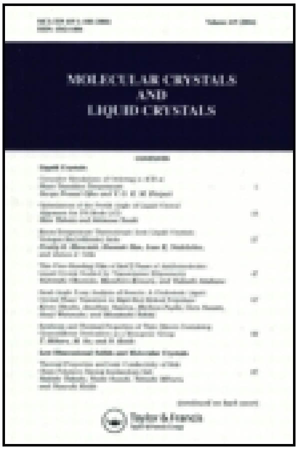

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Order in the Nematic Mesophase

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Abstract—The degree of order, $\mathcal{O}_{33}$, of a paramagnetic probe, vanadyl acetylacetonate, has been measured in the nematic mesophase of eight liquid crystals. Significant deviations from a common curve are observed when $\mathcal{O}_{33}$ is plotted as a function of the reduced temperature. Calculations using the specific form suggested by Maier and Saupe for the intermolecular potential function, describing both solvent-solvent and solute-solvent interactions, fail to provide a quantitative account of the deviations. The calculations do, however, account qualitatively for the behaviour of different solutes aligned in the same nematic mesophase. The deviations appear to depend, in a systematic way, on the nematic-isotropic transition temperature which suggests that a modification to the intermolecular potential could describe the experimental results.

1. Introduction

The equilibrium properties of fluids composed of spherically symmetric molecules can be calculated from a knowledge of the distribution functions. The pair distribution function $n^{(2)}(\mathbf{r}_1; \mathbf{r}_2)$, where $n^{(2)}(\mathbf{r}_1; \mathbf{r}_2)\,d\mathbf{r}_1\,d\mathbf{r}_2$ is the probability of finding one molecule in each of the volume elements $d\mathbf{r}_1$ and $d\mathbf{r}_2$ at positions $\mathbf{r}_1$ and $\mathbf{r}_2$, is particularly important. When the symmetry of the molecule is less than spherical the intermolecular potential function is orientation dependent and it is necessary to extend the concept of radial distribution to include angular correlations.[1] For example, $n^{(2)}(\mathbf{r}_1,\omega_1; \mathbf{r}_2,\omega_2)\,d\mathbf{r}_1\,d\mathbf{r}_2\,d\omega_1\,d\omega_2$ is now the probability of finding a molecule in each of the volume elements $d\mathbf{r}_1$ and $d\mathbf{r}_2$ with orientations between ω_1 and $\omega_1 + d\omega_1$ and between ω_2 and $\omega_2 + d\omega_2$. In isotropic fluids the angular correlation extends only over a few molecules and the pair distribution function $n^{(2)}(\mathbf{r}_1,\omega_1; \mathbf{r}_2,\omega_2)$

is independent of ω_1 and ω_2 for large values of the intermolecular separation.

This is not the situation in the nematic mesophase of a liquid crystal where the angular correlation extends over many thousands of molecules and in the presence of a constraint, such as an electric[2] or magnetic field,[3] extends throughout the sample. The orientation dependent properties of the system can be calculated from the singlet orientation distribution function because $\rho^{-1}n^{(1)}(\mathbf{r}_1,\omega_1)\,d\omega_1$ is the probability that a molecule has an orientation between ω_1 and $\omega_1 + d\omega_1$, where ρ is the number density. Thus the average value of a property $f(\omega_1)$ is

$$\langle f(\omega_1)\rangle = \rho^{-1}\int f(\omega_1)n^{(1)}(\mathbf{r}_1,\omega_1)\,d\omega_1 \tag{1}$$

It is possible to expand $n^{(1)}(\mathbf{r}_1,\omega_1)$ in terms of multiple products of the direction cosines[1], l_i, of a molecular axis system $i, j, k, \ldots$ and the preferred molecular orientation dictated by the constraint:

$$n^{(1)}(\mathbf{r}_1,\omega_1) = (4\pi)^{-1}\rho[1 + 3\sum_i \mathcal{O}_i l_i + 5\sum_{i,j}\mathcal{O}_{ij}l_il_j + 7\sum_{i,j,k}\mathcal{O}_{ijk}l_il_jl_k + \ldots] \tag{2}$$

