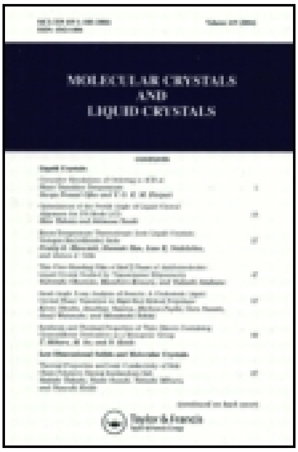

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A Novel Esr Approach to Accurately Probe Transition Temperatures in Liquid Crystalline Systems

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A NOVEL ESR APPROACH TO ACCURATELY PROBE TRANSITION TEMPERATURES IN LIQUID CRYSTALLINE SYSTEMS

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Abstract Using the spin probe predeuterated-2,2,6,6-tetramethyl-4-piperidone-N-oxide (PD-Tempone) at mole fractions about 10^{-5} the transition temperatures of 'pure' 4-cyano-4'-n-pentylbiphenyl (5CB) and four dilute solutions of 3,3-diethylpentane (Et_4C) at mole fractions between 0.02 and 0.08 in 5CB were determined. This fast approach relies on the smaller coupling constant obtained for the spin probe in the orientationaly ordered nematic phase relative to the isotropic phase. Using an especially designed sample holder in conjunction with a temperature control and monitoring system the temperatures of our samples were controlled to within ± 0.02 °C. The results were used to obtain the phase diagram for the 5CB-Et_4C system in the concentration range studied.

INTRODUCTION

The addition of a nonmesomorphic solute impurity to a nematogenic solvent leads, with few exceptions[1,2], to a depression in the nematic-to-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-to-isotropic transition. Phase diagrams like the one shown in figure 1 were obtained from visual[3-7] and density[8,9] studies at low mole fractions x_2 ($0.005 \approx x2 \leq 0.06$) of the nonmesomorphic solute. T_N^* ($=T_N/T_{NI}$) and T_I^* ($=T_I/T_{NI}$) are reduced temperatures where T_N and T_I are, respectively, the Kelvin temperatures at which the isotropic phase just appears on heating (or just disappears on cooling) and the nematic phase just disappears on heating (or just appears on cooling) and T_{NI} is the Kelvin nematic-to-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 stability.

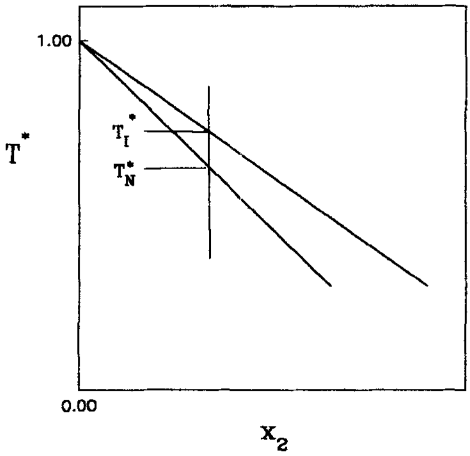

FIGURE 1 Typical phase diagram for a nonmesomorphic solute at low mole fraction, x_2, in a nematogenic solvents.

In this study the transition temperatures of 'pure' 5CB and four binary mixtures of Et_4C at low mole fractions, x_2 (between 0.02 and 0.08), in 5CB were determined by ESR spectroscopy using PD-Tempone (at mole fraction about 10^{-5}) as probe. It has been found by us[11] that at such low mole fractions PD-Tempone probes the nematic-to-isotropic phase transition without appreciably perturbing it. This approach depends on the knowledge that, as a result of a liquid crystal potential, a smaller coupling constant is obtained for the spin probe in the orientationaly ordered nematic phase than in the isotropic phase.[12] This creates a spectral doublet in the high and low field lines within the two-phase region. Using such spectra alongside broad spectra (obtained with a much larger modulation amplitude) not showing the high and low field doublets at temperatures where the nematic and isotropic phases coexist, allow us to pin point T_N and T_I. Finally through the use of the especially designed sample holder shown in figure 2 in conjunction with a temperature control and measurement system, the temperatures measured in this study were accurate to within ± 0.02 °C. Such accuracy is comparable or better than that achieved in visual[3-7] and density[8,9] studies.

