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Thermodynamics of Solutions with Liquid Crystal Solvents. VIII. Solute Induced Nematic-Isotropic Transitions[†]

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An experimental approach has been devised which permits the study of the effect of nonmesomorphic solutes of different sizes and shapes on nematic phase stability. The apparatus consists of a vacuum microbalance system which employs a Cahn RG Electrobalance to determine the weight of volatile solute absorbed by a known weight of nematic material at a given temperature and solute partial pressure. From such measurements, solute activity coefficients (γ_2) were determined as a function of solute mole fraction (x_2) at several set temperatures (T) below the nematic-isotropic transition temperature (61.2°C) of the pure nematogen *p*-methoxybenzylidene-*p'*-*n*-propylaniline (MBPA). The solute probes studied were *n*-heptane, benzene and carbon tetrachloride. For all three systems the observed behavior was: ln γ_2 decreased sharply with increasing x_2 in the nematic region, became discontinuous at a mole fraction $\bar{x}_2$ corresponding to the solute induced transition point, and then decreased gradually (approaching zero) with increasing x_2 in the isotropic region. From studies at different T values, $\mathrm{d}T/\mathrm{d}\bar{x}_2$ was determined for all three solutes. These experimental results are discussed in terms of the solute molecular characteristics and in light of recent theoretical results obtained from a statistical mechanical lattice model of a two component mixture of non-interacting rigid rods of different size. This study provides additional evidence of the important role of repulsive forces in governing nematic stability.

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INTRODUCTION

It has been shown by several statistical mechanical treatments[1,2] that a model incorporating only the asymmetric repulsive forces resulting from the rod-like shape of the molecules is sufficient to produce a stable anisotropic (aligned) phase under certain conditions. In real nematic liquids these asymmetric repulsive interactions are most likely coupled with attractive interactions in a complicated manner.[2,3] Similarly, the solution properties of a non-mesomorphic solute dissolved in a nematic solvent, while almost certainly determined in part by solute and solvent shape, may also depend on those attractive interactions which are found in isotropic solutions, such as dispersion and dipole–dipole interactions.

Several techniques; electron spin resonance spectroscopy (esr), gas-liquid chromatography (glc), and thermometry; have been used to investigate the interaction of nematic materials with compounds which have no tendency to exhibit anisotropic phases. The effect of solute concentration on the nematic order parameter has been measured by esr;[4] infinite dilution activity coefficients and heats of solution of numerous solutes in nematic solvents have been studied by glc;[5] and the phase diagrams of many nonmesomorphic/mesomorphic systems have been determined.[6–9]

In order to gain a more complete understanding of solute induced nematic-isotropic transitions, the present investigation of the solution properties at finite concentrations of three nonmesomorphic solutes in *p*-methoxybenzylidene-*p*′-*n*-propylaniline (MBPA) at five temperatures was undertaken. The three nonpolar solutes chosen–*n*-heptane, benzene and carbon tetrachloride–have sufficiently diverse molecular characteristics to permit a further assessment of the relative importance of molecular size, shape and polarizability. In a subsequent paper[10] a statistical mechanical treatment of a binary mixture of rigid rods of two different length-to-breadth ratios placed on a simple cubic lattice[11] will be described, and the results of this treatment will be compared with the experimental results presented here.

EXPERIMENTAL SECTION

Nematic solvent

p-Methoxybenzylidene-*p*′-*n*-propylaniline (MBPA) was synthesized by the condensation of *p*-*n*-propylaniline and anisaldehyde (Eastman) in absolute ethanol.[12] The product was recrystallized three times from petroleum ether and four times from absolute ethanol at –5 to –25°C. Precautions were taken to prevent hydrolysis of the Schiff base linkage. Following removal of the residual ethanol by evaporation under high vacuum, individual samples were sealed in glass vials under high vacuum. A purity of greater than 99.7% was estimated with a differential scanning calorimeter (Perkin Elmer model 1 B) using the procedure described by the manufacturer.[13]

Solutes

Research grade *n*-heptane (99.92%) and research grade benzene (99.90%) were purchased from Phillips Petroleum Company and were used without further purification. Both solutes were stored over sodium and distilled twice under high vacuum to remove trace amounts of dissolved gases. Carbon tetrachloride (Baker Analyzed Reagent Grade) was distilled on an 8 in. Widmer column to remove trace amounts of carbon disulfide and chloroform. The CCl_4 was distilled twice under high vacuum to remove dissolved gases and stored over KOH pellets which had been heated to 200°C under 1×10^{-3} torr for several hours to remove most of the hydrated water.