In magnetic resonance experiments using a nematic mesophase as the solvent we are normally concerned with certain second rank interactions, such as the nuclear dipolar coupling and the anisotropic hyperfine coupling, which are averaged to zero in isotropic fluids. To calculate the contribution of such interactions to the static spin Hamiltonian the average values of the products of two direction cosines are required.[4] For example,

$$\langle l_il_j\rangle = \int l_il_jn^{(1)}(\mathbf{r}_1,\omega_1)\,d\omega_1 \tag{3}$$

and substitution of the expansion for $n^{(1)}(\mathbf{r}_1,\omega_1)$ shows that only the coefficients $\mathcal{O}_{ij}$ determine $\langle l_il_j\rangle$. In fact the $\mathcal{O}_{ij}$ are just the elements of the ordering matrix defined by Saupe[5] as

$$\mathcal{O}_{ij} = \frac{3\langle l_il_j\rangle - \delta_{ij}}{2} \tag{4}$$

Clearly a magnetic resonance experiment, in which only second rank interactions are involved, cannot be used to determine all of the singlet distribution function.

The magnitude of the ordering matrix is determined by the angular part, U, of the intermolecular potential energy function and so experimental values of $\mathcal{O}$ might allow us to determine the form of U. Provided dispersion forces are responsible for the potential then U can be written in a form containing a single parameter which determines the depth of the potential well.[6] In order for such a potential to yield the required phase transition it is necessary to adopt the Bragg-Williams approximation[7] and assume that U is proportional to the degree of order.[6] According to this model the degree of order should be a universal function of the reduced temperature, T^*, (T/T_K) where T_K is the isotropic-nematic transition temperature. Previous determinations of $\mathcal{O}$ show that this prediction is largely correct.[8,9] However, it is not clear if the small deviations from the common curve are due to the differences in the methods of obtaining $\mathcal{O}$ or to the existence of a more complicated potential function.

We have attempted to solve this problem by measuring the alignment of a paramagnetic probe, vanadyl acetylacetonate, using electron resonance, in eight nematic mesophases with quite different molecular structures. The electron resonance technique has several advantages[10] when studying the nematic mesophase and here the ability to determine the alignment in different liquid crystals in a systematic and consistent manner is particularly important. There is, however, one disadvantage, for the alignment of the solute must be related to the order of the solvent, and to do this we have to extend the model for the nematic mesophase.

2. Procedure and Results

The samples of the eight liquid crystals were obtained commercially and used without further purification since, in every case, the nematic-isotropic transition points were in close agreement with the literature values. The mole fraction of vanadyl acetylacetonate in solution was always less than 10^{-3} and the solutions were degassed before sealing under vacuum. The electron resonance spectra were measured using a Varian E-3 spectrometer and a Varian E-4557 variable temperature unit. The sample temperature was measured with a copper/constantan thermocouple taped to the sample tube and connected to a Digitec millivoltmeter.

The effective vanadium coupling constant, $\langle a \rangle$, was obtained from the total width of the spectrum in the nematic mesophase, and if $\langle a_f \rangle$ is in gauss the component of $\mathcal{O}$, for the solute, perpendicular to the molecular plane, is given by[10]

$$\mathcal{O}_{33} = \frac{g\beta(\langle a_f \rangle - a_f)}{2(hA'_\perp - g'_\perp \beta \langle a_f \rangle)} \tag{5}$$

In this expression g is the isotropic g-factor, a_f the isotropic vanadium hyperfine splitting (in gauss), $g'_\perp$ is the in-plane component of the anisotropic g-factor and $A'_\perp$ the in-plane component of the anisotropic hyperfine tensor. The following values were used for these quantities[11]:

$$\begin{aligned} A'_\perp &= 108.9 \text{ MHz}, \\ g'_\perp &= 0.013, \\ g &= 1.969 \end{aligned} \tag{6}$$

together with the isotropic coupling constant measured above the nematic-isotropic transition point. The calculated degree of order is plotted as a function of reduced temperature in Figs. 1 and 2. The nematic-isotropic transition temperatures used to calculate the T^* were obtained from the electron resonance spectra by noting the temperature at which the spacing between the hyperfine lines decreased sharply. In all cases this was within a few degrees of the transition temperature determined directly. The names of the liquid crystals used in this study, together with their nematic-isotropic transition temperatures, are given in Table 1.