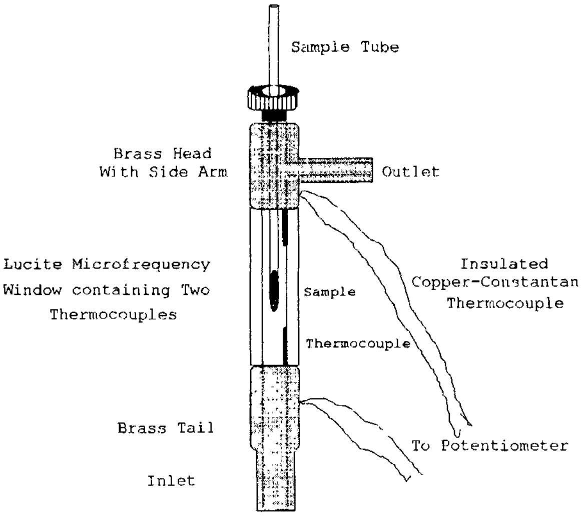

FIGURE 2 The brass-lucite ESR sample holder.

EXPERIMENTAL

5CB was obtained from BDH Chemicals. It was assessed to be highly pure because it exhibited a sharp nematic-to-isotropic transition temperatures (to within ± 0.1 °C). PD-Tempone was obtained from Molecular Probes. Et_4C was obtained from Chemical Samples. All these chemicals were used without further purification.

In an earlier ESR study we have shown[11] that at mole fractions about 10^{-5} PD-Tempone does not perturb the nematic-to-isotropic transition of 5CB. Such a solution of PD-Tempone in 5CB was used as 'solvent' to prepare four solutions with Et_4C mole fractions between 0.02 and 0.08. Each of these solutions was prepared by adding the appropriate number of Et_4C microliters, using a PB600-1 Repeating Dispenser fitted with a 50 microliter Hamilton syringe, to a known weight of 5CB in a tightly stoppered vial. Samples from these solutions were introduced into the ESR tube using very narrow mouthed disposable droppers. The ESR tubes were simply sealed with parafilm. The heights of the solution samples in the ESR tubes were adjusted to be between 1 and 1.5 cm. At these heights the whole sample is within the active region of the microwave cavity.

The temperature of the ESR sample was maintained by circulating dimethylpolysiloxane from a LAUDA RCS-20D circulator and constant temperature bath through an especially designed sample holder (see figure 2) placed inside the microwave cavity. The temperature of the circulating liquid could be controlled to within ± 0.02 °C. The dimensions of the sample holder, particularly those of the microwave frequency window that is inside the Bruker TE102 rectangular cavity are a compromise between the requirements of unhindered flow of dimethylpolysiloxane and the maximum possible quality factor for the ESR microwave cavity. Copper-Constantan thermocouples embedded in the Lucite window of the sample holder (see figure 2) just above and below the sample showed that long term temperature fluctuations and the temperature gradient across the sample were within ± 0.02 °C.