Apparatus and procedure

A vacuum microbalance system (Figure 1) was built for the accurate determination of the weight of solute vapor absorbed by a nonvolatile solvent (in this case a nematic liquid crystal) at a fixed temperature and vapor pressure of solute. The weighing mechanism employed was a Cahn RG Electrobalance modified according to the manufacturer's suggestions for working at elevated temperatures. The Pyrex vacuum bottle housing the balance and all of the associated vacuum lines which would contain solute vapor at pressures above its ambient vapor pressure were wrapped with chromel heating wire and asbestos tape and were maintained above 55°C to prevent condensation of the solute vapor. To prevent changes in the pressure due to changes in the temperature of the solute vapor, the temperature of the balance housing was monitored with four thermocouples and maintained within 0.3 degrees of 55.6°C for 15 min. before each measurement was taken by adjusting the current in the heating wires with a Variac. The wrapped balance vacuum bottle was secured in two securely mounted double yoke cradles to prevent movement of the balance during loading of the sample. With the precautions described above, the weight of solute absorbed was measured with an accuracy of ±0.2%. The vapor pressure of the volatile solute in equilibrium with that dissolved in the nonvolatile nematic solvent was measured with a thermostated 13 mm i.d. mercury manometer and a precision cathetometer (Gaertner Scientific model M912). When measuring the vapor pressure of CCl_4, the mercury slowly reacted with the CCl_4 at the liquid-vapor interface.[14] Therefore, a wide bore manometer (1 in. precision bore) was used to minimize the meniscus correction.

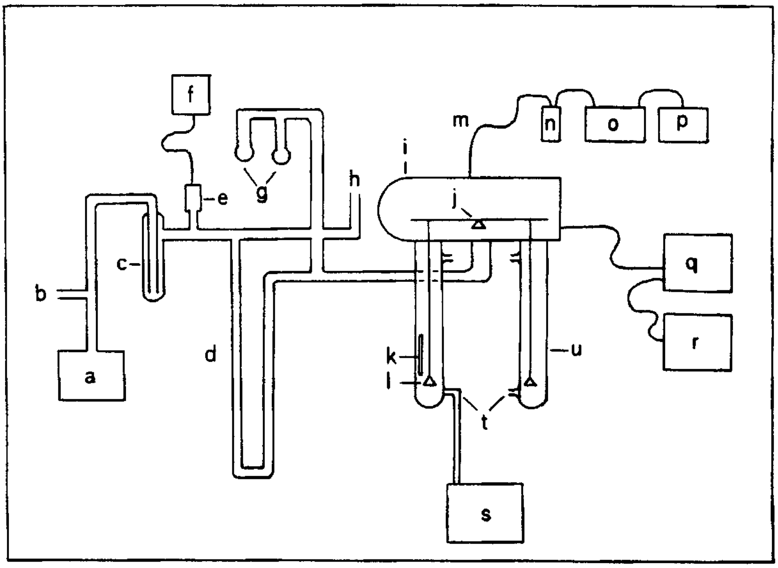

FIGURE 1 Schematic of the vacuum microbalance system and related vacuum and thermostating equipment. (a) vacuum pump; (b) air inlet; (c) liquid nitrogen trap (d) thermostated manometer (bath not illustrated); (e) Pirani head; (f) Pirani gauge; (g) bulbs for storing and distilling solutes; (h) to Mcleod gauge; (i) heated vacuum bottle; (j) electrobalance; (k) thermometer; (l) sample pan; (m) thermocouple leads; (n) ice bath; (o) potentiometer; (p) null meter; (q) console of electrobalance; (r) I mV.recorder; (s) thermostated circular; (t) connections to copper tubing (only one of three tubes is illustrated); (u) jacketed hangdown tube.

