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Nematic Order in *p*-azoxyanisole and its Dependence on Pressure, Volume and Temperature

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Abstract—The extension of the Maier–Saupe treatment of nematic liquid crystals discussed in previous papers is able to give a quantitative description of the following properties of p-azoxyanisole: (a) the volume change at the nematic–isotropic transition point T_c, (b) the temperature variation of the long range orientational order parameter s_1 at constant pressure, (c) the temperature variation of s_1 at constant volume, (d) the volume variation of s_1 at constant temperature, and (e) the pressure invariance of s_1 at T_c.

1. Introduction

The effect of pressure on the long range orientational order in a nematic liquid crystal was first investigated by Deloche *et al.*,⁽¹⁾ who found that the order parameter $s_1 = (3\,\overline{\cos^2\theta} - 1)/2$ in p-azoxyanisole (PAA) at the nematic–isotropic transition point T_c has a constant value of 0.40 ± 0.015 from 1–3 k bar. This result was confirmed by McColl and Shih⁽²⁻⁴⁾ in their detailed PVT studies on the same compound, but their value of s_1 at T_c was 0.35 ± 0.01. The latter authors also made the interesting observation that the thermal range of the nematic phase at constant volume is about 2.5 times that at constant pressure. They concluded that this experimental fact cannot be accounted for adequately by the Maier–Saupe theory⁽⁵⁾ of nematic liquid crystals, and therefore used an alternative model⁽¹⁾ including both dispersion and steric effects to interpret the temperature variation of s_1 at constant volume. The aim of this paper is to show that the extension of the Maier–Saupe theory developed by us previously,⁽⁶,⁷⁾ which involves a higher order term in the potential function can give a consistent quantitative explanation of the dependence of the order parameter on pressure, volume and temperature.

2. Application of the Molecular Statistical Theory to *p*-azoxyanisole

Deloche *et al.*(1) suggested that the free energy expression in the Maier–Saupe theory should consist of two parts: (a) the Van der Waals attractive contribution and (b) the steric repulsive contribution. To estimate (b), these authors regarded the molecules to be hard rods and assumed(1a) that the free energy contribution due to steric effects is proportional to s_1^2. The model then becomes formally similar to the Maier–Saupe theory so that it also leads to a universal value of $s_1 \simeq 0.43$ at T_c. From a calculation of the heat of transition Deloche *et al.* concluded that the repulsive and attractive contributions are of the same order of magnitude.

McColl and Shih(3) applied this model to interpret their observations. The calculation involves two unknown parameters which they adjusted to give the right temperature variation of s_1 at constant volume. Their analysis also leads to the conclusion that the attractive and steric contributions are about equal. However it is not at all clear how their theoretical curve extends below the limit of $s_1 \simeq 0.43$. (see also Ref. 1a).

It had been emphasized by us in earlier studies(6,7) that since the geometrical anisotropy of the molecule is an essential criterion for the occurrence of the nematic phase, the repulsive interactions should also be included in evaluating orientational order. Our approach differed from that of Deloche *et al.*(1) in that instead of assuming the molecules to be perfectly hard rods (for which the pair potential is either 0 or ∞) we worked out the repulsive contribution to the orientational energy by replacing each molecule by $(2n+1)$ centres of repulsion (where n is an integer). According to this model, the potential energy function (including the dipole–dipole and the dipole–quadrupole contributions to the dispersion energy) can be expressed in the form

$$U_i = -V^{-\gamma}\left[Bs_1\frac{3\cos^2\theta_i - 1}{2} + D\left(s_1\frac{5\cos^4\theta_i - 1}{4} + s_2\frac{3\cos^2\theta_i - 1}{2}\right)\right] \quad (1)$$

neglecting higher terms. Here s_2 is a new long range order parameter defined as $(5\,\overline{\cos^4\theta}-1)/4$. (Priestley and Pershan(8) have recently suggested an experimental method of determining s_2 from Raman scattering.) We rewrite (1) as

$$U_i = -V^{-\gamma}[a'x_i^4+b'x_i^2+c']$$

where $x_i = \cos\theta_i$; $x = \cos\theta$; $a' = \frac{5}{4}Ds_1$; $b' = \frac{3}{2}(Bs_1+Ds_2)$ and $c' = -\frac{1}{4}[2Bs_1+D(s_1+2s_2)]$.

