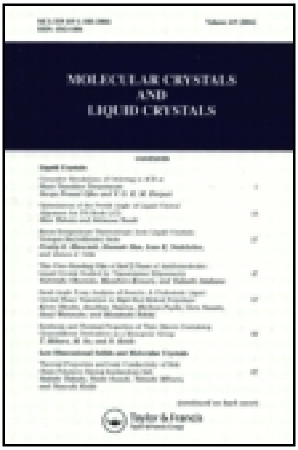

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The Effect of Quasispherical Solutes on the Nematic to Isotropic Transition in 7CB

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Density as a function of temperature was measured in the nematic and isotropic phases of p-*n*-heptyl-p′-cyanobiphenyl (7CB). Similar measurements were made on dilute solutions of the quasispherical solutes Et_4C(tetraethylmethane) and R_4Sn ($R = C_2H_5$, n-C_3H_7 and n-C_4H_9) in 7CB. Addition of these solutes to 7CB led, as expected, to a depression in its nematic-isotropic (*NI*) transition temperature and to the formation of a two-phase region. From these density measurements, β_N and β_I, the moduli of the slopes of the nematic and isotropic boundary lines in the reduced *NI* transition temperature (T^*) *vs* solute mole fraction (x_2) diagrams, were obtained. These thermodynamic results are contrasted with values for the same solutes in p-*n*-pentyl-p′-cyanobiphenyl (5CB). Indications that a curvature may exist at very low solute mole fractions in the T^* *vs* x_2 diagram are discussed.

INTRODUCTION

With few exceptions,[1,2] non-rodlike solute impurities depress the nematic-to-isotropic transition temperature in liquid crystals.[3,4] In addition, as expected from the first order nature of the phase transition, the presence of such impurities leads to the appearance of a two-phase region. The phase diagram shown in Figure 1 is typically obtained for a nonmesomorphic solute/nematogenic solvent mixture at moderately low solute mole fractions ($0.01 < x_2 < 0.06$) where $T^* = T/T_{NI}$, T^* being the reduced temperature and T_{NI} the nematic-to-isotropic transition temperature of the "pure" liquid crystalline solvent. The slopes of the nematic and isotropic boundary lines

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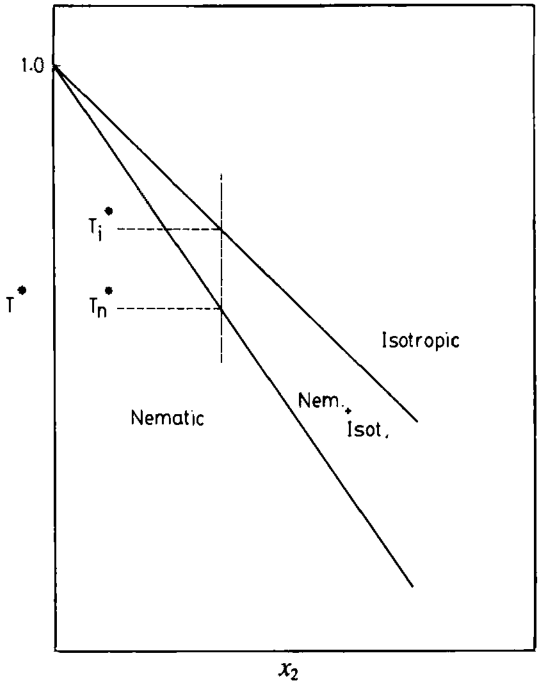


FIGURE 1 Reduced temperature (T^*)-solute mole fraction (x_2) diagram typically obtained from studies on mixtures with moderately low solute mole fractions ($0.01 \approx x_2 < 0.06$).

(of moduli β_N and β_I respectively) reflect the solute's ability to destabilize the nematic phase.

In the past β_N and β_I values were obtained from measurements using a microbalance apparatus[5] and, more commonly, from visual[3,4,6] methods. Moduli of *limiting* slopes ($x_2 \rightarrow 0$) of the nematic and isotropic boundary lines, β_N^∞ and β_I^∞ respectively, have also been obtained using an approach that involves a combination of gas-liquid chromatography (*GLC*) and differential scanning calorimetry (*DSC*). Unfortunately the high uncertainties (up 20%) in this method limit its use to that of rapid scanning of a variety of solutes in nematic solvents.