The experimental measurements were made as follows. A sealed glass vial containing the MBPA was broken open in a dry box to minimize the hydrolysis of the purified MBPA. A 2 mg sample was hermetically sealed in a D.S.C. pan for determination of the purity. Approximately 120 mg of MBPA were transferred to a weighed sample pan. The granular sample was melted and crystallized to facilitate handling. To minimize exposure to the atmosphere, the sample and the sample pan were placed between two weighed plastic cups and transferred from the dry box to a desiccator. The sample, still sealed between the plastic cups, was weighed and returned to the desiccator. The weighed MBPA sample on the balance pan and a balance pan containing tare weights were suspended in separate jacketed hangdown tubes. Water circulating through the jacketed hangdown tubes maintained the sample temperature to within ±.02°C as measured with a calibrated Anschuetz thermometer suspended next to the sample pan in the hangdown tube. The system was evacuated to 2×10^{-4} torr and, after a suitable time for degassing the nematic liquid, solute vapor was introduced. Equilibrium was achieved in 3 to 5 h, at which time the weight change measured on the recorder in 1/2 h was less than 0.1% of the total weight of solute absorbed. The sample temperature, the weight of solute absorbed, and the vapor pressure of the volatile solute were measured. More solute vapor was introduced and the procedure repeated. The system was pumped to 2×10^{-4} torr every other day and the nematic sample was changed every three weeks, at which time the purity of the nematic sample was always found to be greater that 99.4%.

The experimental apparatus had previously been used to study two systems which will be discussed only briefly here. The first system, hexane and squalane at 30°C, was studied to test the reliability of the experimental apparatus. The extrapolated infinite dilution activity coefficient value of 0.65 was in good agreement with those obtained by similar static measurements by Martire, Pecsok and Purnell,[15] 0.67; and by Ashworth and Everett,[16] 0.65. The results of the second system, heptane and 4,4′-dihexyloxyazoxybenzene at 90.10°C, have been reported in the literature.[17] For this system the extrapolated infinite dilution activity coefficient value of 3.49 was in good agreement with the value of 3.54 obtained by Chow and Martire by glc.[5]

Results

The enthalpy of the solid-nematic transition, 4.1±.1 kcal/mole, and the enthalpy of the nematic-isotropic transition, 97 ± 5 cal/mole, of MBPA were measured by differential scanning calorimetry. The transition temperatures, 44.8-45.3°C and 60.2°C, were observed visually in a thermostated water bath with a calibrated Anschuetz thermometer.

Solute activity coefficients, corrected for the non-ideality of the vapor phase, were calculated from the well known equation[15]

$$\log \gamma_2 = \log \left(\frac{P}{x_2 P_2^\circ}\right) - \frac{(B_{22} - V_2^\circ)(P_2^\circ - P)}{2.3RT} \qquad (1)$$

where P is the equilibrium vapor pressure of the system (equal to the solute partial pressure), x_2 is the solution mole fraction of the solute, P_2° is the saturated vapor pressure of the solute, B_{22} is the second virial coefficient of the solute and V_2° is the molar volume of the solute. The standard corrections for the heights of the mercury menisci, the thermal expansion of mercury, the altitude and the latitude were applied to the height of mercury which was measured to ±.02 mm. x_2 was computed from the weight of MBPA and the weight of solute, after applying to the recorded weight pickup a blank correction, a bouyancy correction, and a correction for the force on the sample pan due to the evaporation of MBPA during the evacuation of the balance chamber. P_2° was calculated from the Antoine equation using constants compiled by Dreisbach.[18] B_{22} for benzene and carbon tetrachloride were interpolated from smoothed data listed by Dymond and Smith.[19] B_{22} for heptane was calculated from the McGlashan and Potter corresponding states equation.[20] V_2^0 was calculated from the law of rectilinear diameter using data compiled by Dreisbach.[17]

Log γ_2 values for carbon tetrachloride which were calculated from Eq.(1) are shown in Figure 2. Logarithms of the activity coefficients of each solute at each temperature in each phase were fitted by a least squares procedure to the empirical equation

$$\log \gamma_2 = Ax_1^2 + Bx_1^3 + Cx_1^4 \tag{2}$$

which satisfies the Gibbs-Duhem relation where x_1 is the solvent mole fraction. The empirical parameters A, B and C are listed in Table I, and plots of log γ_2 vs x_2 are presented in Figures 3, 4 and 5.

It is clear from these Figures that the concentration of solute required to induce the nematic-isotropic transition increases as the temperature decreases. In Figure 6 the nematic-isotropic transition temperature of each solute-solvent combination is plotted versus the mole fraction of solute. The symbol $\vdash\!\!\!-\!\!\!-\!\!\!\dashv$