3. Interpretation

The points in Figs. 1 and 2 show quite clearly that, although the degree of order of the solute approximates to a universal function

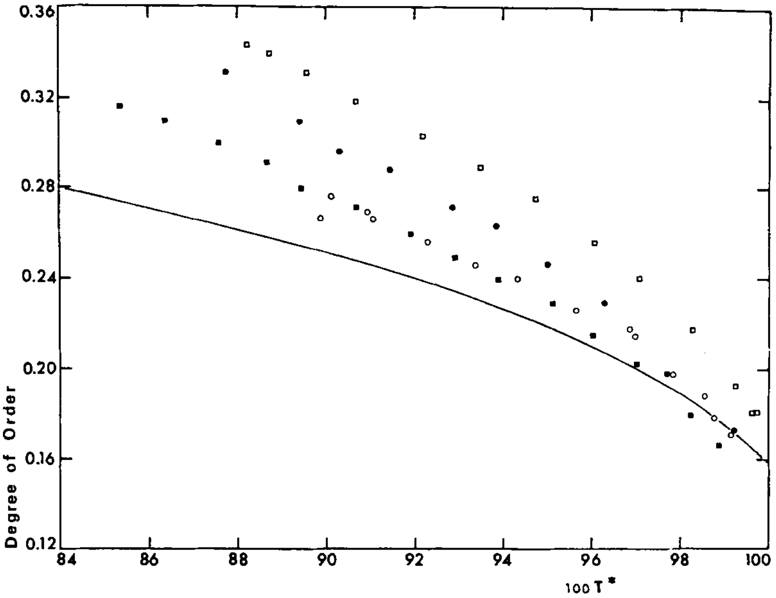

Figure 1. The ordering matrix element, $-\mathcal{O}_{33}$, plotted as a function of reduced temperature; the name of the liquid crystal corresponding to a particular symbol is given in Table 1. The solid line was calculated using Eqs. (11) and (17) with β equal to -0.465.

Table 1 The Nematic Liquid Crystals and their Nematic-isotropic Transition Points

Compound	Symbol in Figs. 1 and 2	Transition Point (°K)
4(*p*-methoxybenzylidine) aminophenyl acetate	◆	368
4,4′-di-*n*-hexyloxyazoxybenzene	●	399
4,4′-di-methoxyazoxybenzene	□	408
4-*n*-heptyloxybenzoic acid	◇	414
4-*n*-octyloxybenzoic acid	○	414
4(*p*-methoxybenzylidene)aminobiphenyl	▽	438
bis(*p*-methoxybenzylidene) hydrazine	△	445
4(*p*-methoxybenzylidene) aminoazobenzene	■	451

