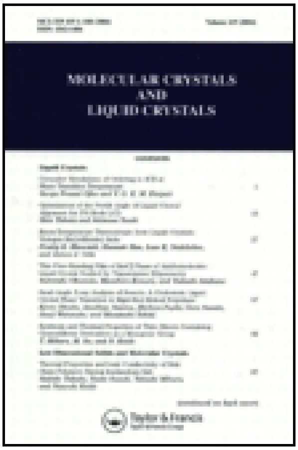

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

The Phase Transition Behavior of Mixtures of Nematic Liquid Crystal with Non-Mesogenic Solute Molecules

Zhang Shu-lin [a] , Zhou He-tian [a] , Song Zeng-fu [a] , Rong Zu-xiu [a] , Hua Dao-hong [a] & Wang Shu-kun [a]
[a] Department of Physics, Peking University, Beijing, China

Version of record first published: 14 Oct 2011.

To cite this article: Zhang Shu-lin , Zhou He-tian , Song Zeng-fu , Rong Zu-xiu , Hua Dao-hong & Wang Shu-kun (1981): The Phase Transition Behavior of Mixtures of Nematic Liquid Crystal with Non-Mesogenic Solute Molecules, Molecular Crystals and Liquid Crystals, 70:1, 183-194

To link to this article: http://dx.doi.org/10.1080/00268948108073589

Mol. Cryst. Liq. Cryst., 1981, Vol. 70, pp. 183–194
0026-8941/81/7001-0183 $06.50/0

Printed in the United States of America

The Phase Transition Behavior of Mixtures of Nematic Liquid Crystal with Non-Mesogenic Solute Molecules†

ZHANG SHU-LIN, ZHOU HE-TIAN, SONG ZENG-FU, RONG ZU-XIU, HUA DAO-HONG, and WANG SHU-KUN

Department of Physics, Peking University, Beijing, China

(*Received July 31, 1980; in final form October 22, 1980*)

The magnetic birefringence and the refractive indices have been measured for the following binary solution systems: (1) Tetrabutyl-tin/MBBA. (2) Cyclohexene/MBBA. (3) Azobenzene/MBBA. The reciprocal of Cotton-Mouton coefficients η and the order parameters S as a function of the temperature T for these systems have been calculated from this experimental data. The supercooling temperature T^* and the order parameters at a given temperature decrease with increase of the mole fraction X_B of solute. The slope of the η vs. T does not change for different concentrations and different kinds of solutes within our experimental accuracy.

INTRODUCTION

The phase transition behavior of a solution of a non-mesogenic solute in a liquid crystal solvent is both theoretically and technically an interesting problem. The phase diagram and the phase separation phenomena of such a binary solution system have been studied from a phase transition thermodynamical point of view by several workers.[1] There are also some works on the effect of non-mesogenic solutes on the ordering of liquid crystals.[2] Some workers[3] have noticed the effects of impurities on pretransition behavior. However the effects of the geometrical shape and concentration of the non-mesogenic solute on the pretransition behavior and nematic ordering have not been studied in great detail. In this work we have studied the following three systems: (1) Tetrabutyl-tin [$Sn(CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_3)_4$, spherical shape]/MBBA; (2) Cyclohexene[$CH_2(CH_2)_3CH{:}CH$, spheroidal shape]/MBBA; (3) Azobenzene [$C_6H_5N{:}N \cdot C_6H_5$, nearly linear shape]/MBBA. We have measured their

---

†Presented at the Eighth International Liquid Crystal Conference, Kyoto, July 1980.

magnetic birefringence in the isotropic phase and their refractive indices in the nematic phase. The experimental results are then discussed by use of a generalized thermodynamical theory for binary solutions.

EXPERIMENTAL

1 Sample preparation

The MBBA used in our experiment were provided and purified by Beijing Chemical Reagent Institute (B.C.R.I). Its clearing point is 45.6° C. The solute compounds are commercially available, Tetrabutyl-tin were purified by B.C.R.I before doping.

MBBA were degassed in vacuum (10^{-3} mmHg) at a temperature above clearing point before doping. Tetrabutyl-tin and Cyclohexene were injected into MBBA with a microsyringe and the weights injected were determined by their room-temperature density. Azobenezene was added directly to MBBA after weighing. The samples were fully mixed by a supersonic-stirrer.