An ER-200-SRC series spectrometer was used to obtain the ESR spectra. The magnetic field sweep was calibrated with a Bruker-ER 035 M NMR gaussmeter with an accuracy of 2 mG. The frequency was measured with a Model 5342A Hewlett Packard frequency counter. Both microwave power and modulation amplitude were verified to be at least 10 times below the onset of broadening. The scan speed and time constant were also carefully chosen so as not to introduce any artifact by scanning. Using a scan range of 70G a hard copy of the ESR spectrum was obtained. Also recorded on the hard copy is the field computed by the Sweep Address Compute (SAC) for the peak maxima. SAC is supplied as an integral number N within the range $0 \leq N \leq 4095$ which is equivalent to the Field Compute (FC) command in the sense that one can calculate the actual field. It allows for an accurate relative calibration of recorded spectra especially for small sweep widths where the FC will not work due to its limited display resolution. On increasing the modulation by a factor of 10 or more a much broader spectrum was obtained. Pairs of sharp and broad spectra were obtained at different temperatures in the heating and cooling cycles across the nematic and isotropic phases of the sample after allowing adequate time for equilibration (about 20 minutes) at each temperature. The temperature was raised (or lowered) in steps of 0.5 °C (or less) when away from transition temperatures and in steps of 0.05 °C (or less) in the neighborhood of transition temperatures. For all the systems studied the data for the heating and cooling cycles were close and reproducible. These pairs of spectra allowed us to pin-point t_N (T_N in Kelvin) and t_I

(T_I in Kelvin). This was done in the following manner. As a result of the existence of a liquid crystal potential, a smaller coupling constant a_N is obtained for the spin probe in the orientationally ordered nematic phase (see spectrum (a) in figure 3) than the coupling constant a_I obtained in the isotropic phase (see spectrum (d) in figure 3).

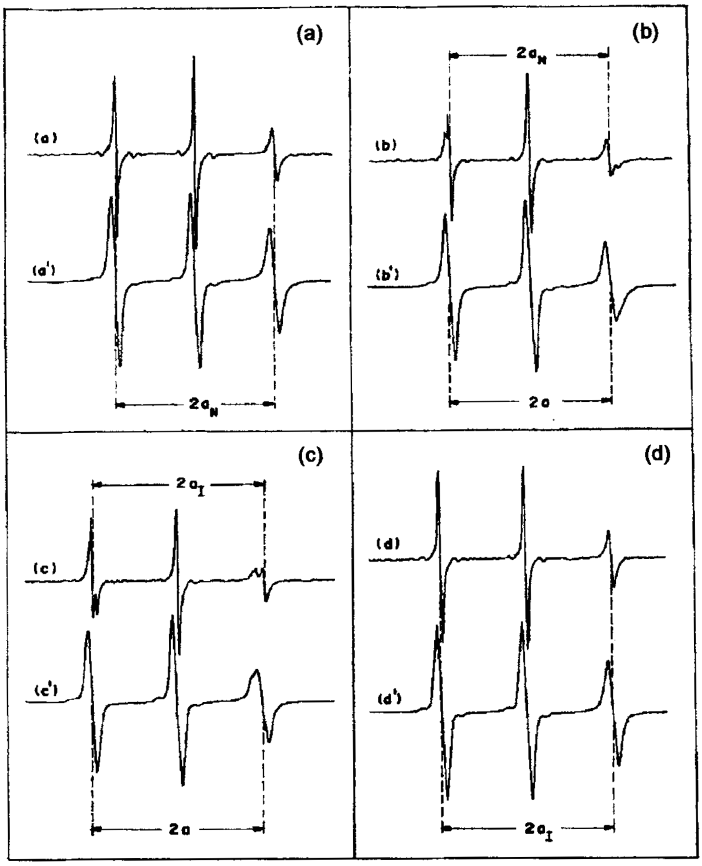

FIGURE 3 Representative sharp and broad ESR spectra for PD-Tempone in the nematic (a and a'), isotropic (d and d'), the two-phase region close to the nematic coexistence line (b and b') and the two-phase region close to the isotropic coexistence line (c and c') in the $5CB-Et_4C$ system.

From such spectra the variations of a_N and a_I with t are mapped out in the nematic (○) and isotropic (□) phases respectively (see figure 4).