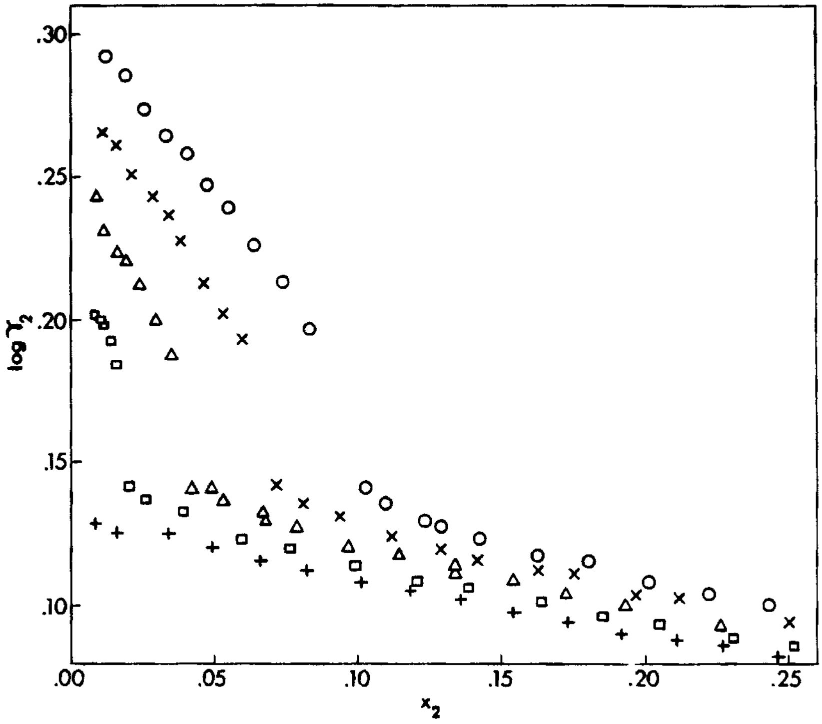

FIGURE 2 Logarithm of the solute activity coefficient (experimental points) vs. solute mole fraction for carbon tetrachloride in MBPA at five temperatures. + 62.10°C; □ 57.10°C; △ 52.10°C; X 46.30°C; ○ 40.10°C.

indicates the mole fraction (average over both phases) region over which the two phases were observed in equilibrium. No experimental measurements of log γ_2 were taken whenever the two phases coexisted. Although thermodynamic arguments predict that the transition should occur between two phases of different composition at a fixed solute vapor pressure, the two phases were visually observed to coexist over a solute vapor pressure range of less than 2 torr. Thus the thermodynamically predicted difference in the compositions of the two phases in equilibrium is approximately 30% less than is indicated in Figure 6 (see later).

DISCUSSION

The solute activity coefficient is a measure of the deviation of the solution from

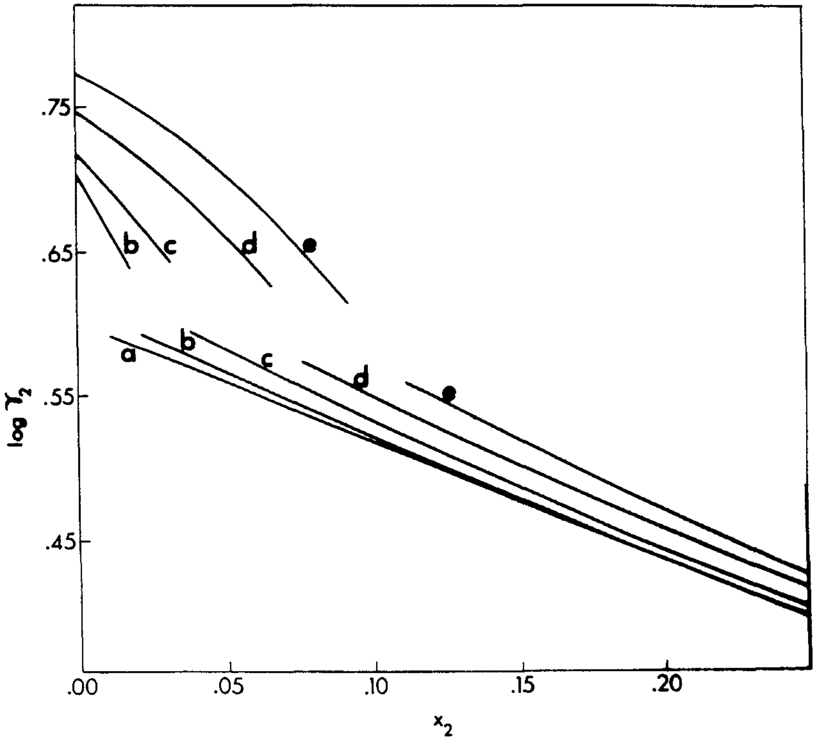

FIGURE 3 Logarithm of the solute activity coefficient (logγ_2) vs. solute mole fraction (x_2) for *n*-heptane in MBPA. (a) 58.10°C; (b) 56.10°C; (c) 52.90°C; (d) 46.30°C; (e) 40.10°C.

