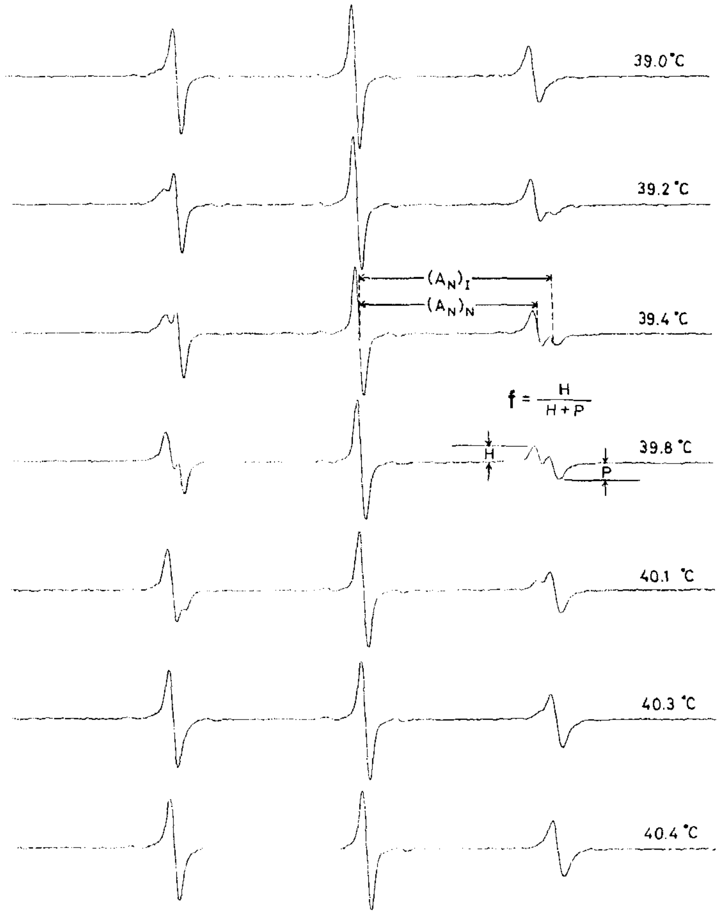


Figure 2. E.S.R. spectra of tempone in the 7CB–Pr_4Sn mixture at temperatures defining the two phase region accompanying the nematic–isotropic transition, centred at about 39·8°C. The three main lines are due to the hyperfine splitting (A_N) from a single ^{14}N nucleus. The subscripts N and I denote nematic and isotropic phases, respectively. (Spectrometer settings were as follows; signal average = 1 time; digitization = 4000 points, field set = 3444 G; scan range = 50 G; scan time = 500 ms; modulation frequency = 100 kHz; modulation amplitude = 0·12 G; gain = $1·25 \times 10^4$; time constant = 0·5 ms; microwave power = 14 dB and microwave frequency = 9·6826 GHz.)

phase increases, the contribution to the doublet from tempone in the isotropic phase increases at the expense of the contribution from tempone in the nematic phase. At 39·8°C, a temperature in the middle of the two phase region, the contributions from tempone in the nematic and isotropic phases are nearly equal. At the temperature on the boundary between the two phase region and the isotropic phase region, T_I, the doublet reverts to a singlet with a coupling constant characteristic of tempone in the isotropic phase. From T_N^* $(= T_N/T_{NI})$ and T_I^* $(= T_I/T_{NI})$ the moduli of the slopes of the nematic and isotropic boundary lines β_N $(=(1 - T_N^*)/x_2)$ and β_I $(=(1 - T_I^*)/x_2)$, respectively, are calculated. The results are given in the table.