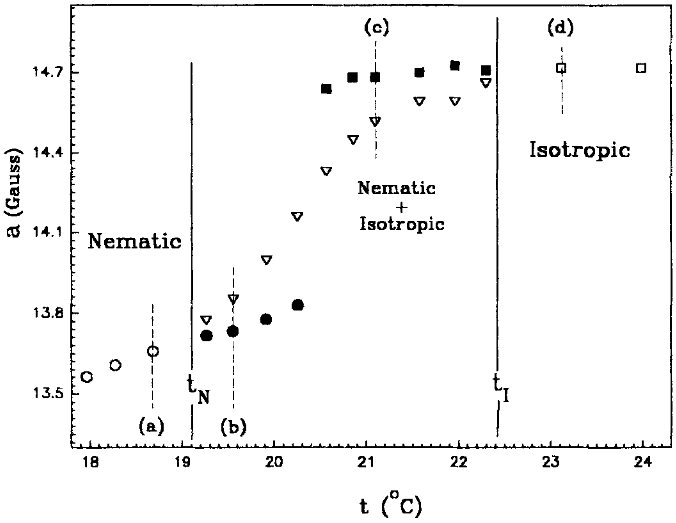

FIGURE 4 a versus t plot for a solution with a 0.058 mole fraction of 3,3-diethylpentane in 5CB showing a_N versus t in the nematic phase (○) and the two-phase region (●), a_I versus t in the isotropic phase (□) and the two-phase region (■), and a versus t (Δ) in the two-phase region. The points through which the dotted vertical lines (a), (b), (c) and (d) correspond to spectra (a), (b), (c) and (d) in figure 3.

At temperatures within the two-phase region a spectral doublet is observed in the high and low field lines of the sharp spectra. From sharp spectra at temperatures within the two-phase region and close to its boundary with the nematic phase the coupling constant due to PD-Tempone in the nematic phase is determined from its contribution to the doublet (spectrum (b) in figure 3). Similar measurements give the variation of a_N with t (●) in this region (see figure 4). Similarly from sharp spectra at temperatures within the two-phase region and close to its boundary with the isotropic phase the coupling constant due to PD-Tempone in the isotropic phase is determined from its contribution to the doublet (spectrum (c) in figure 3). Again similar measurements give the variation of a_I with t (■) in this region (see figure 4). At temperatures within the two-phase region the broad spectra give the variation of an overall coupling constant a with t (points (Δ) in figure 4). The convergence of the a_N versus t line in the nematic phase with the a_N versus t and a versus t lines in the two-phase region pinpoints t_N. Similarly the convergence of the a_I versus t line in the isotropic phase with the a_I versus t and a versus t lines in the two-phase region pinpoints t_I.

a versus t plots, obtained in the manner just described, are given in figure 5 for the 5CB-Et_4C system.

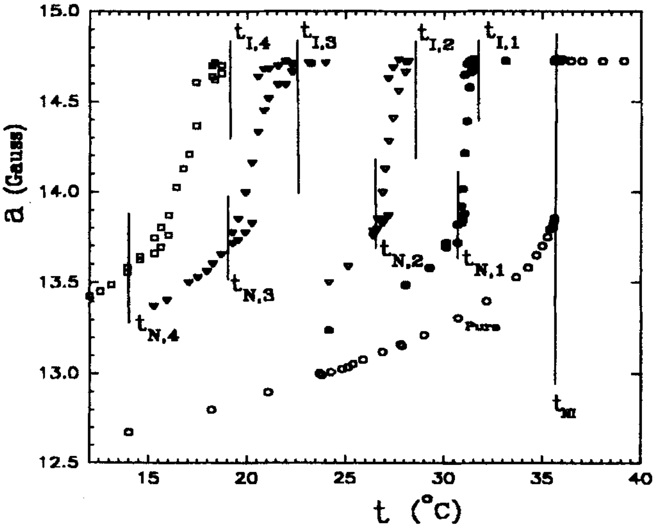

FIGURE 5 a versus t plots for 'pure' 5CB and four binary mixtures with different mole fractions x_1 to x_4 of ET_4C in 5CB.