The Helmholtz free energy due to orientational order

$$F_s = NkT[\tfrac{1}{2}(\overline{ax_i^4}+\overline{bx_i^2}-c)-\ln\textstyle\int\exp(ax_i^4+bx_i^2)\,\mathrm{d}x_i] \tag{2}$$

where $a = a'/kTV^{\gamma}$, etc. Putting $\partial F_s/\partial s_1 = \partial F_s/\partial s_2 = 0$ leads to the conditions $\overline{x_i^2} = \overline{x^2}$, $\overline{x_i^4} = \overline{x^4}$. Equating the Gibbs free energy to zero at T_c gives

$$\Delta V = -2F_s/(\partial F_s/\partial V)_{T_c}$$

or

$$\frac{\Delta V}{V} = \frac{2\ln\int\exp(ax^4+bx^2)\,\mathrm{d}x-\left[\frac{a}{5}(5\overline{x^4}+1)+\frac{b}{3}(3\overline{x^2}+1)\right]}{\frac{\gamma}{2}\left[\frac{a}{5}(5\overline{x^4}-1)+\frac{b}{3}(3\overline{x^2}-1)\right]}.$$

The data at atmospheric pressure are quite insensitive to the exact value of γ. Indeed, even the Maier–Saupe potential which has a V^{-2} dependence gives reasonably satisfactory results. In the absence of precise information on this point we had assumed in previous calculations an average V^{-3} dependence for the sum of the dispersion and repulsion energies. The constants B and D which fitted the volume change $\Delta V/V$ at T_c and gave good values of s_1 as a function of temperature at atmospheric pressure (derived from optical data) were

$$B = 4.5448\times10^{-6}\,\text{erg cm}^9$$

$$D = -1.0460\times10^{-6}\,\text{erg cm}^9$$

With these constants, the ratio of thermal range of the nematic phase at constant volume to that at constant pressure turns out to be 2.3 in fairly good agreement with the reported value of about 2.5.

However the absolute values of s_1 from the refractive index data differ from those obtained from NMR measurements. The optical data(9,10) give $s_1 = 0.33$ at T_c whereas from NMR measurements

Deloche *et al.* report a value of 0.40 ± 0.015 at T_c, and McColl and Shih a value of 0.35 ± 0.01. Therefore, in order to have an objective test of the theory, we shall throughout consider only the s_1 values of McColl and Shih and recalculate the dependence of the order parameter on pressure, volume and temperature.

McColl and Shih also established experimentally that for PAA

$$(\partial \ln T/\partial \ln V)_{s_1} = -4. \tag{3}$$

According to our theory, s_1 is determined by a and b (see Eq. (2)). If a and b are to be kept constant while T and V are varied, as is implied in (3), it is clear that TV^{γ} = constant, or $(\partial \ln T/\partial \ln V)_s = -\gamma$. Thus, in terms of our theory, (3) leads to the value $\gamma = 4$ for PAA. Hence, although our previously assumed value of $\gamma = 3$ gives a reasonably good fit with the data, it would be more appropriate to take $\gamma = 4$ in the present calculations. For atmospheric pressure data, we make use of the density measurements of Maier and