In this study β_N and β_I are obtained from the variation of density as a function of temperature (in the nematic, isotropic and two-phase regions) for a "pure" liquid crystal (Figure 2) and a mixture of it and a non-mesomorphic solute impurity (Figures 3a–3d). The nematic-to-isotropic transition temperature, T_{NI}, is that at which a sharp change in the density of the "pure" liquid crystal occurs (see Figure 2). T_N and T_I are the tem-

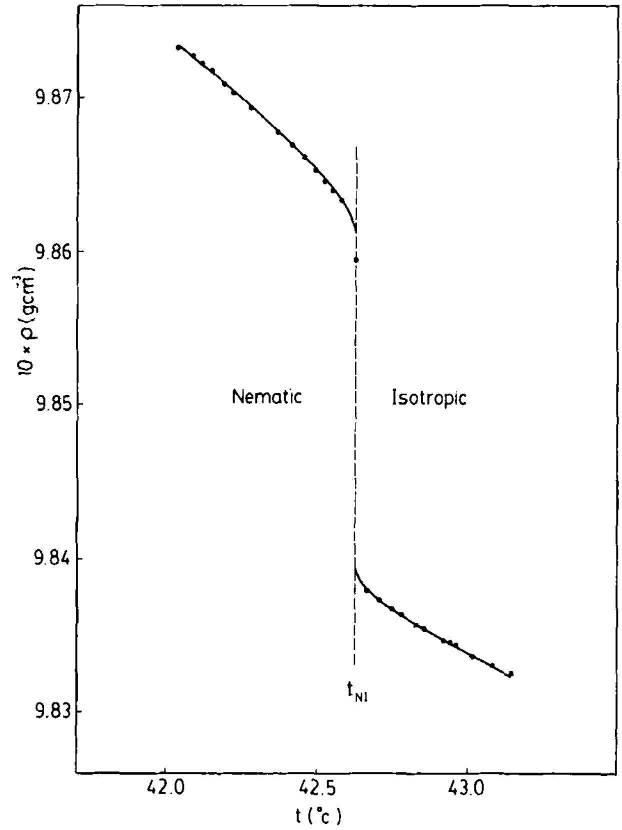
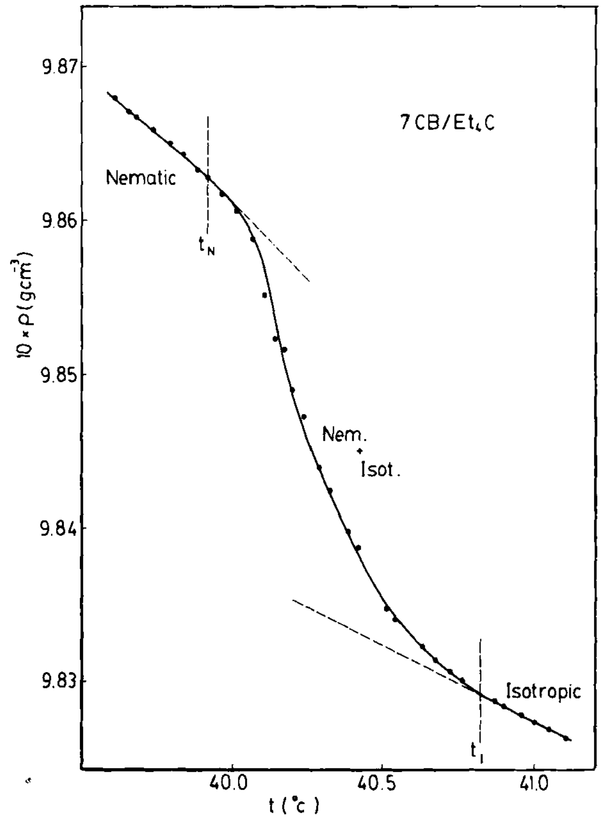


FIGURE 2 Density (ρ) in g cm^{-3} as a function of temperature for 7CB.

peratures at which the two-phase region begins (isotropic phase appears) and ends (nematic phase disappears) respectively (Figures 3a–3d). Different variations of density with temperature exist in the nematic region just before T_N is reached and the part of the two-phase region immediately after T_N. T_N is determined from the intersection of best fits for the data in the two regions. T_I is similarly determined using best fits to the data in the part of the two-phase region just preceding T_I and in the isotropic region. β_N and β_I are obtained using the relationships[4]

$$\beta_N = -\left(\frac{\Delta T^*}{\Delta x_2}\right)_N = (1 - T_N/T_{NI})/x_2 \quad \ldots \quad \ldots \qquad (1)$$

$$\beta_I = -\left(\frac{\Delta T^*}{\Delta x_2}\right)_T = (1 - T_I/T_{NI})/x_2 \quad \ldots \quad \ldots \qquad (2)$$