Following Wu and McConnell [12] this splitting of the high and low field spectral lines into two signals (one due to tempone in the nematic phase (indicated as H in figure 2) and the other due to tempone in the isotropic phase (P in figure 2)) a spectral

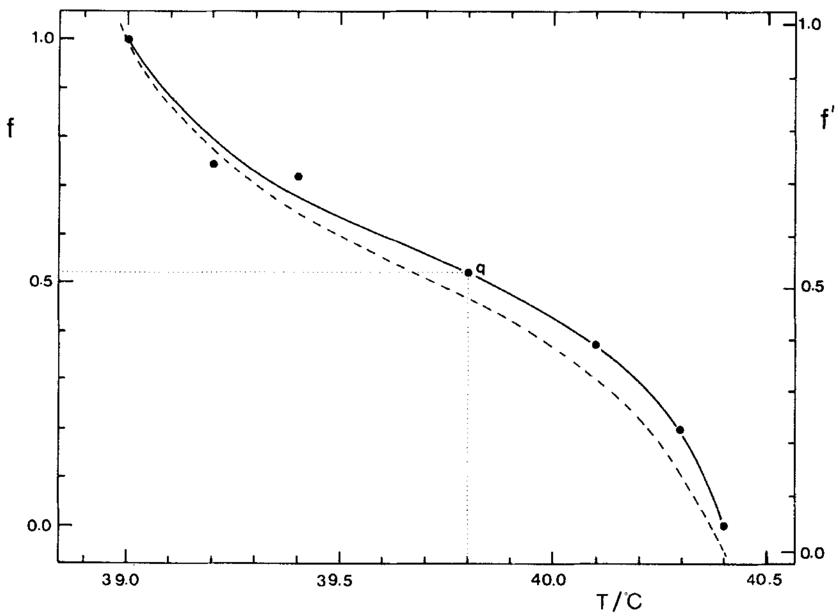


Figure 3. The tempone spectral parameter, f, versus temperature for the two phase region of the 7CB–Pr_4Sn mixture is represented by the continuous line. The broken line gives f' versus temperature for the same system.

parameter $f\,(=H/(H + P))$, which is a measure of the fraction of tempone dissolved in the nematic phase, was calculated at several temperatures in the two phase regions of the systems studied. At plot of f against temperature is given in figure 3 for the 7CB–Pr_4Sn system; below T_N, $f = 1$ and above T_I, $f = 0$.

The approach of Wu and McConnell [12] gives correct f values if the nematic phase and isotropic phase spectral lines contributing to the doublet are lorentzian, of equal peak-to-peak widths and have $h/p = H/P$. h and p are the peak-to-peak heights of the contributing nematic phase and isotropic phase spectral lines, respectively. Our systems meet the first two conditions. The third requirement is met only approximately since the overlap between each pair of contributing spectral lines spreads slightly beyond their peak-to-peak centres. For this reason our f values needed to be related to a true spectral parameter f'. To achieve this, spectra of different simulated intensities for tempone in nematic and isotropic phases were used. $f'\,(=h/(h + p))$ and f were obtained, respectively, before and after the digital addition of a nematic phase spectral line to an isotropic phase spectral line. The f' and f values were found to be related by