ideal behavior, that is, from Raoult's law. The solute activity coefficient is related to the partial molar excess Gibbs free energy, $\bar{G}_2^E$, by the expression

$$RT \ln \gamma_2 = \bar{G}_2^E = \bar{H}_2^E - T\bar{S}_2^E = \left(\frac{\partial G^E}{\partial x_2}\right)_{T,P} \tag{3}$$

where

$$G^E = H - (x_1 H_1 + x_2 H_2) - TS + T(x_1 S_1 + x_2 S_2) + RT(x_1 \ln x_1 + x_2 \ln x_2). \tag{4}$$

H and S are the enthalpy and entropy of the mixture; H_1, H_2, S_1 and S_2 are the enthalpies and entropies of the pure components; and $-R(x_1 \ln x_1 + x_2 \ln x_2)$ is the ideal entropy of mixing. Clearly, factors which increase the enthalpy or decrease the entropy of the solution with respect to that of the separate pure components will contribute to a more positive $\ln \gamma_2$.

From Figures 3, 4 and 5 it is evident that plots of the logarithm of the solute activity coefficient versus the solute mole fraction have certain common features. For all three solutes $\log \gamma_2$ is considerably larger in the nematic phase than in the isotropic phase. Following the arguments of Chow and Martire,[5] this

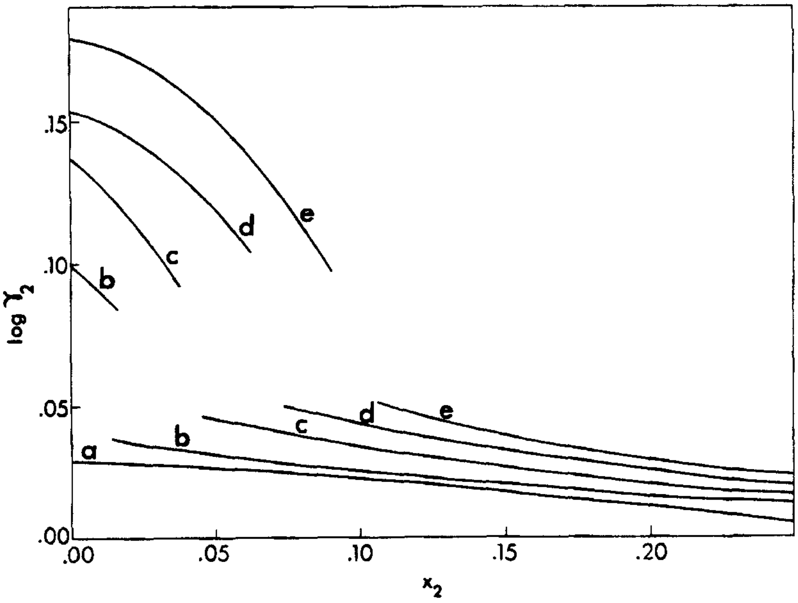

FIGURE 4 Logarithm of the solute activity coefficient ($\log \gamma_2$) vs. solute mole fraction (x_2) for benzene in MBPA. (a) 62.10°C; (b) 57.10°C; (c) 52.10°C; (d) 46.30°C; (e) 40.10°C.

may be attributed to three factors which are clearly coupled, but which will be considered separable in the following discussion.

Rotational effect

Asymmetric (i.e., "rodlike") solute molecules tend to become partially ordered in the nematic phase and hence have lower rotational entropies than in their own pure isotropic states. The more anisotropic the attractive and repulsive forces experienced by the solute molecules, the greater the loss of rotational entropy upon solution, the more negative the excess entropy, and the more positive the value of log γ_2.

Conformational effect

The pure *n*-alkanes, in this case *n*-heptane, have an appreciable population of