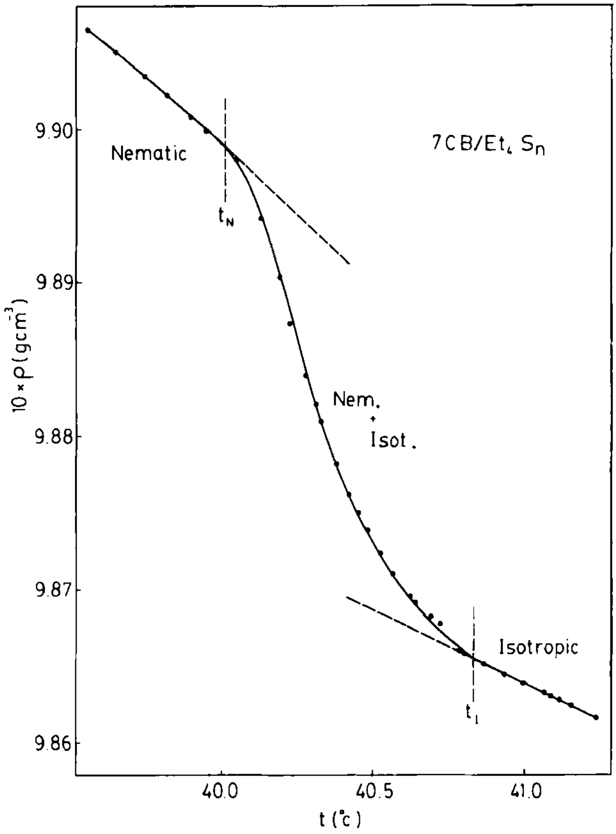
(*a*)

FIGURES 3a–3d Density (ρ) in *g* cm^{-3} as a function of temperature for dilute mixtures of quasispherical solutes in 7CB.

The liquid crystalline solvent studied is p-*n*-heptyl-p′-cyanobiphenyl (7CB). The solute probes used are Et_4C (tetraethylmethane) and R_4Sn (R = C_2H_5, n-C_3H_7 and n-C_4H_9). Solute size is the only variable for such quasispherical solute molecules with alkyl surfaces. The results of this work are contrasted with an earlier visual study[4] for the same solutes in p-*n*-pentyl-p′-cyanobiphenyl (5CB).

EXPERIMENTAL SECTION

Chemicals The tetraalkyl (quasispherical) solutes are the same as those used in an earlier study[4] with 5CB as solvent. For easy reference the solutes



(*b*)

FIGURE 3 *Continued*

TABLE I

The solutes and their properties

Solute[a]	Source	$\rho_{25^\circ C}$[b]	V_2^*[c]	D_2^3[d]
Et_4C	Chemical Samples	0.752	98.9	2.36
Et_4Sn	*K* and *K*[e]	1.189	121.0	2.89
Pr_4Sn	*K* and *K*[e]	1.107	162.0	3.87
Bu_4Sn	Aldrich	1.057	202.9	4.85

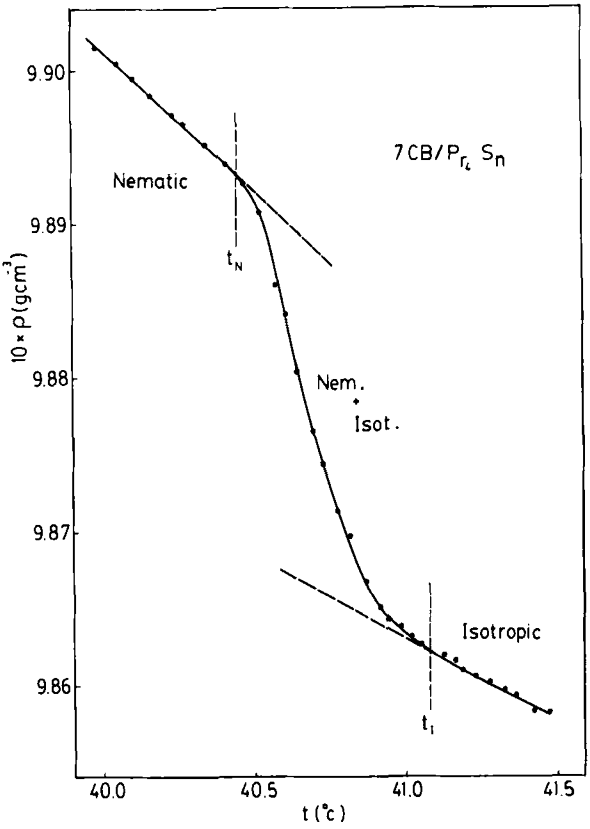
[a] *Et* = ethyl, *Pr* = *n*-propyl, *Bu* = *n*-butyl.

[b] Pure solute density in *g* cm^{-3}.