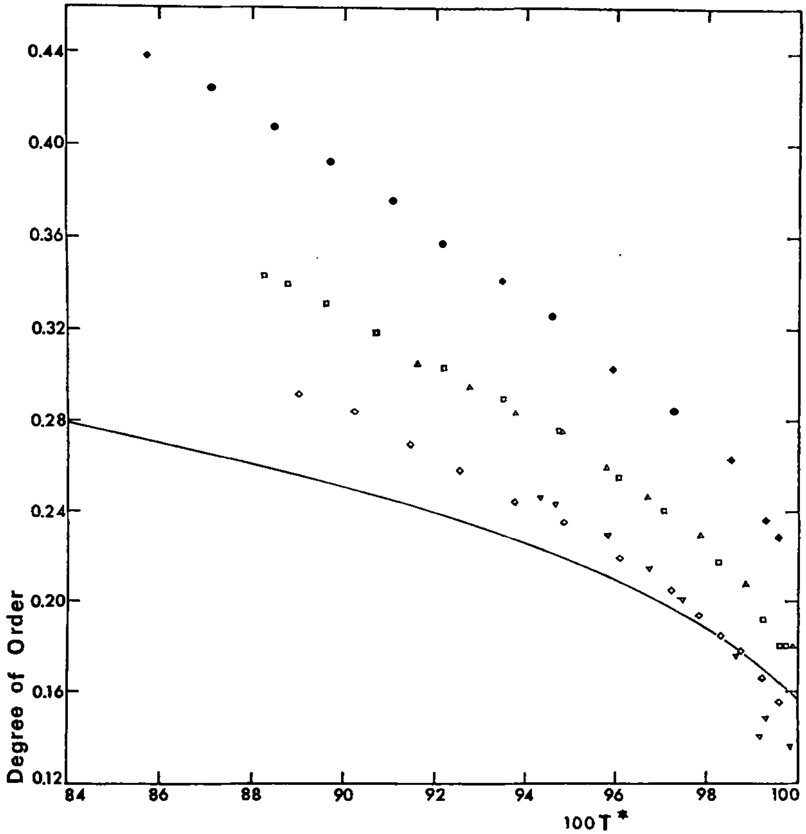

Figure 2. The ordering matrix element, $-\mathcal{O}_{33}$, plotted as a function of reduced temperature; the name of the liquid crystal corresponding to a particular symbol is given in Table 1. The solid line was calculated using Eqs. (11) and (17) with β equal to -0.465.

of the reduced temperature, there are significant deviations. Before the implication of these deviations on the form of the intermolecular potential function can be judged it is necessary to see how the order of the solute is determined by that of the solvent. Because of the low concentration of the probe we need only consider the interaction of the solute with a potential generated entirely by the solvent. By analogy with the pure nematic mesophase we begin by assuming that the orientational potential energy of a solute molecule is[6]

$$U(l_1,l_2,l_3) = -\frac{\mathcal{O}_S}{2V^2}\sum_{i=1}^{3}\epsilon_i(3l_i^2 - 1) \tag{7}$$

where the subscripts refer to the molecular axes 1, 2 and 3, the ϵ_i measure the strength of the intermolecular interaction and V is the molar volume. This form of the solute potential contrasts with that employed by Saupe[12] who appears to ignore both the volume and order dependence of the potential by simply writing

$$U = -\sum_{i=1}^{3}\epsilon_i l_i^2 \tag{8}$$

The geometry of vanadyl acetylacetonate[13] suggests that the molecule possesses cylindrical symmetry about axis 3 perpendicular to the molecular plane. This implies that $\epsilon_1 = \epsilon_2$ and so

$$U = -\frac{\mathcal{O}_S}{2}\frac{\delta\epsilon}{V^2}(3l_3^2 - 1) \tag{9}$$

where $\delta\epsilon$ is $\epsilon_3 - \epsilon_1$ and the element of the ordering matrix for the solute is

$$\mathcal{O}_{33} = \frac{3}{2}\left[\int_0^1 l_3^2 \exp\left(\frac{\mathcal{O}_S\delta\epsilon(3l_3^2 - 1)}{2kTV^2}\right)dl_3 \Bigg/ \int_0^1 \exp\left(\frac{\mathcal{O}_S\delta\epsilon(3l_3^2 - 1)}{2kTV^2}\right)dl_3\right] - \frac{1}{2} \tag{10}$$