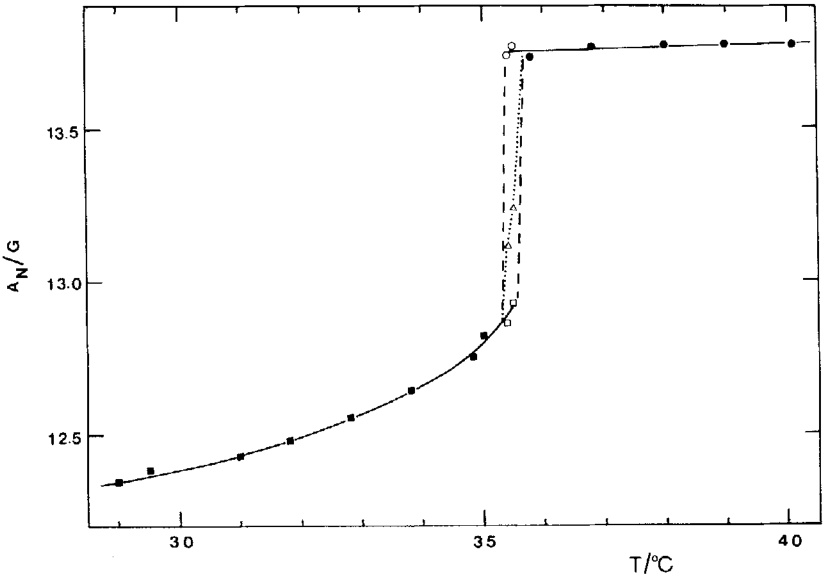
$$f' = -0{\cdot}0513 + 1{\cdot}0249f$$

($r = 0{\cdot}9958$), so the shift in f, $\Delta f\,(=f - f')$, increases from 0·026 at $f = 1$ to 0·051 at $f = 0$. The f' versus temperature curve shown in figure 3 was generated from this relationship.

These spectral simulations also showed that the hyperfine splittings A_N and A_I, measured in the manner illustrated in figure 2, are unaffected by overlap between spectral lines.

In figure 4 (a)–(d) plots of ^{14}N hyperfine splitting versus temperature are given for tempone dissolved in (a) pure 5CB, and in the systems (b) 5CB–Et_4C, (c) 5CB–Bu_4Sn

and (*d*) 7CB–Pr_4Sn. In these plots the two phase regions are bounded by the broken lines and continuous lines represent the nematic (■) and isotropic (●) phase regions. In the two phase regions $(A_N)_N$ and $(A_N)_I$ are represented by □ and ○, respectively. f versus temperature plots like that shown in figure 3 are inserted into the two phase regions of the plots in figure 4 as dotted (△) lines. Points q in figures 3 and 4 (*d*), both for the 7CB–Pr_4Sn system, help to illustrate this insertion procedure. The position of q along pr in figure 4 (*d*) is fixed by the requirement that pq/pr equal the f value for point q in figure 3.



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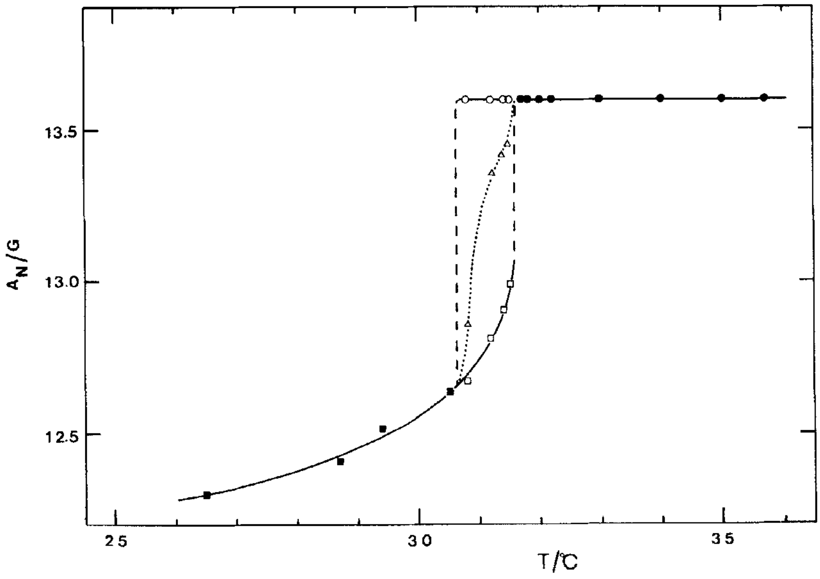