[c] Hard-core volume in cm^3 mol^{-1}, estimated from the group contribution method of Bondi.[9]

[d] D_2 is a reduced diameter, i.e., it is relative to the diameter of the short axis of the solvent molecule, which is taken to be spherocylindrical in shape.[3]

[e] *K* and *K* Rare and Fine Chemicals is the Life Science Division of ICN Pharmaceuticals, Inc.

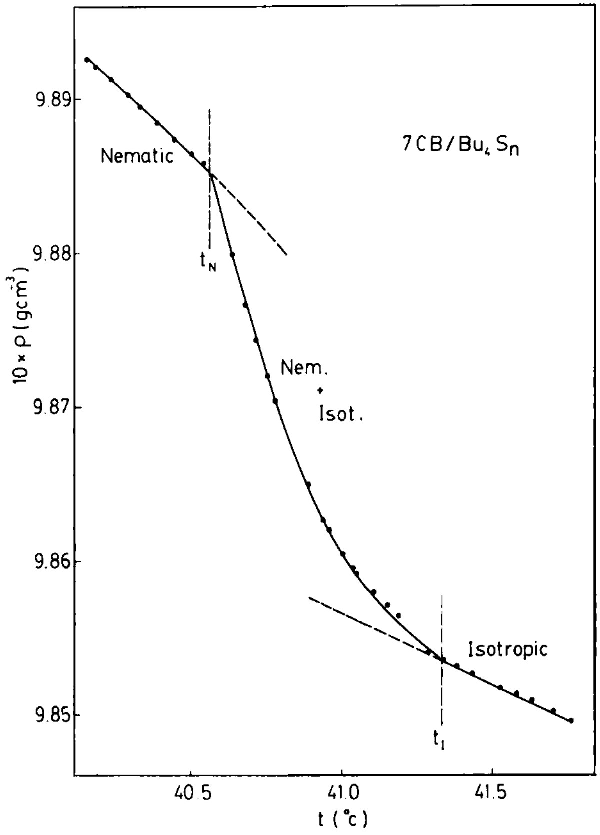


(*c*)

FIGURE 3 *Continued*

and their properties are listed in Table I. All solutes had a purity of at least 98% and were used without further purification. 7CB was obtained in sealed containers from BDH Chemicals. From the sharpness of its nematic to isotropic transition the 7CB sample was assessed to be highly pure and was used as supplied. The properties of 7CB, along with those of 5CB are given in Table II.

Apparatus and procedure The density measurements were made using an Anton Paar digital precision density system (a DMA 602 measuring cell and a DMA 60 density meter). The instrument was calibrated at intervals of 0.05°C or less over the full range of temperatures studied using air and deionized distilled water. Temperature control was achieved using a Heto



(*d*)

FIGURE 3 *Continued*

TABLE II

Properties of liquid crystalline solvents

Solvent	t_{NI}(°C)	V_1^{*a}	m_1^{b}
5CB	35.5	155.9	2.8
7CB	42.6	176.4	2.95

[a] Hard-core volume (from Ref. 9) in cm^3 mol^{-1}.
[b] Molecular length-to-breadth ratio estimated from molecular models.

(type CB7 equipped with a PT-regulator) thermostated circulation system. The temperature within the density cell was measured using an Anton Paar (DT 100-40) digital precision thermometer. The position of the sensor of the digital thermometer within the density cell affects the density measurement and was, therefore, unchanged throughout the study. Measurements were made only after enough time was allowed (usually 25 min) to attain a constant reading on the density meter and a temperature that is constant to within ±0.01°C. Under these conditions, the accuracy of our density measurements was better than 1.0×10^{-5} gm cm^{-3}.

The solutions studied were prepared by adding 10 μL of the solute in question to the isotropic phase of about 1 gm of accurately weighed 7CB and shaking to ensure thorough mixing. The mole fractions of the solutes are given in Table IV. The liquid sample (7CB or 7CB/tetraalkyl mixture) is introduced into the U-shaped glass tube (of capacity 0.7 cm^3) of the density measuring cell. By slowly heating the sample and visually observing the measuring cell good estimates of T_{NI} (in the case of "pure" 7CB) and T_N and T_I (in the cases of the 7CB/tetraalkyl mixtures) are made. Unfortunately density measurements[8] (and in turn more precise values of T_{NI}, T_N and T_I) can only be made with the shutter of the sample compartment of the density cell closed. Once the temperature range of interest is determined densities at small temperature intervals (averaging 0.05°C) were measured.