A more convenient form of $\mathcal{O}_{33}$ can be obtained by integrating by parts to give

$$\mathcal{O}_{33} = \frac{3}{4\gamma}\left[\left(e^{\gamma} \Bigg/ \int_0^1 e^{\gamma l_3^2}\,dl_3\right) - 1\right] - \frac{1}{2} \tag{11}$$

and evaluating the integral by expanding the exponential and integrating term by term:

$$\int_0^1 e^{\gamma l_3^2}\,dl_3 = 1 + \sum_{i=1}^{\infty}\gamma^i/i!\,(2i + 1) \tag{12}$$

where

$$\gamma = 3\,\delta\epsilon\mathcal{O}_S/2kTV^2. \tag{13}$$

Evaluation of the formulae demands values of $\mathcal{O}_S$ as a function of temperature. These can be obtained theoretically in the following way. The orientational potential energy of a liquid crystal molecule is also given by an equation analogous to Eq. (7) and, if the molecules are rod-like, the potential reduces to

$$U = -\frac{\mathcal{O}_S}{2}\frac{\delta\epsilon_0}{V^2}(3l \;\; - 1) \tag{14}$$

where 3 now corresponds to the long axis of the molecule. The order of the solvent is

$$\mathcal{O}_S = \frac{3}{4\alpha\mathcal{O}_S}\left[\left(e^{\alpha\mathcal{O}_s} \Big/ 1 + \sum_{i=1}^{\infty} (\alpha\mathcal{O}_S)^i/i!(2i+1)\right) - 1\right] - \frac{1}{2} \tag{15}$$

where

$$\alpha = 3\,\delta\epsilon_0/2kTV^2 \tag{16}$$

Equation (15) can be solved numerically in two ways, both of which involve termination of the summation when the value of the sum is 10^4 times the next term. The first method is straightforward and involves iteration. Unfortunately the convergence is slow and it became necessary to find an alternative technique. This involves the SIMPLEX minimization routine[14] which is used to solve Eq. (15) until the error in $\mathcal{O}_S$ is less than 10^{-5}. The SIMPLEX procedure is faster than iteration and the values of $\mathcal{O}_S$ calculated for given α are in complete agreement. Some caution must be exercised when examining the solutions for Eq. (15). For all values of α, $\mathcal{O}_S$ equal to zero is a solution and for α greater than 7.5 there is a further solution corresponding to a stable ordered phase. When α is less than 7.5 but greater than a certain value, α'_K, there are two non-zero solutions, the smaller of the two corresponds to a metastable condition and has been ignored. Below α'_K the only real solution to Eq. (15) is $\mathcal{O}_S$ equal to zero.[7]

The molar volumes of the pure liquid crystal and the dilute solution of the probe are essentially identical and so Eqs. (13) and (16) can be combined to give

$$\gamma = \alpha\beta\mathcal{O}_S \tag{17}$$

where β is the ratio $\delta\epsilon/\delta\epsilon_0$. The parameter β is a measure of both solute-solvent and solvent-solvent interactions, which should change in our experiments with different nematic mesophases. Variations in β may therefore account for the deviations from a common curve in Figs. 1 and 2. We have therefore calculated $\mathcal{O}_{33}$ as a function of α for various values of β using the theoretical values of $\mathcal{O}_S$, together with Eqs. (11) and (12). The summation was again terminated when the ratio of the sum to the next term was greater than 10^4. To compare these calculations with experiment we must relate α to the reduced temperature, T^*. At the nematic-isotropic transition point α takes a certain value α_K which is related to the transition temperature by

$$\alpha_K = \frac{3\delta\epsilon_0}{2kT_K V_K^2} \tag{18}$$

and so the ratio α_K/α is just $T^* V^{*2}$ where V^* is the reduced molar volume. In the absence of a volume change at the transition point, α_K can be calculated by finding the value of α which makes the orientational free energy for the system, ΔF, vanish. The potential function given in Eq. (14) can be used to calculate the molar orientational energy $\langle U \rangle$ and the partition function from which the molar entropy, and hence ΔF, can be obtained. According to our calculations $\alpha_K = 6.812$ in complete agreement with the earlier result of Maier and Saupe.[15] It is important to note that the calculated degree of order exhibits a discontinuity when $\alpha_K = 6.725$; the difference between this and the value of 6.812 means that it should be possible to superheat the nematic melt past the true transition point.