The phase transition temperature of the samples were visually observed in a thermostat. We also measured their densities under various temperatures by the specific weight method.

2 The measurement of magnetic birefringence

The magnetic birefringence was measured by the rotating-analyzer technique.[4] The magnetic field was provided by a conventional electromagnet. In the experiment the applied magnetic field was about 9000 G. Its stability was better than 10^{-2}. The optical modulating frequency was 33.33 Hz. The photoelectrical detector was a photodiode (2DU1). The lock-in amplifier used in our experiment was produced by Lushan Electronic Instrument Factory in China and its resolvability of phase shift is 0.1°. The sample cell was made from a glass tube 8 mm long with an inner diameter of 6 mm, and both of its ends were closed with glass windows stuck on by the hot pressing method with polyester film as an adhesive.

3 The measurement of refractive indices

The refractive indices in nematic phase were measured by the wedged sample method. The light source was a He-Ne laser. The wedged cell was made from two flat glasses separated at one end by a molybdenum wire of 0.6 mm diameter. The alignment of the liquid crystal molecules was obtained by evaporating SiO film onto the slides. The distance from the sample to the reflected light spot on the wall was 13.5 meters.

4 Temperature control

The temperature of the sample was electronically controlled to better than 0.01° C for a period of 10–20 minutes.

RESULTS

1 The magnetic birefringence and the Cotton-Mouton coefficient

In the isotropic phase, the magnetic birefringence Δn_M is

$$\Delta n_M = \lambda\delta/2\pi d \qquad (1)$$

where δ is the phase difference between the signal light beam and the reference light beam caused by Δn_M, λ is the wave length of the light source, d is the length of the sample cell. The reciprocal of Cotton-Mouton coefficient $H^2/\Delta n_M$ as a function of temperature T is presented in Figures 1–3.

2 The refractive indices and the order parameters in the nematic phase

In the nemactic phase, we measured the heights $h_{e,o}$ of the light spots of the extraordinary ray and the ordinary ray, and calculated the refractive indicies n_e and n_o by the equation

$$n_{e,o} = \sin(h_{e,o}/l)/\sin(2\beta) \qquad (2)$$

where l the distance from samples to reflected light spots on the wall, β the

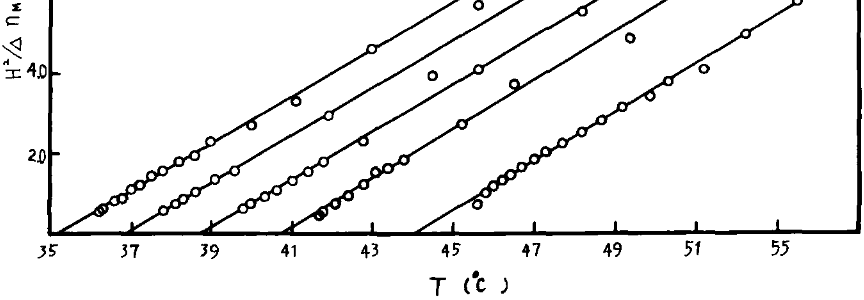

FIGURE 1 The reciprocal of the Cotton-Mouton coefficient ($H^2/\Delta n_M$) is shown as a function of temperature (T) for Tetrabutyl-tin/MBBA system. *a*. Pure MBBA; *b*. X_B 0.0040; *c*. X_B 0.012; *d*. X_B 0.018; *e*. X_B 0.024.