RESULTS

Our results for the density of "pure 7CB as a function of temperature are presented in Figure 2. The nematic-to-isotropic transition is relatively sharp occurring over a two-phase region of about 0.06°C. This fact is illustrated (though exaggerated for the sake of clarity) by points J and K in Figure 8 which have T^* ($T = T/T_{NI}$) values smaller and larger than 1.0 respectively. t_{NI} (42.63°C) is the temperature within this two-phase region at which the *bulk* of this "pure" 7CB sample changes to the isotropic phase. The temperature at which the isotropic (lower density) phase first appears is slightly ($\simeq$0.03°C) below t_{NI}. This initial formation of the isotropic phase is believed to contribute to the slight dip preceding t_{NI} in the ρ *vs* t plot (Figure 2).

To obtain the volume change at the nematic-to-isotropic transition the reciprocal of the density in each phase was fitted to a quadratic function of $|T - T_{NI}|^{1/2}$ where T is the temperature and T_{NI} is the transition temperature. This procedure is suggested by Klement and Cohen.[10] The extrapolations necessary to obtain the transitional volume change are 0.06 and 0.04°C on the nematic and isotropic sides of the transition respectively. The estimated accuracy of the extrapolated volume change is ± 0.00004 cm^3 g^{-1}. As Table III shows our results for 7CB are in good agreement with those of Dunmur and Miller.[11]

The results for density as a function of temperature for a mixture of each of the quasispherical solute impurities (Et_4C, Et_4Sn, Pr_4Sn and Bu_4Sn) in 7CB are represented in Figures 3a–3d. As expected, the addition of a solute impurity to 7CB broadened its nematic-to-isotropic transition region and depressed the temperature of the transition. From best fits of the data in the neighborhood of the onset and completion of the transition t_N and t_I were obtained. Using Eqs. 1 and 2, β_N and β_I were calculated. The results for the four mixtures are given in Table IV.

Plots of β_N *vs* D_2^3 and β_I *vs* D_2^3, for 7CB and 5CB,[4] are given in Figures 4 and 5 respectively. D_2 is the diameter of the solute molecule relative to the short axis of the (spherocylindrical) solvent molecule.[3] The functional form $\beta = aD_2^b$, which has the proper limit for the β's ($\beta \rightarrow 0$) as $D_2 \rightarrow 0$, was used although the data is also reasonably well correlated through a simple linear fit (see Table V).

DISCUSSION

Results of earlier studies[3,4,6] on the effect of the nonmesomorphic solute impurities on the nematic-to-isotropic transition temperature in liquid crystals are corroborated by the results of this novel density measurement approach. For each of the 7CB/tetraalkyl mixtures (Figures 3a–3d) a two-phase region is observed over a temperature range that falls below T_{NI}, the relatively sharp nematic-to-isotropic transition temperature of "pure"

TABLE III

Transitional temperature, densities, and volume change for 7CB

	t_{NI}(°C)	densities (g cm^{-3}) nematic	 isotropic	$\Delta V/V_{nem}$
This work	42.63	0.98609	0.98404	0.00220
Dummer and Miller[11]	42.7	0.98621	0.98406	0.0022

TABLE IV

Results from analysis of ρ vs. t measurements with 7CB as solvent

Solute	Mole fraction of solute	β_N	β_I
Et_4C	0.0151	0.568 ± 0.004	0.383 ± 0.004
Et_4Sn	0.0129	0.645 ± 0.004	0.442 ± 0.004
Pr_4Sn	0.0102	0.677 ± 0.005	0.481 ± 0.004
$BuSn$	0.00770	0.854 ± 0.006	0.535 ± 0.004

TABLE V

Correlation coefficients of linear least square fits for the variation of β's with solute size

Type of fit	Correlation coefficient 5CB[a]	 7CB
β_N *vs* D_2^3	0.995	0.959
$\ln \beta_N$ *vs* $\ln D_2$	0.998	0.953
β_l *vs* D_2^3	0.995	0.982
$\ln \beta_l$ *vs* $\ln D_2$	0.997	0.986

[a] Obtained from results in Ref. 4.

7CB. The trends of increasing β_N and β_l with solute size (Figures 4 and 5) have also been observed. For each of the solutes studied, in qualitative agreement with the results of all model calculations,[12–16] larger values are obtained in the 5CB solvent with the smaller molecular length-to-breadth radio m_1, (Figures 4 and 5). Figures 6 and 7 (from Ref. 4 with the 7CB results added) indicate the qualitative agreement between the experi-