Now in Figs. 1 and 2 the experimental degrees of order are plotted as a function of reduced temperature whereas, for constant β, the theory predicts that $\mathcal{O}_{33}$ should be a universal function of

T^*V^{*2}. Although this difference in the ordinate might be thought to account for the observed deviations this is not the case. According to the principle of corresponding states[16] the reduced molar volume should be a universal function of T^* and, provided this is so, changing from T^* to T^*V^{*2} will shift all the points at a given reduced temperature equally. Precise measurements[15,17] of the density of three nematic mesophases support this prediction; the universal curve is shown in Fig. 3.

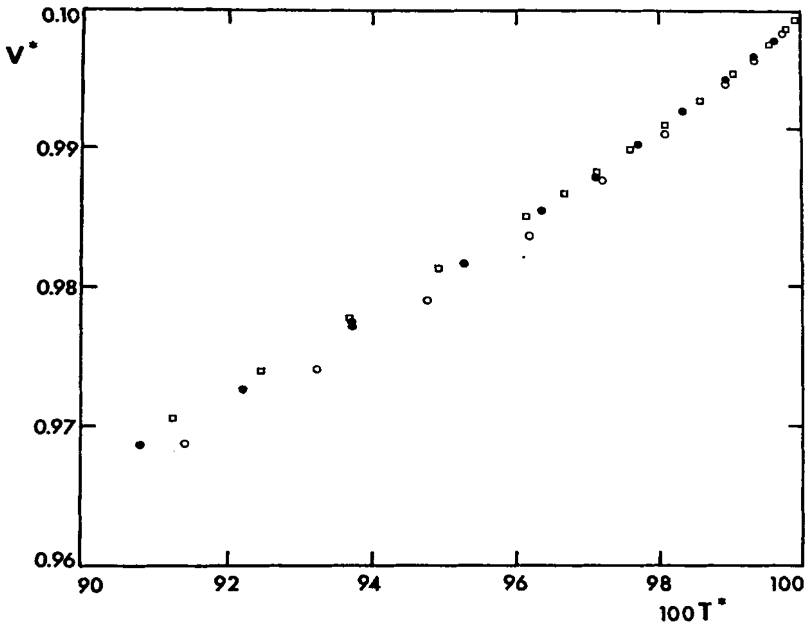

Figure 3. The reduced molar volume plotted as a function of reduced temperature for p-azoxyanisole (□), undeca-2,4-diene-1-carboxylic acid (○), and nona-2,4-diene-1-carboxylic acid (●).

The computed results for $\mathcal{O}_{33}$ are plotted as a function of α_K/α in Fig. 4 for β equal to -0.50, -0.71, -1.00, -1.38, and -2.05. Negative values of β were chosen because in vanadyl acetylacetonate the molecular plane tends to be aligned parallel to the magnetic field and so ϵ_1 must be greater than ϵ_3, making

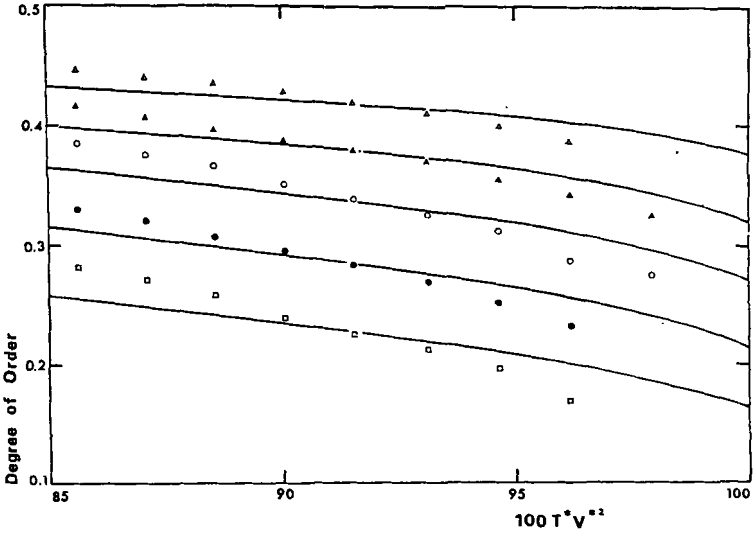

Figure 4. The solute order, $-\mathcal{O}_{33}$, plotted as a function of the reduced variable $T^* V^{*2}$. The solid lines are theoretical curves calculated with the values of β given in Table 2 and the experimental points are for the vanadyl chelates named in Table 2.