Five plots are shown; one for 'pure' 5CB giving t_{NI} and the rest are at four different mole fractions x_1 to x_4 and give four temperatures $t_{N,1}$ to $t_{N,4}$ for the boundary of the nematic phase with the two-phase region in each of the four mixtures and four temperatures $t_{I,1}$ to $t_{I,4}$ for the boundary of the isotropic phase with the two-phase region in each of the four mixtures.

RESULTS AND DISCUSSION

T_N, T_I and T_{NI} are the Kelvin equivalents of t_N, t_I and t_{NI}. Thus from the a versus t plots T_N^* and T_I^* versus x_2 plots may be obtained. In this manner the T^* versus x_2 plot shown in figure 6 for the 5CB-Et$_4$C has been obtained from the a versus t plots shown in figure 5 for the same system.

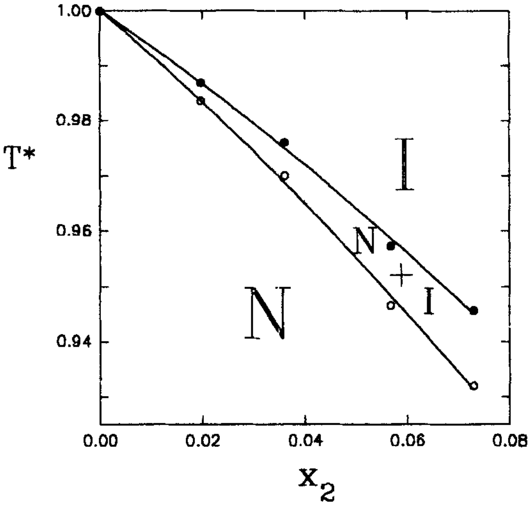

FIGURE 6 The T^* versus x_2 plot for 5CB-Et$_4$C system at low Et$_4$C mole fractions.

Although the T_N^* versus x_2 and T_I^* versus x_2 plots shown in figure 6 were virtually linear (linear least squares fits gave correlation coefficients of 0.9983 and

0.9988, respectively) second and third order polynomial least squares fits were made. The correlation coefficients for the polynomial fits were only very slightly better than those for the linear fits, thus although the coexistence lines in these phase diagrams may be curved as has been theoretically predicted[13], such curvature could not yet be experimentally verified with any degree of certainty and comments regarding curvature of the coexistence lines remain conjectural in nature. The curves shown in figure 6 are from second order least squares fits.

From the linear T_N^* versus x_2 and T_I^* versus x_2 fits β_N and β_I the moduli of the respective slopes were obtained. The results along with those obtained from previous studies are given in Table I.

TABLE I β_N and β_I for the 5CB-Et$_4$C system.

Mole Fraction Range in this study	β_N		β_I	
	this study	other study	this study	other study
0.020-0.073	0.945	0.728[a] 0.754[b]	0.756	0.627[a] 0.563[b]

[a] Reference 4 and [b] Reference 9

In spite of the variations between the various methods we have a high degree of confidence in the results of this ESR study. Taking into account the care with which the experiments were carried out and the accuracy with which our samples' temperatures were controlled, we suspect that the apparent agreement between the previous studies[4,9] does not necessarily reflect their greater accuracy. We attribute our higher β values for 3,3-

diethylpentane to the greater ability of the ESR technique to probe the transition.

CONCLUSIONS

This paper provides a technique for carrying out ESR studies where the sample temperature may be controlled to better than ± 0.02 °C. Also described is a novel approach for pinpointing the temperatures at which the nematic-to-isotropic transitions start and end in 'pure' liquid crystals and liquid crystals doped with impurities. This allows us to obtain phase diagrams for these systems and β_N and β_I, the moduli of the slopes of the coexistence lines (assumed linear) on the nematic and isotropic sides, respectively, of the two-phase region. These values are of considerable practical importance, since small amounts of similar solutes are often added to nematogenic mixtures used in liquid-crystal displays to adjust viscosity-electrical conductivity characteristics. Additionally knowledge of β_N and β_I values is needed to test various theories.[4,13] Such considerations are postponed for a future publication.

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