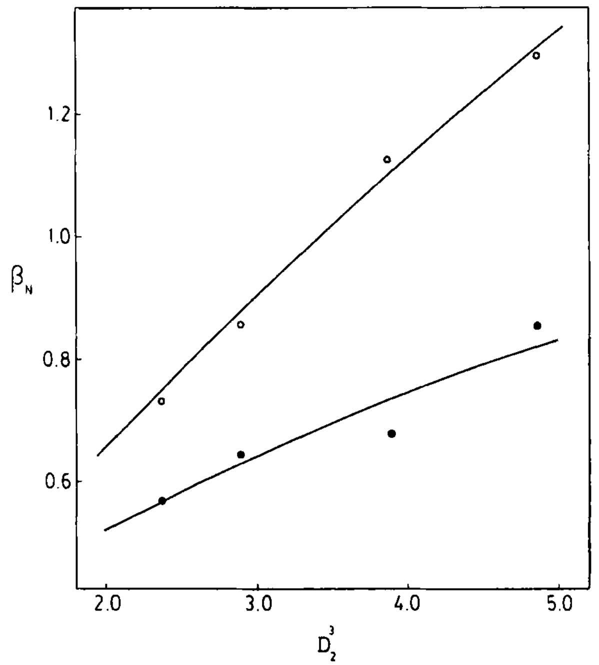


FIGURE 4 β_N *vs* solute size D_2^3 for tetraalkyl solutes in 7CB (●) and 5CB[4] (○). Fitted curves from linear least-square analysis of $\ln \beta_N$ as a function of $\ln D_2$. In 7CB: $\beta_N = 0.365D_2^{1.53}$. In 5CB $\beta_N = 0.382D_2^{2.34}$

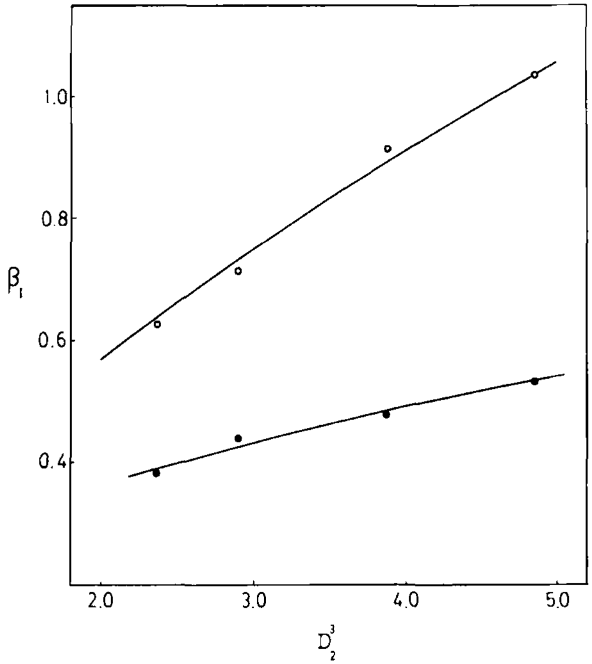


FIGURE 5 β_l *vs* solute size D_2^3 for the tetraalkyl solutes in 7CB (●) and 5CB[4] (○). Fitted curves from linear least-square analysis of $\ln \beta_l$ as a function of $\ln D_2$. In 7CB: $\beta_l = 0.268D_2^{1.32}$. In 5CB $\beta_l = 0.359D_2^{2.02}$.

mentally observed trends and the trends predicted by various statistical mechanical theories[12–16] based on rigid-rod solvent molecules. A description of these theories is given elsewhere.[4] In addition, Figures 4 and 5 indicate that the rates of increase of β_N and β_I with solute size is greater in 5CB, the solvent molecule with the smaller m_l, value. Clearly, as theory[16] predicts, "longer solvent rods can accommodate a higher concentration of solute spheres before the nematic order is destroyed".

Next we examine the reasonableness of the 7CB results from our density study in the light of the results for 5CB from the visual[4] study. Firstly, we note that 5CB (m_l = 2.8) and 7CB (m_l = 2.95) have very close length-to-breadth ratios (m_l) assuming they are rigid spherocylinders of equal diameters. Secondly, the increased flexibility of the *n*-heptyl tail in 7CB (over the *n*-pentyl tail in 5CB) tends to make the effective m_l value of 7CB even closer in value to that of 5CB. Thirdly, the 5CB and 7CB homologs which were obtained from the same source (BDH Chemicals) had equally sharp nematic-to-isotropic transitions and thus may be assumed to contain approximately equal amounts of similar impurities intrinsic to the method of