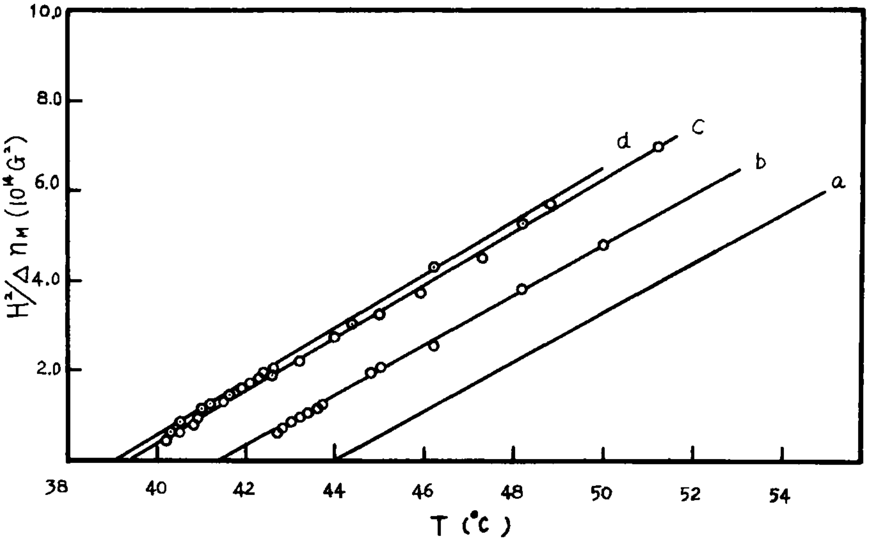

FIGURE 2 The reciprocal of the Cotton-Mouton coefficient ($H^2/\Delta n_M$) is shown as a function of temperature (T) for Cyclohexene/MBBA system. (The pure MBBA is the same with Figure 1). *a*. Pure MBBA; *b*. X_B 0.0043; *c*. X_B 0.012; *d*. X_B 0.014.

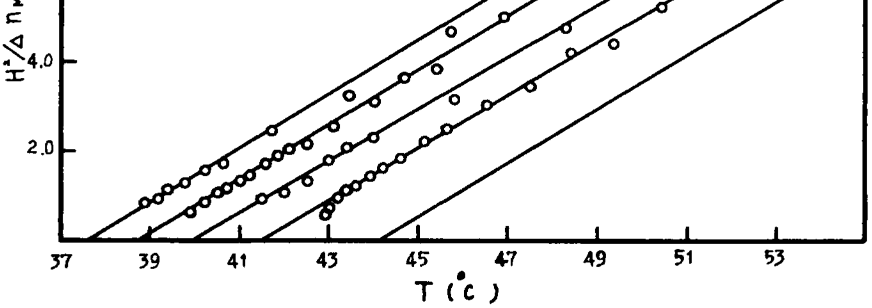

FIGURE 3 The reciprocal of the Cotton-Mouton coefficient ($H^2/\Delta n_M$) is shown as a function of temperature (T) for Azobenzene/MBBA system. (The pure MBBA is the same with Figure 1). *a*. Pure MBBA; *b*. X_B 0.0047; *c*. X_B 0.011; *d*. X_B 0.018; *e*. X_B 0.028.

wedged angle of the sample cell. According to Vuks model[6] if we suppose that the anisotropy of refractive indices results only from the ordering alignment of liquid crystal molecules, and neglect the anisotropy of non-mesogenic molecules, then the order parameter would be equal to

$$S = (1/4\pi)M(N\zeta X_A)^{-1}(\gamma_\parallel - \gamma_\perp)^{-1}(n_e - n_o)/(n_e^2 + 2n_o^2 + 6) \tag{3}$$

where N is Avogadro's number, ζ is the density of the solution, M is the molecular weight, $\gamma_\parallel - \gamma_\perp$ is the anisotropy of principal polarizabilities for liquid crystal molecules, X_A is the mole fraction of the nematic solute. The density ζ is the value measured by our experiment (or its extrapolated value), and $(\gamma_\parallel - \gamma_\perp)$ is obtained by extrapolation from our measuring values of n_e and n_o following Haller's method.[7] The order parameter S as a function of temperature T is shown in Figures 4–6.

DISCUSSION

In our experiments, the solution of the non-mesogenic solutes in the nematic solvents is a binary system, the mole fractions of solvent (MBBA) and solute (the non-mesogenic molecule) are respectively;

$$\begin{aligned} X_A &= N_A/(N_A + N_B) \\ X_B &= N_B/(N_A + N_B) \end{aligned} \tag{4}$$