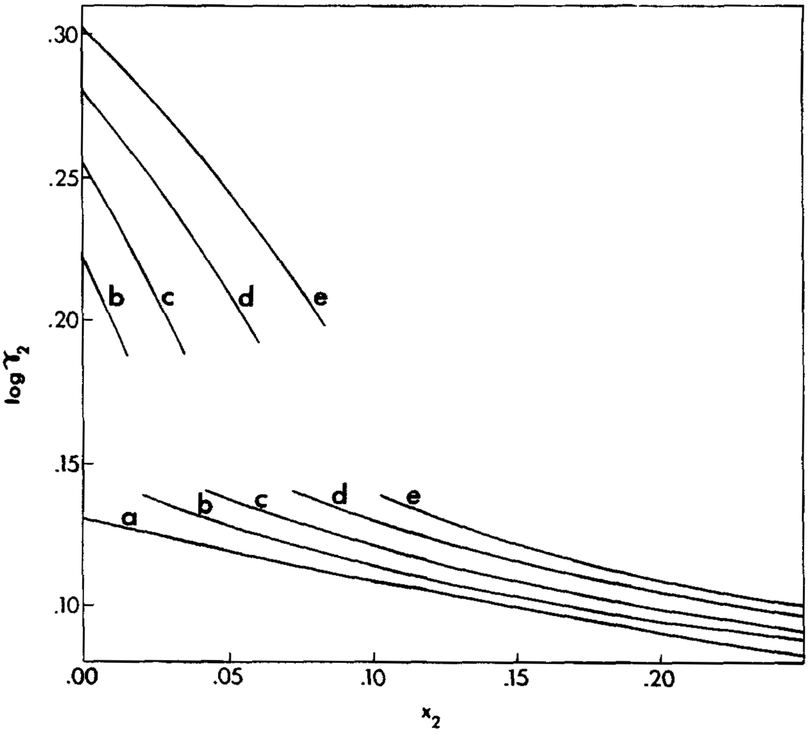

FIGURE 5 Logarithm of the solute activity coefficient (logγ_2) vs. solute mole fraction (x_2) for carbon tetrachloride in MBPA. (a) 62.10°C; (b) 57.10°C; (c) 52.10°C; (d) 46.30°C; (e) 40.10°C.

molecules in conformations other than the zigzag or exclusively trans conformation. Upon solution in the nematic phase, the more rodlike trans conformation will become more highly populated at the expense of the other less rodlike ones. This leads to a loss of internal rotational entropy, a negative contribution to the excess entropy, and therefore, a positive contribution to log γ_2.

Potential energy effect

The strongest attractive interactions between two nematic molecules will occur when the two molecules are parallel. This is the basic assumption in the Maier-Saupe mean field theory of nematic behavior.[21] As a second component, a nonmesomorphic component, is added to a nematic material, it will disorder the nematic molecules and hence the probability of strong lateral interactions will decrease. The solute-solvent interaction will only partially compensate for the loss of the strong solvent-solvent and the weaker solute-solute interaction, and hence lead to a positive contribution to log γ_2.

Each effect described above will decrease as the nematic phase becomes more disordered, either by increasing the temperature or by increasing the solute concentration. These effects are of little or no importance in the isotropic phase. The solute behavior in the isotropic phase is similar to that observed for similar solutes in nonmesomorphic solvents.[22] No unusual behavior was observed in the isotropic phase near the transition, but a small post-transitional affect may have been hidden by random experimental errors. The magnitude of log γ_2 in the isotropic phase is determined by the strength of the attractive forces between the solute and the solvent molecules and by an entropic term analogous to the Flory-Huggins mixing term for flexible polymers.[23,24] This term, which accounts for the size difference between the solute and the solvent molecules, results in a more positive $\bar{S}_2^E$ for benzene and carbon tetrachloride, which are of approximately equal size, than for *n*-heptane, which has a larger molar volume and a larger hard core volume[25] (see Table II). Furthermore the attractive forces between the alkane, heptane, and the polar, highly conjugated MBPA are certainly much weaker than the attractive forces between the individual components. This, together with the entropic size term described above, gives heptane a comparatively larger activity coefficient in both the nematic and isotropic phases. In the nematic phase, the rotational and conformational effects should also contribute to the larger activity coefficient observed for *n*-heptane. The interaction of the diffuse electron clouds on the chlorine atoms with the two benzene rings in MBPA, together with the size effect, gives carbon tetrachloride a considerably lower activity coefficient than heptane in both the nematic and the isotropic phases. Of the three solutes, benzene, with its polarizable pi electrons, most closely resembles the MBPA; and thus has the smallest activity coefficient.