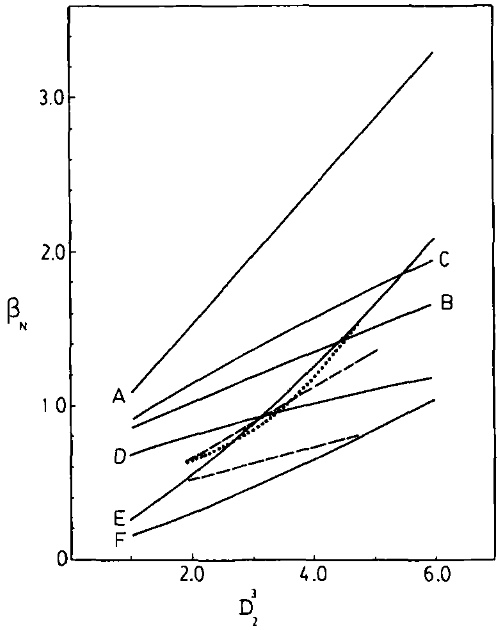


FIGURE 6 β_N *vs* solute size D_2^3. Lattice model[3,4,12]: $A(m_1 = 5)$ and $B(m_1 = 10)$; virial expansion[3,4,13]: $C(m_1 = 5)$ and $D(m_1 = 10)$; molecular-field theory[3,4,14,15]: $E(m_1 = 3)$ and $F(m_1 = 5)$. Dotted line: van der Waals theory[16] with $m_1 \approx 3$. Solvent molecules treated as rigid rods. Dashed lines: smoothed experimental results for tetraalkyl solutes in 5CB[4] (upper line) and 7CB (lower line).

their synthesis.[17] On the basis of the above β values from the visual study[4] on 5CB and this density study on 7CB are expected to be closer in value than is observed (see Figures 4 and 5). This somewhat large difference in the β values is well outside the combined errors of these equally accurate methods.

Next we examine the density and visual methods more closely. The results of this density study are, for each solute, obtained from measurements on a *single* 7CB/tetraalkyl mixture at a lower x_2 value than the *least* concentrated mixture of the same solute in the visual study. On the other hand the results of the visual study are obtained from linear least square fits of T^* *vs* x_2 for each of the coexistence lines. Hereafter, values from the density and visual studies will be referred to as β_D and β_V respectively. That the T^* *vs* x_2 plots were virtually linear[4] (with correlation coefficients in excess of 0.999) reflects nearly constant β_V values within the range of x_2 values studied.

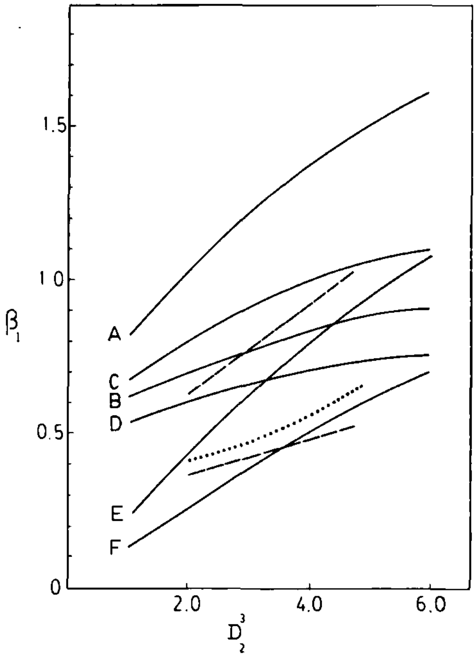


FIGURE 7 β_I vs solute size D_2^3. Codes for curves A–F, dotted line and dashed lines are given in legend to Figure 6.

Any curvature that may be present in the T^* vs x_2 diagrams is thus not clearly revealed by the visual studies. On the other hand, model calculations[12,16,18] on systems of quasispherical solutes in nematogenic solvents predict the type of curvature shown in Figure 8 (and referred to as "type-1" curvature in Ref. 18). Such curvature can make the $\beta_{N,D}$ and $\beta_{I,D}$ values (slopes of lines AM[19] and AN[19] respectively) respectively smaller than $\beta_{N,V}$ and $\beta_{I,V}$ (slopes of the lines BE and CF respectively) for even the same solute-nematogenic solvent system. If "type-1"[18] curvature exists $\beta_{N,D}$ and $\beta_{I,D}$ will depend on x_D (see Figure 8), the solute mole fraction used in the density study and reach their minimum values $\beta^{\infty}_{N,D}$ and $\beta^{\infty}_{I,D}$ respectively as $x_D \rightarrow 0$. The poor correlations of the plots of our results ($\beta_{N,D}$ or $\beta_{I,D}$ vs D_2 and ln $\beta_{N,D}$ or ln $\beta_{\mathrm{I,D}}$ vs ln D_2) relative to the correlations of the visual study results ($\beta_{N,V}$ or $\beta_{I,V}$ vs D_2^3 and ln $\beta_{N,V}$ or ln $\beta_{I,V}$ vs ln D_2) reflect this dependence suggesting the possible existence of "type-1"[18] curvature in the T^* vs x_2 diagrams for systems of quasispherical solutes in 7CB. The correlations of the various plots are given in Table V. Considering the 7CB results alone, the poorer correlations of the $\beta_{N,D}$ vs D_2^3 plots relative to the