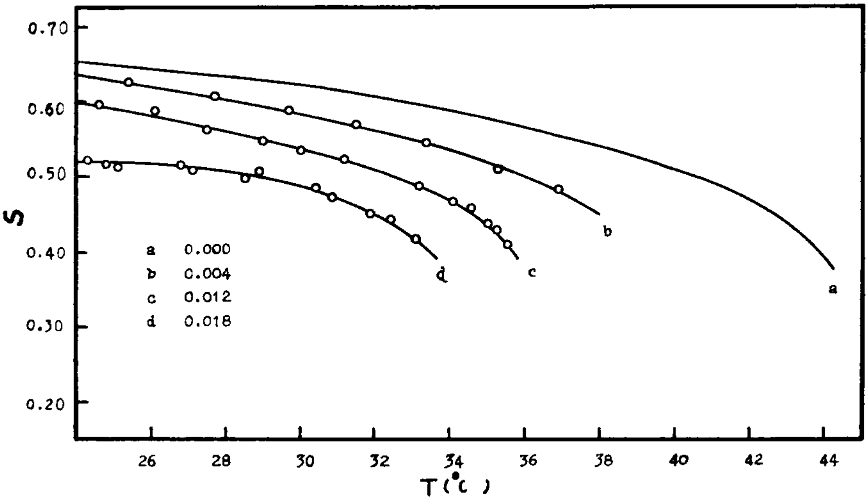

FIGURE 4 Order parameter (S) as a function of temperature (T) for Tetrabutyl-tin/MBBA. (The pure MBBA is the same with Figure 5). *a*. Pure MBBA; *b*. X_B0.0040; *c*. X_B0.012; *d*. X_B0.018.

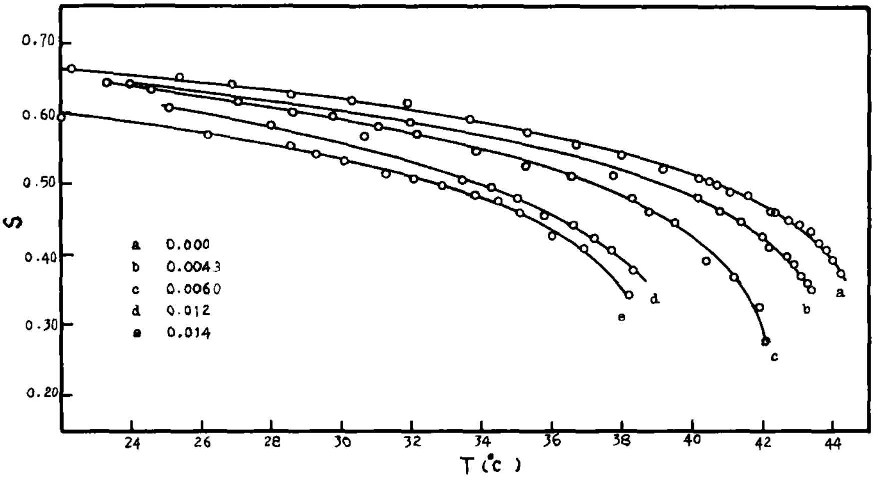

FIGURE 5 Order parameter (S) as a function of temperature (T) for Cyclohexene/MBBA. *a*. Pure MBBA; *b*. X_B 0.0043; *c*. X_B 0.0060; *d*. X_B 0.012; *e*. X_B 0.014.

where N_A and N_B are the mole number of solvents and solutes respectively. In our experiments the value of X_B is from 0 to 0.028. We can neglect the interaction between the molecules of the solute, and assume that the system satisfies the condition of ideal dilute solutions. Then we can generalize the usual theory of the thermodynamics[8] for ideal solutions and extend it to the binary systems,

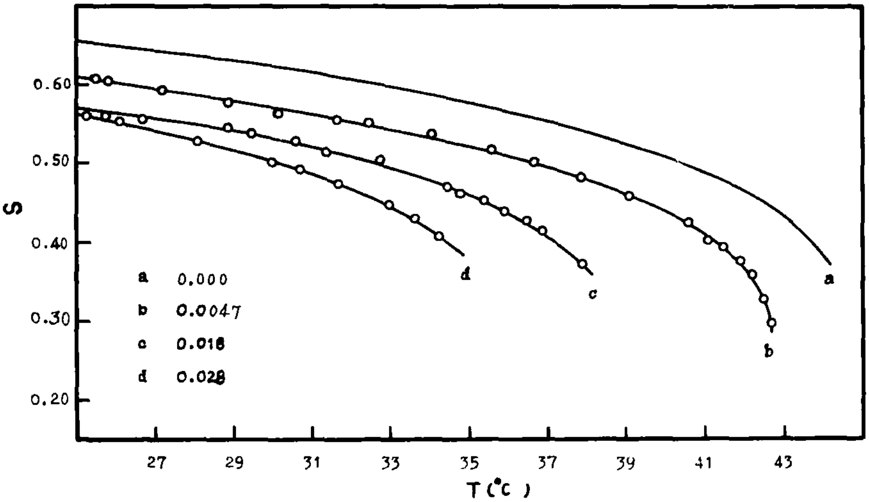

FIGURE 6 Order parameter (S) as a function of temperature (T) for Azobenzene/MBBA. (The pure MBBA is the same with Figure 5). *a*. Pure MBBA; *b*. X_B 0.0047; *c*. X_B 0.018; *d*. X_B 0.028.