The nematic-isotropic transition temperatures in Figure 6 are to a first approximation linearly dependent on the solute mole fractions. The slopes of the transition temperature versus the solute mole fraction in Table II indicate that carbon tetrachloride molecules are slightly more effective, on a numerical basis, in disrupting the nematic phase than are benzene or *n*-heptane molecules. However, when the transition temperatures are plotted versus the solute hard core volume fractions, thus correcting for the size differences between the solute molecules, *n*-heptane yields the least negative slope. Therefore the long cigar shaped *n*-heptane molecules are less effective per unit volume in disrupting the nematic order than the spherical carbon tetrachloride or the oblate spheroidal benzene molecules. The depression of the nematic-isotropic transition temperature of *p*-methoxybenzylidene-*p*'-*n*-butylaniline by l-hexanol reported by Cladis, Rault and Burger,[9] when converted to °C per volume fraction, is 400±10. Therefore, *n*-heptane and l-hexanol, two compounds which have approximately the same size, shape and flexibility, have roughly the same ability to disrupt the ordered nematic phase.

At the solute induced transition the solute activity coefficient, the enthalpy of the transition, the rate of the depression of the transition temperature (dT/dx_2), and the difference in the solute mole fractions of the two phases in equilibrium are related through the equation[6]

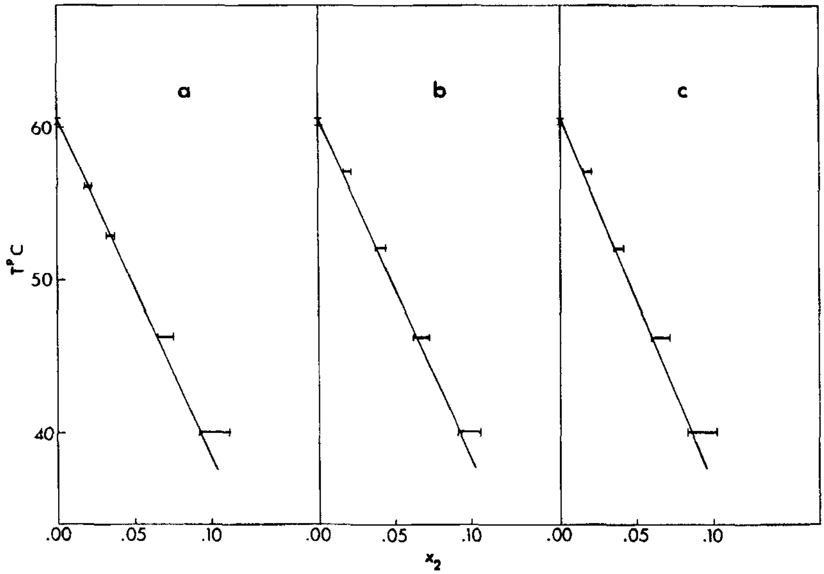

FIGURE 6 Nematic-isotropic transition temperature (T) vs. solute mole fraction (x_2) for (a) *n*-heptane; (b) benzene and (c) carbon tetrachloride in MBPA.

$$x_2' - x_2 = \frac{\left(\frac{\mathrm{d}T}{\mathrm{d}x_2}\right)_p (H_m' - H_m)}{T\left(\frac{\mathrm{d}\mu_1}{\mathrm{d}x_2} - \frac{\mathrm{d}\mu_2}{\mathrm{d}x_2}\right)} \tag{5}$$

where the unprimed values refer to the nematic phase, the primed values refer to the isotropic phase, H_m and H_m' are the enthalpies of the two phases, and μ_1 and μ_2 are the chemical potentials of the two components in the nematic phase. For solute mole fractions less than 0.1, $H_m' - H_m$ should be approximately equal to the enthalpy of the nematic-isotropic transition ($\Delta H_{N\text{-}I}$) for the pure nematic compound. Applying the Gibbs-Duhem relation and expressing the solute chemical potential in terms of ln γ_2, one obtains[11]

$$x_2' - x_2 = \frac{\left(\frac{\mathrm{d}T}{\mathrm{d}x_2}\right)_p (1 - x_2)\Delta H_{N\text{-}I}}{RT^2\left[\frac{1}{x_2} + \left(\frac{\partial \ln \gamma_2}{\partial x_2}\right)_{T,P}\right]} \tag{6}$$

From the above equation and the results in Table I, the calculated differences in the solute mole fraction of the two phases in equilibrium at 40.1°C are 0.018±0.001 for heptane, 0.014±0.001 for benzene, and 0.013±0.001 for carbon tetrachloride. These calculated differences are approximately 30% smaller than those which were observed under the conditions of our experiment (see Figure 6).