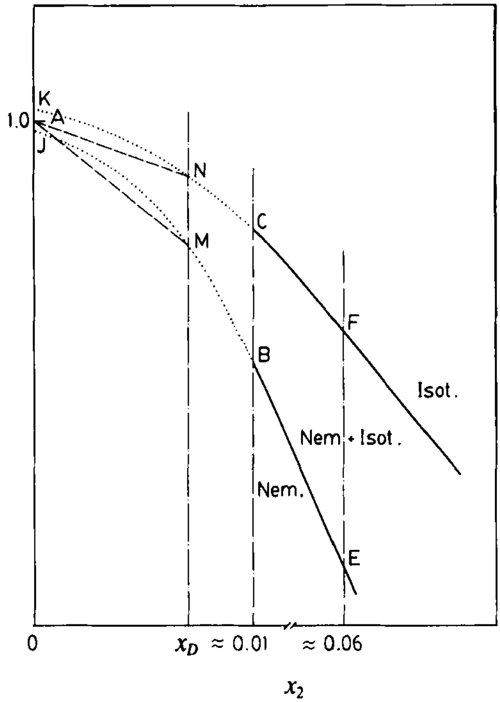


FIGURE 8 A T^* vs x_2 diagram exhibiting "type-1"[18] curvature and exaggerated at low mole fractions for the sake of clarity.

$\beta_{I,D}$ vs D_2^3 plots point to the possibility of greater curvature in the coexistence line on the nematic side of the two-phase region.

Density studies are being carried out on 5CB and 5CB/3,3-diethylpentane mixtures. The results of these studies will be contrasted with visual studies[4] on the same system.

Acknowledgment

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References

1. J. W. Park, C. S. Bak and M. Labes, *J. Amer. Chem. Soc.*, **97**, 4398 (1975).
2. G. Sigaud, M. F. Achard, F. Hardouin and H. Gasparoux, *Chem. Phys. Lett.*, **48**, 122 (1977).
3. D. E. Martire, G. A. Oweimreen, G. I. Ågren, S. G. Ryan and H. T. Peterson, *J. Chem. Phys.*, **64**, 1456 (1976).

4. G. A. Oweimreen and D. E. Martire, *J. Chem. Phys.*, **72**, 2500 (1980).
5. H. T. Peterson and D. E. Martire, *Mol. Cryst. Liq. Cryst.*, **25**, 89 (1974).
6. B. K. Kronberg, D. F. R. Gilson and D. Patterson, *J. Chem. Soc., Faraday II*, **72**, 1673 (1976).
7. G. A. Oweimreen, G. C. Lin and D. E. Martire, *J. Phys. Chem.*, **83**, 211 (1979).
8. What is actually measured is the period of vibration (electromagnetically induced) of the U-shaped glass tube containing the sample. The density of the sample is obtained by comparing the square of this period to the squares of the periods for air and distilled deionized water (of accurately known densities) at the same temperature.
9. A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964).
10. W. Klement and L. H. Cohen, *Mol. Cryst. Liq. Cryst.*, **27**, 359 (1974).
11. D. A. Dunmur and W. H. Miller, *J. de Physique*, Colloque C3 40, C3-141 (1979).
12. G. I. Ågren and D. E. Martire, *J. Phys. (Paris)*, **36**, CI-141 (1975).
13. G. I. Ågren, *Phys. Rev.*, **A11**, 1040 (1975).
14. R. L. Humphries and G. R. Luckhurst, *Proc. R. Soc. London Ser.*, **A352**, 41 (1976).
15. D. E. Martire, in *The Molecular Physics of Liquid Crystals* edited by G. R. Luckhurst and G. W. Gray (Academic, London, 1979), Chap. 11.
16. M. A. Cotter and D. C. Wacker, *Phys. Rev.*, **A18**, 2676 (1978).
17. G. W. Gray, K. J. Harrison, J. A. Nash, J. Constant, D. S. Hulme, J. Kirton and E. P. Raynes, *Liq. Cryst. Org. Fluids*, **2**, 617 (1974).
18. F. Dowell, *J. Chem. Phys.*, **69**, 4012 (1978).
19. Because of intrinsic impurities that defy purification methods a small two-phase region exists at even $x_2 = 0$. Strictly speaking $\beta_{N,D}$ and $\beta_{I,D}$ are equal to the slopes of the lines *JM* and *KN* (in Figure 8) respectively.