and write the Gibbs free energy of this system as:

$$G = X_A\bar{G}_{Ap} + X_B\bar{G}_{Bp} + RT(X_A \ln X_A + X_B \ln X_B) + X_B\delta\bar{G}_B, \tag{5}$$

where G is the mole Gibbs free energy of this solution, $\bar{G}_{Ap}$ and $\bar{G}_{Bp}$ are the mole Gibbs free energy of the pure solvent and pure solute respectively. R is the gas constant. $\delta\bar{G}_B$ is a function of T, P, $\cdots$ and S† only, and independent of X_B. Thus, we can rewrite Eq. (5) as:

$$\begin{aligned} G(T,P,S,X_B) = X_A\bar{G}_{Ap}(T,P,S) + X_B\bar{G}_{Bp} + RT(X_A \ln X_A \\ + X_B \ln X_B) + X_B\delta\bar{G}_B(T,P,S) \end{aligned} \tag{5'}$$

and the value of the order parameter in the equilibrium state of this system is determined by:

$$\partial G/\partial S = 0 \tag{6}$$

Then, we can discuss the properties of the pretransition and the nematic phase for this system by using the theoritical above mentioned formulas and our experimental data.

1 The pretransition behavior

According to the model of de Gennes,[9] in the pretransition region the Gibbs free energy of the pure solvent (pure liquid crystal) can be expanded into a power series of the order parameter S:

$$\bar{G}_{Ap} = \bar{G}_{Ap}^{(0)} + \frac{1}{2}\bar{A}S^2 + \frac{1}{3}\bar{B}S^3 + \frac{1}{4}\bar{C}S^4 + \cdots \tag{7}$$

The coefficient $\bar{A}$ is approximated to:

$$\bar{A} = \alpha(T - T_c^*) \tag{8}$$

where T_c^* is called "supercooling temperature." Generalizing the idea of de Gennes to this system, which is approximated to an ideal dilute solution, we assume further that the function $\delta\bar{G}_B$ can be expanded into a power series of the order parameter S:

$$\delta\bar{G}_B = \delta\bar{G}_B^{(0)} + \frac{1}{2}\bar{A}'S^2 + \frac{1}{3}\bar{B}'S^3 + \frac{1}{4}\bar{C}'S^4 + \cdots \tag{9}$$

Analogous to Eq. (8), $\overline{A'}$ can be expanded as;

$$\overline{A'} = \overline{A'_0} + \alpha'(T - T_c^*) \tag{10}$$

---

† We assumed here that the macroscopical description of the ordering phenomena of this liquid crystal system used only one order parameter $S = \langle P_2(\cos\Theta)\rangle$.

Substituting Eqs. (7)–(10) into Eq. (5′), we have

$$G = (X_A\overline{G}_{Ap}^{(0)} + X_B\overline{G}_{Bp} + X_B\delta\overline{G}_B^{(0)}) + RT(X_A \ln X_A + X_B \ln X_B) + \frac{1}{2}\alpha_X[T - (T_c^* - \Delta T_c^*)]S^2 + \frac{1}{3}(X_A\overline{B} + X_B\overline{B'})S^3 + \frac{1}{4}(X_A\overline{C} + X_B\overline{C'})S^4 + \cdots \quad (11)$$

where

$$\alpha_X = \alpha + (\alpha' - \alpha)X_B \quad (12)$$

$$\Delta T_c^* = \overline{A_0'}X_B/\alpha_X$$

We now use this form to discuss the magnetic birefringence of this solution. If we neglect the contribution from the anisotropic susceptibility of the solute molecules, the Gibbs free energy of this system in an applied magnetic field H can be written as:

$$G_H = G - \frac{1}{3}NX_A\Delta\chi H^2S \quad (13)$$

Where G is the function in Eq. (11), $\Delta\chi$ is the anisotropic part of the susceptibility of the MBBA molecule, N is Avogadro's number. As the ordering induced by the applied magnetic field is very small, the function G can be approximated to the square term of S. From $\partial G_H/\partial S = 0$, we thus obtain the following result:

$$S_H = X_AN\Delta\chi H^2/[3\alpha_X\{T - (T_c^* - \Delta T_c^*)\}] \quad (14)$$