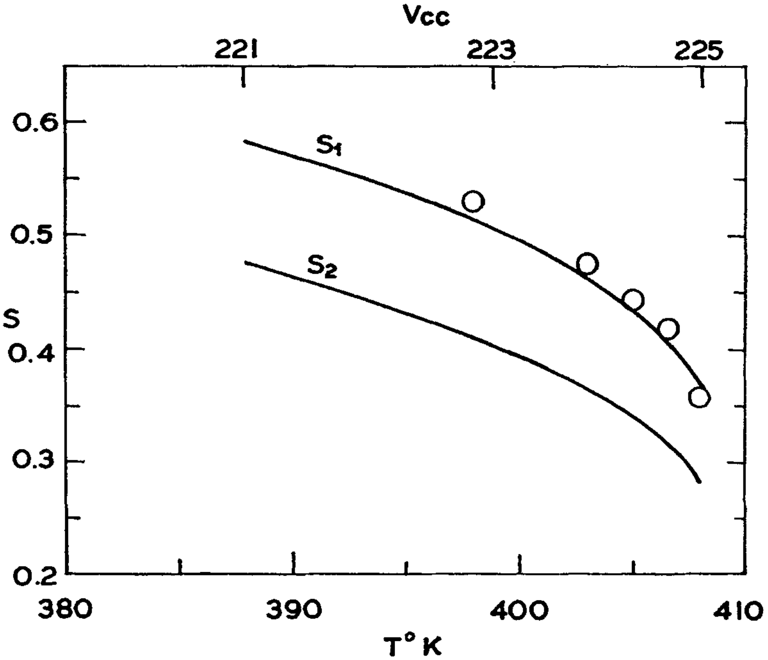

Figure 1. Orientational order parameters s_1 and s_2 of *p*-azoxyanisole vs. temperature at constant (atmospheric) pressure. Curves represent theoretical variation and circles experimental data of McColl and Shih.(2,3)

Saupe,(5) according to which the molar volume of PAA is 221 cm³ at $T_c - 20\,°\mathrm{K}$. Since McColl and Shih report a volume of 221 cm³ at $T_c - 18\,°\mathrm{K}$ at atmospheric pressure, our calculated nematic range extends 2 °K below the experimental value. Bearing this fact in mind we shall proceed to compare theory and experiment. The parameters B and D which fit the experimental(5) $\Delta V/V = 0.0035$ and give the best overall agreement for the variation of s_1 with temperature are

$$B = 9.377 \times 10^{-4}\,\mathrm{erg\ cm}^{12}$$

$$D = -1.774 \times 10^{-4}\,\mathrm{erg\ cm}^{12}.$$

Figures 1–3 present the theoretical curves for the temperature variation of s_1 at constant (atmospheric) pressure, the temperature variation of s_1 at constant molar volume, and the volume variation of s_1 at constant temperature. (The corresponding curves for s_2 are

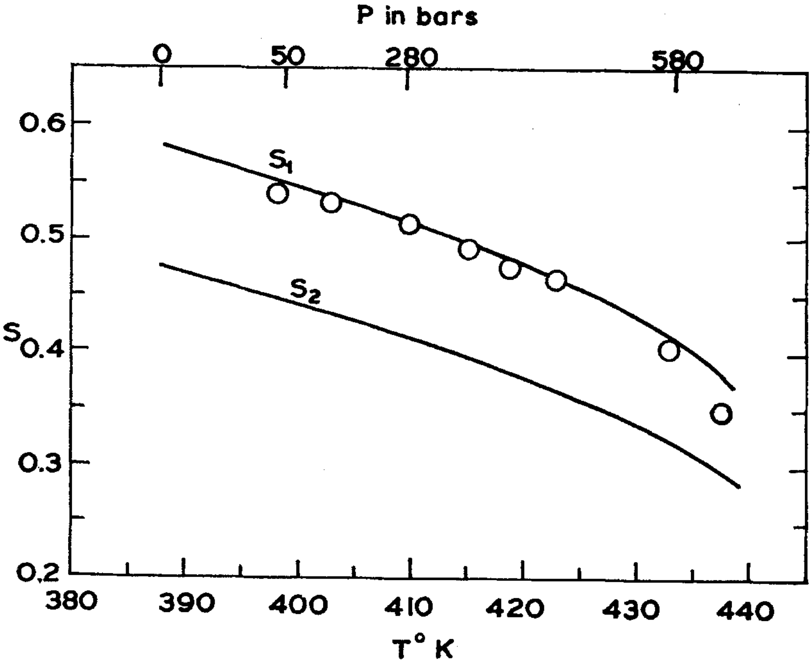

Figure 2. Orientational order parameters s_1 and s_2 of p-azoxyanisole vs. temperature at the constant molar volume of 221 cm³. Curves represent theoretical variation and circles experimental data of McColl and Shih.(2,3)