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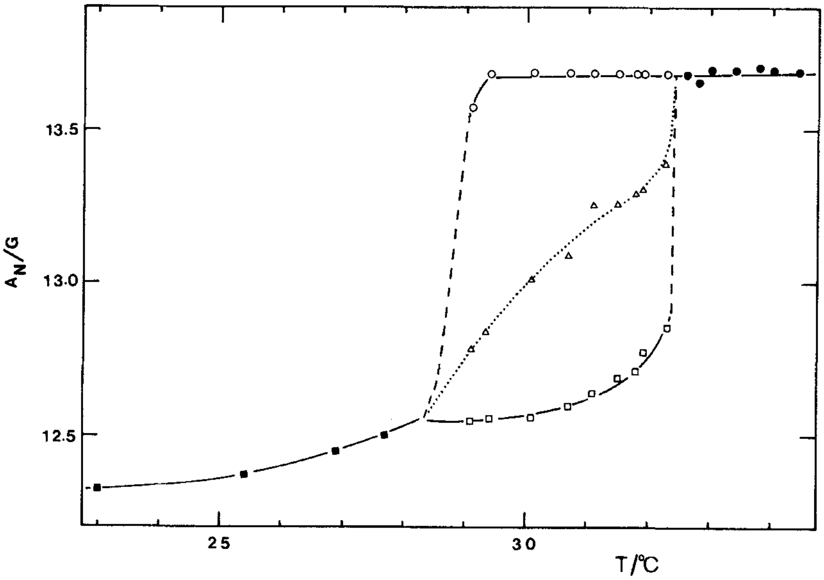
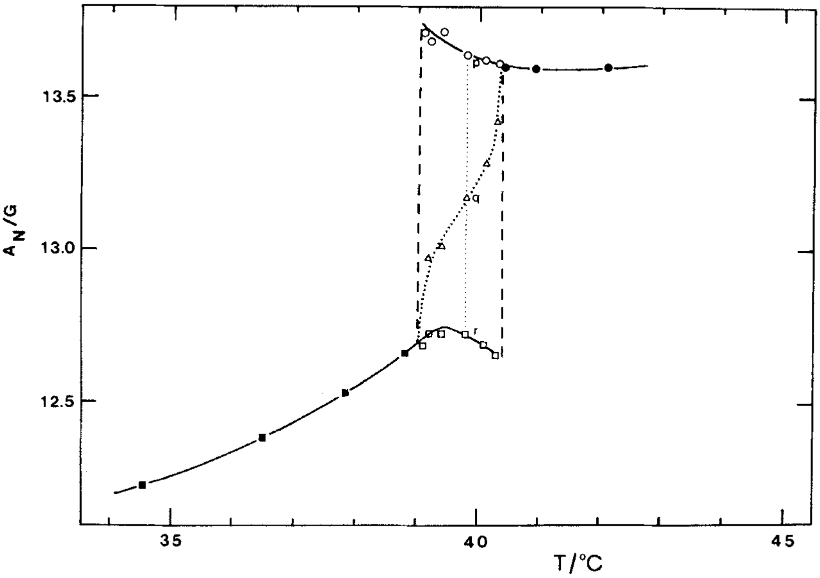


(c)



(d)

Figure 4. Plots of ^{14}N hyperfine splitting, A_N, versus temperature for (a) pure 5CB and for the mixtures; (b) 5CB–Et_4C (c) 5CB–Bu_4Sn and (d) 7CB–Pr_4Sn. ■ and ● denote the nematic and isotropic phases, respectively, and □ and ○, respectively, the nematic and isotropic phases within the two phase region bounded by the broken lines. The dotted (△) line is an f versus temperature plot similar to that of figure 3 and inserted as explained in the text.

Since the extent of the two phase region obtained for 'pure' 5CB in this study (figure 4 (*a*)) is comparable with, if not even smaller than, the extent of the two phase region obtained for pure 5CB in other studies [4, 8], the contribution of tempone to the depression of the nematic–isotropic transition and the extent of the two phase region can be assumed to be negligible. Since the same procedure was used to introduce tempone into all the mixtures studied, we can assume that tempone acted purely as a probe and had no appreciable effect on the nematic–isotropic transitions of the systems studied.