Similar to the consideration in deducing Eq. (3), if the optical anisotropy of this solution is assumed to be due to the optical anisotropy of MBBA molecules alone, the expression of the reciprocal of the Cotton–Mouton coefficient can be written as:

$$\eta_X = \frac{H^2}{\Delta\eta_M} = \eta_0\frac{\alpha_X}{\alpha}\frac{1}{X_A^2}[T - (T_c^* - \Delta T_c^*)] \quad (15)$$

Where η_0 is defined by the following equation:

$$\eta = \eta_0(T - T_c^*) \quad (16)$$

and η is the reciprocal of the Cotton-Mouton coefficient of the pure solvent.

From our experimental results we may conclude that

1) In the error range of our experiment, the straight lines, which represent the dependence of η_X on the temperature T for various solutions with various

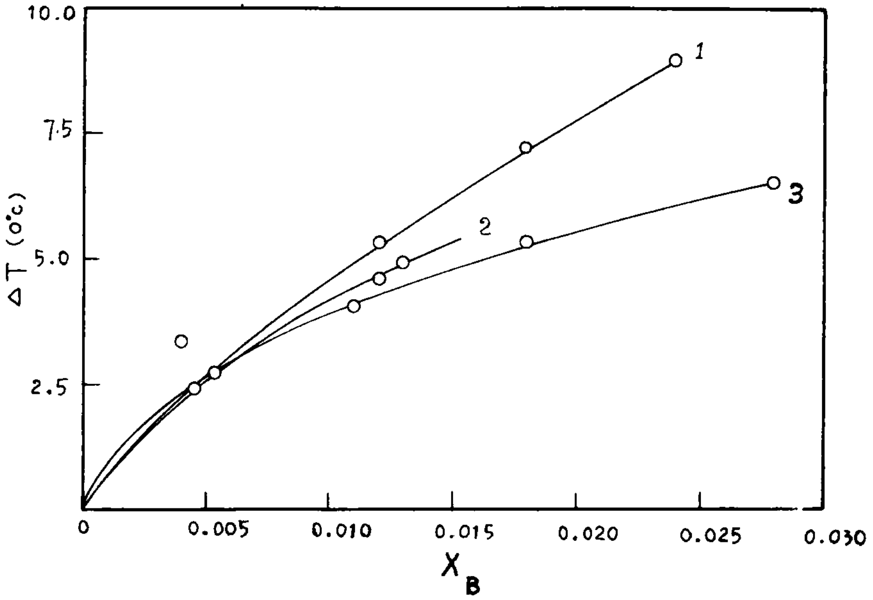

FIGURE 7 ΔT^* vs. mole fraction of solute (X_B) for the samples: 1. Tetrabutyl-tin; 2. Cyclohexene; 3. Azobenzene.

kinds of solute and various mole fraction of solutes, have approximately the same slope as the pure solvent. According to Eqs. (15) and (12), this means that $\alpha_X/(\alpha X_A^2) \approx 1$. Considering $X_B \ll 1$ the above formula implies $\alpha' \approx \alpha$.

2) From Eq. (12), for $X_B \ll 1$, the value $\Delta T_c^*(X_B)$ is proportional to X_B, and the proportionality constant is approximately $\overline{A_0'}/\alpha$. Figure 7 shows the dependence of ΔT_c^* on X_B. The experimental results show that the relation above mentioned is satisfied approximately and for a high mole fraction of the solute the effect of the various solutes on ΔT_c^* is in this order: Tetrabutyl-tin, Cyclohexene, Azobenzene. But for a low mole fraction of solutes, Azobenzene has the greatest effect on ΔT_c^*.