$\delta\epsilon$ negative. On the other hand in a nematic mesophase composed of rod-like molecules $\delta\epsilon_0$ is positive. The results plotted in Fig. 4 show, quite clearly, that changing the magnitude of β simply raises or lowers the curve for the solute order. Because the series of curves are essentially parallel, changes in the parameter β cannot account for the results given in Figs. 1 and 2, where the $\mathcal{O}_{33}$ are comparable at the transition point and then diverge for lower values of the reduced temperature. This particular inadequacy of the theory is emphasized in Figs. 1 and 2 by a comparison of the theoretical curve, calculated with β ($-$ 0.465) chosen to fit the experimental degree of order at the transition point, with the results at lower reduced temperatures.

In our experiments the use of different liquid crystal solvents and the same paramagnetic probe may result in different values of β. However, a comparison of the calculations with the experimental degrees of order suggests that changing the solvent but not the solute does not alter β, possibly because $\delta\epsilon$ and $\delta\epsilon_0$ are affected in the same way.[10] On the other hand if the structure of the probe was altered and the order measured in the same mesophase $\delta\epsilon_0$ would remain constant and $\delta\epsilon$, and hence β, must change. Glarum and Marshall[18] have measured $\mathcal{O}_{33}$ for a number of vanadyl chelates, whose structures are given in Table 2, dissolved in *p*-azoxyanisole. Their results are indeed a series of near parallel curves as our calculations predict. We have plotted $\mathcal{O}_{33}$ for five of the chelates as a function of $T^* V^{*2}$ by using the common curve in Fig. 3 to calculate the reduced molar volume. The points shown in Fig. 4 approximate quite closely to the theoretical curves calculated for the β's given in Table 2. As expected the magnitude of β increases with the size of the chelate and in fact the ratio of the effective area of the molecular plate to β, given in Table 2, is approximately constant. The exception is the 3-phenyl-2,4-pentanedione complex for which the ratio is too large; presumably the substituent phenyl groups produce a marked deviation from planarity thus invalidating the theoretical analysis. The calculations also provide an explanation for the interesting observation that the alignment of a large solute molecule can be greater than that of the solvent.[18]

TABLE 2 The Vanadyl Chelates and the Corresponding β Values

Chelate	Symbol in Fig. 4	β	Area/β (Å^2)
3-phenyl-2,4-pentanedione	□	− 0.50	− 490
2,4-pentanedione	●	− 0.71	− 132
benzoylacetone	○	− 1.00	− 162
dibenzoylmethane	▲	− 1.38	− 148
di-2-naphthoylmethane	△	− 2.05	− 152

Although the general agreement between the theory and experiment illustrated in Fig. 4 is good, it is also clear that the experimental value of the slope, $d\mathcal{O}_{33}/d(T^* V^{*2})$, is greater than the theoretical slope. This and the family of curves in Figs. 1 and 2 suggest that the potential function Eq. (14) must be modified. In principle the dipole-dipole, induction and repulsion interactions are also anisotropic and should be included with the dispersion contribution in the potential function.[19] The inclusion of these terms introduces several adjustable parameters and it might seem doubtful if the values required to fit the results could be simply related to the molecular structure of the mesophase. However, examination of Figs. 1 and 2 shows that liquid crystals with similar isotropic-nematic transition points have similar degrees of order. Further, the lower T_K then the higher is the value of $\mathcal{O}_{33}$ for a given reduced temperature. These observations are encouraging and we intend, therefore, to investigate the possibility of explaining our results with the fuller potential.

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