also shown in the diagrams.) The overall agreement between theory and experiment can be seen to be quite satisfactory. The theoretically predicted thermal range of the nematic phase at constant volume is about 2.5 times that at constant pressure, in excellent

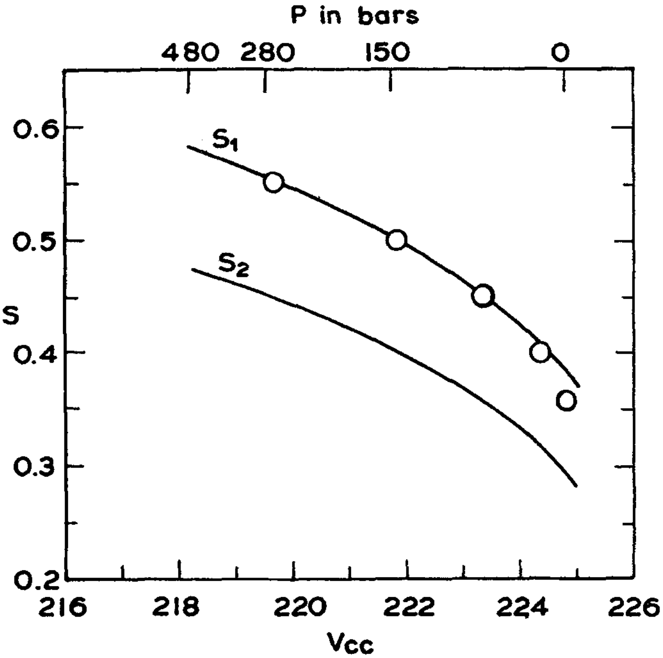

Figure 3. Orientational order parameters s_1 and s_2 of *p*-azoxyanisole vs. molar volume at the constant temperature of 408 °K. Curves represent theoretical variation and circles experimental data of McColl and Shih.(2,3)

accord with observations. The volume range of the nematic phase at constant temperature is about 1.5 times that at constant pressure.

The result that s_1 at T_c is invariant with pressure follows naturally from theory. The Gibbs free energy

$$G_s = F_s + \left(\frac{\partial F_s}{\partial V}\right)_{Tc} \frac{\Delta V}{2}$$

is determined by the two parameters a and b which in turn determine s_1 and s_2. The vanishing of G_s occurs for a particular set of values a, b and hence of s_1, s_2, and if we ignore the variation of ΔV with pressure, the transition will be determined by the same values of a, b

(and s_1, s_2) at all pressures. Now $\Delta V/V$ itself is so small that it makes only a minor contribution to the theoretical value of s_1 at T_c. For example, according to the Maier–Saupe theory, $s_1 = 0.443$ at T_c for PAA ($\Delta V/V = 0.0035$), whereas if we put $\Delta V/V = 0$, s_1 has a universal value of 0.4292 at T_c at all pressures.(5) Consequently, any variation in $\Delta V/V$ is not likely to affect the order parameters substantially.

We may conclude therefore that the extension of the Maier–Saupe theory can adequately account for all existing data on long range nematic order and its dependence on pressure, volume and temperature. However, it is too early to say whether the potential function used in this theory is in fact a realistic representation of the attractive and repulsive forces between molecules in nematic systems, but it is encouraging to find from preliminary studies that the empirically determined parameters B and D do in fact bear a relationship with the molecular structure and properties.(11,12) Of course, it is well known that the mean field treatment cannot be expected to give a complete description of the nematic phase. Attempts to extend the treatment to include short range correlations have been made recently.(13,14)

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