3) For pure MBBA, close to the transition point, the dependence of η on $\dot{T}$ begins to depart from a straight line, and the curve bends down, similar phenomena have been reported in references.[3] This may be an effect induced by critical fluctuations. However, we note that in almost all our doped samples this tendency becomes weaker. We think that this is due to the occurrence of phase separation. When phase separation occurs, the concentration of the solute in the isotropic phase rises, and the corresponding ΔT_c^* is also raised, as shown in Eq. (12). This effect cancels out effect of the 'bending down' induced by critical fluctuation.

2 The nematic phase

According to Eqs. (5) and (6), the order parameter of the pure solvent $S_0(T,p)$ is given by:

$$\frac{\partial \bar{G}_{Ap}}{\partial S} = 0 \tag{17}$$

and the order parameter of the binary system $S(T,p,X_B)$ is given by:

$$X_A \frac{\partial \bar{G}_{Ap}}{\partial S} + X_B \frac{\partial \delta \bar{G}_B}{\partial S} = 0 \tag{18}$$

Introducing

$$\Delta S = S(T,p,X_B) - S_0(T,p) \tag{19}$$

and expanding Eq. (18) in ΔS, then to a first order approximation in X_B, we have:

$$\Delta S(T,p,X_B) = -\frac{\dfrac{\partial \delta \bar{G}_B(T,p,S_0)}{\partial S}}{\dfrac{\partial^2 \bar{G}_{Ap}(T,p,S_0)}{\partial S^2}} X_B \tag{20}$$

Note that the extreme value determined by Eq. (18) must be a minimum, thus, the relation

$$\frac{\partial^2 \bar{G}_{Ap}}{\partial S^2} > 0$$

is satisfied and this holds for any kind of solute. Therefore it is evident that if the change of the free energy $\delta \bar{G}_B$, induced by the interaction between the solvents and solutes, increases as the order parameter S increases, the order parameters S of liquid crystal will decrease when the solution is doped with the solute. In the opposite condition, the value of S will increase when the solution is doped with the solute.

From our experimental data, we obtained the following results:

1) From Figures 4–6, we see that for all kinds of solutes used in our experiment, the change of order parameters $\Delta S < 0$, this means that for these solutes,

$$\frac{\partial \delta \bar{G}_B}{\partial S} > 0$$

2) As shown in Figure 8, which represents the order parameters S at the given temperatures as a function of X_B, the characters of various solutes are

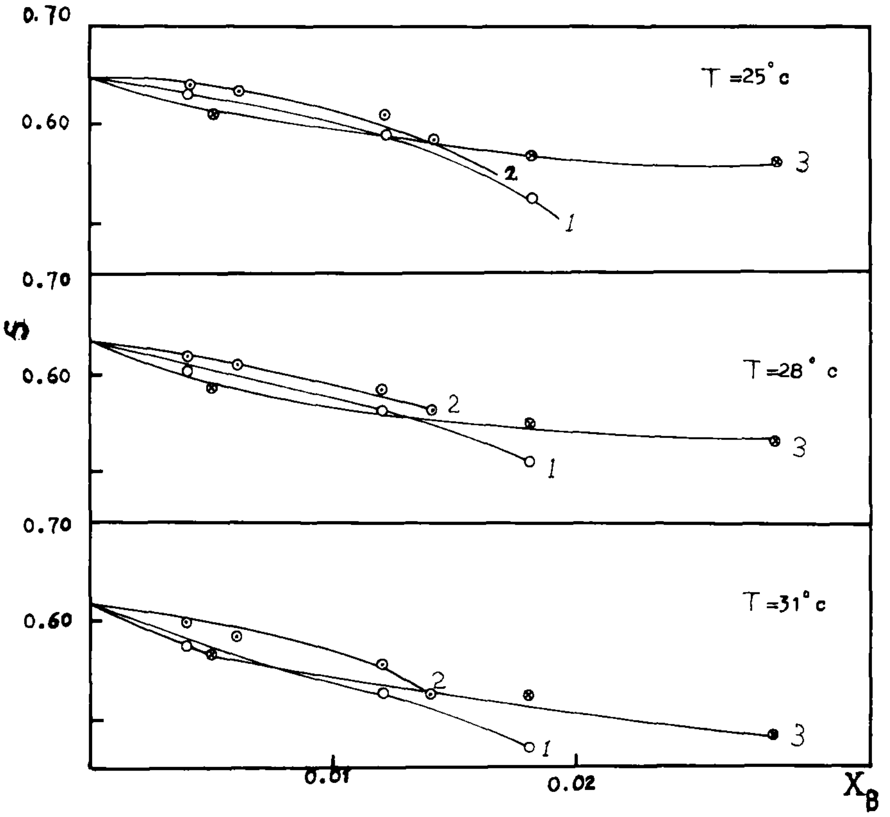

FIGURE 8 Order parameter (S) vs. mole fraction of solute (X_B) at several temperatures for the samples: 1. Tetrabutyl-tin; 2. Cyclohexene; 3. Azobenzene.