Despite the fact that ($\mathrm{d}T/\mathrm{d}x_2$) values comparable to the ones reported here were found by Dave *et al.*[6-8] for several nonmesomorphic/mesomorphic binary systems, no two phase region was observed. Given Eq. (6) and the fact that nematic-isotropic transitions are indeed first order (i.e., that $\Delta H_{N\text{-}I}$ is non-zero), we conclude that one of their alternative explanations,[6] i.e., that their method of investigation was not sensitive enough to detect the presence of the small two phase region, is the correct one. The thermodynamic results of the present study and a statistical mechanical treatment of a binary mixture of rods[10] both clearly indicate the existence of a two phase region when a non-mesomorphic material induces an aligned-isotropic transition.

CONCLUSIONS

Thermodynamic data from solute activity coefficient measurements at finite solute concentrations have been used to show that solute size and solute shape are the dominant criteria in determining the magnitude of the depression of the nematic-isotropic transition temperature by the solute. This conclusion is consistent with recent theoretical results obtained from an athermal lattice model of a binary mixture of rods of different lengths.[10]

The importance of solute size and shape in determining the magnitude of the solute activity coefficient in the nematic phase relative to its magnitude in the isotropic phase is less well understood. In the isotropic phase of a nematogenic

TABLE I

Solute activity coefficients. Least squares fit to the empirical equation
$\log \gamma_2 = Ax_1^2 + Bx_1^3 + Cx_1^3$

	T°C	A	B	C	% Standard deviation of γ_2
Heptane					
Nematic	40.10	− 9.5144	21.2870	−11.0000[a]	.5
	46.30	− 9.9521	21.6980	−11.0000	.5
	52.90	−10.9142	22.6321	−11.0000	.4
	56.10	−12.3449	24.0494	−11.0000	.1
Isotropic	40.10	1.6050	−1.7620	.8462	.4
	46.30	1.7067	−2.0042	.9587	.5
	52.90	1.6934	−2.0333	.9810	.6
	56.10	1.4399	−1.4304	.6074	.4
	58.10	1.2309	− .9066	.2792	.6
Benzene					
Nematic	40.10	− 9.9325	20.5114	−10.4000[a]	.4
	46.30	−10.1497	20.7033	−10.4000	1.2
	52.10	−10.8760	21.4136	−10.4000	.9
	57.10	−10.8998	21.4000[b]	−10.4000	1.0
Isotropic	40.10	.4058	− .9912	.6820	.2
	46.30	.2940	− .6901	.4728	.3
	52.10	.1036	− .2342	.1884	.3
	57.10	.0781	− .1507	.1133	.6
	62.10	− .2962	.6877	− .3602	.3
Carbon tetrachloride					
Nematic	40.10	− 6.1036	12.5051	− 6.1000[a]	.5
	46.30	− 6.4857	12.8658	− 6.1000	.3
	52.10	− 7.1554	13.5105	− 6.1000	.6
	57.10	− 7.6979	14.0202	− 6.1000	.6
Isotropic	40.10	1.1313	−2.3004	1.3727	.3
	46.30	.8422	−1.5821	.9155	.3
	52.10	.6427	−1.1188	.6345	.3
	57.10	.6416	−1.1157	.6214	.3
	62.10	.3055	− .3332	.1585	.2

[a] C held constant to obtain a reasonable fit.

[b] B must be fixed because there are too few data points.

TABLE II

Slopes of the nematic-isotropic transition temperature versus the solute mole fraction (dT/dx_2), versus the solute hard core volume fraction (dT/dv_2), and the solute hard core volumes (V_2^*) [from tabulated data by Bondi[25]]

Solute	dT/dx_2 °C/mole fraction	dT/dv_2 °C/volume fraction	V_2^* cc/mole
n-Heptane	−222 ± 5	−440 ± 5	78.5
Benzene	−222 ± 5	−660 ± 10	48.4
Carbon tetrachloride	−236 ± 7	−680 ± 10	51.4

The hard core volume of MBPA is 152.4 ± 0.5 cc/mole

compound, the repulsive interactions, together with the attractive interactions which depend both on the magnitude and the anisotropy of the solute molecular polarizability, determine the magnitude of the solute activity coefficient. Most likely attractive interactions and conformational effects play some role in determining the magnitude of the solute activity coefficient in the nematic phase relative to its magnitude in the isotropic phase.[5] However, the overall features of the experimental $\ln \gamma_2$ vs. x_2 curves, such as the sharp decrease in $\ln \gamma_2$ in the nematic phase with increasing solute concentration and the discontinuity in $\ln \gamma_2$ at the transition, can be readily demonstrated through a theoretical model which depends only on the sizes and shapes of the particles.[10] In both the real system and the model system, the increase in $\ln \gamma_2$ in the nematic phase over that in the isotropic phase is relatively insensitive to the size and shape of the solute molecules.

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