Magnetic parameters for perdeuteriated tempone in 'Phase V', equation (2.26a) and the calibration curve in figure 5 from a paper by Polnaszek and Freed [13] were used to estimate the order parameter, S, at different temperatures in the nematic, isotropic and two phase regions of our systems. Except for the 7CB–Pr_4Sn system (see figure 4 (*d*)), the order parameter in the nematic phase of the two phase region generally decreased with increasing temperature in a more drastic manner than had been previously observed [6] by N.M.R. Plots of our estimates of S versus T^* are given in figure 5 for pure 5CB and the 5CB–Bu_4Sn system. The earlier results were rationalized as follows [6]. A decrease in S as a result of an increase in temperature is partially counteracted by an increase in S due to a decrease in the mole fraction of the perturbing solute in the nematic phase (see figure 1). Our results favour the view that the former effect predominates. The low solute mole fractions used in this study (see the table) make the changes in the solute mole fraction in the nematic phase far too small to affect S appreciably. In addition very small amounts of samples are used (filling less than 2·5 cm of the E.S.R. tube) so temperature gradient effects were minimized. The odd behaviour encountered in the 7CB–Pr_4Sn system (see figure 4 (*d*)) is attributed to supercooling effects. In some of the measurements in the two phase region the E.S.R. spectrum was taken while cooling the sample after the temperature at which measurement was intended was overshot slightly.

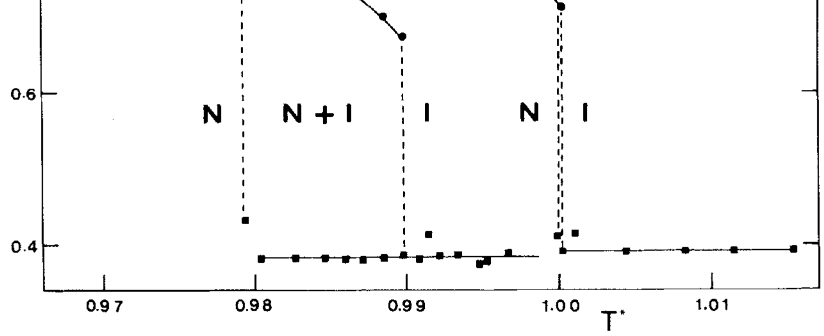


Figure 5. Plots of S versus T^* for (*a*) pure 5CB and (*b*) the 5CB–Bu_4Sn system.

On examining the data in the table we see that, with the exception of the β_N value for the 5CB–Bu_4Sn system, the results from this study and the trends observed are in acceptable agreement with previous visual [3, 4] and density [8, 9] studies. Briefly restated these trends are: (*a*) for the same solute molecule β_N and β_I decrease as the length of the flexible alkyl chain on the liquid-crystalline solvent molecule increases (compare systems 1 and 6 and systems 3, 5 and 7) and (*b*) for the same solvent molecule β_N and β_I increase as the size of the solute molecule increases (compare systems 1, 2 and 3 and systems 6 and 7). Why the β_N value obtained in this study for the 5CB–Bu_4Sn system is much larger than that obtained from the visual study [3, 4] is not clear at present. Probably the much slower heating rate used in the visual study led to superheating and the appearance of the two phase region at a higher temperature (lower β_N) than that encountered in this study. That superheating is possible is suspected from the results of Humphries and Luckhurst [14] which show that the values of A_m, the molar Helmholtz energy function, in the two phase region and in the nematic phase are very close.

The small variations between the results from this study and those from earlier investigations [3, 4, 8, 9] are not unexpected since the temperature control in the earlier studies (better than $\pm 0{\cdot}02°C$) is superior to that achieved in our experiments ($\pm 0{\cdot}1°C$). If better temperature control is achieved this E.S.R. approach should prove to be superior to earlier approaches. Similar future experiments with better temperature control are planned. In addition the data available will be analysed using magnetic parameters (determined from rigid limit computer simulations) for tempone in these systems at 77 K, to obtain information on the liquid crystal potential in the neighbourhood of the nematic–isotropic transition.

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