analogous to that represented in Figure 7. At low concentration, the effect of various solutes on ΔS is in this order: Azobenzene, Tetrabutyl-tin and Cyclohexene, but for higher concentration, the effect of Azobenzene on ΔS is considerably reduced.

CONCLUSION

The results of this work show that the investigation of the physical properties of liquid crystal solutions having solutes of different shape and concentration can provide information about the ordering property and short-range structure of the liquid crystal alignment. We hope that in the future we can carry out work on more kinds of impurities and study other physical properties of phase transition.

Acknowledgment

We would like to thank B.C.R.I and the liquid crystal group of the Department of Chemical Engineering, Qinghua University (especially Prof. Wang Liang-Yu and Mrs. Liu Pai-qian) for their support in various ways to our work. Thanks are also due to Prof. Liu Chu-Tsin and Prof. Lin Lei for their encouragement throughout this work. We are also greatly indebted to Prof. Gan Zi-Zhao for his continuous help and to Mr. Shi Zhi-guang for assistance in performing the experiments.

References

1. (a) J. S. Dave and J. P. Burger, *J. Chem. Soc.*, 4616 (1954); (b) J. S. Dave and K. L. Vasanth, *Mol. Cryst. Liq. Cryst.*, **2,** 125 (1966); (c) P. E. Cladis, J. Rault and J. P. Burger, *Mol. Cryst. Liq. Cryst.*, **13,** 1 (1971); (d) R. L. Humphries and G. R. Luckhurst, *Chem. Phys. Lett.*, **23,** 4,567 (1973); (e) D. E. Martire, G. A. Oweimreen, G. I. Åaren, S. G. Ryan and H. T. Peterson, *J. Chem. Phys.*, **64,** 1456 (1976); (f) S. Yano, K. Terashima, Y. Watanabe and K. Aoki, *J. Phys. (Paris)*, **40,** C3-322 (1979); (g) R. Konrad and G. M. Schneider, *Mol. Cryst. Liq. Cryst.*, **51,** 57 (1979).
2. (a) D. H. Chen and G. R. Luckhurst, *Trans. Faraday Soc.*, **65,** 156 (1969); (b) Koh Fujimura, Shigeru Mita, Shoichi Kondon and Masataami Tkeda, *Mol. Cryst. Liq. Cryst.*, **54,** 191 (1979).
3. (a) T. W. Stinson and J. D. Litster, *Phys. Rev. Lett.*, **25,** 503 (1970); (b) Ken-ichi Muta, Hideo Takezoe, Atsuo Fukuda and Eiichi Kuze, *Japanese J. Appl. Phys.*, **18,** 11, 2073 (1979); (c) Kuon Inoue and Y. R. Shen, *Mol. Cryst. Liq. Cryst.*, **51,** 179 (1979); (d) P. H. Keyes and J. R. Shane, *Phys. Rev. Lett.*, **42,** 722 (1979).
4. Khoon-Cheng Lim and John T. Ho, *Mol. Cryst. Liq. Cryst.*, **47,** 173 (1978).
5. I. Haller, H. A. Huggins and M. J. Freiser, *Mol. Cryst. Liq. Cryst.*, **16,** 53 (1972).
6. (a) M. F. Vuks, *Opt. Spectrosk.*, **20,** 644 (1966); (b) S. Chandrasekhar and N. V. Madhusudana, *J. Phys. (Paris), Suppl.*, **30,** C4-24 (1966).
7. I. Haller, *Prog. Solid-State Chem.*, **10,** 103 (1975).
8. Wang Zhu-xi, Thermodynamics (Renmin Jiouiu, Beijing, 1960), 2nd ed.
9. P. G. de Gennes, *Phys. Lett.*, **A30,** 454 (1969).
10. Lin Lei, *Phys. Rev. Lett.*, **43,** 1604 (1979).