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Scattering of Light by Liquid Crystalline *p*-Azoxyanisole†

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Abstract—Chatelain's theory of light scattering in nematic liquid crystals is modified and extended to obtain expressions for the intensities V_H, H_H, H_V and V_V in three cases, i.e., when the optic axis of the medium lies (i) normal to the scattering plane, (ii) along the direction of the incident light and (iii) perpendicular to incident direction and in the scattering plane. The theory is developed assuming that the molecules are arranged parallel to one another in spherical volume elements, but no specific orientation distribution function is used here. The intensity data available for *p*-azoxyanisole are analysed by modifying the theoretical expressions by an empirical form-factor to represent the effect of the orientation correlation between neighbouring volume elements. From the consistency of the analysis it emerges that the volume elements have a radius of about 800 Å. Also, the average value $\cos^4\theta$ is calculated, θ being the angle between the optic axis and the orientation direction in a volume element.

1. Introduction

The scattering of light in the nematic phase of *p*-azoxyanisole at 125 °C was investigated by Chatelain[1,2] in detail, using plane polarized incident light with the electric vector lying (i) in the plane of scattering and (ii) perpendicular to it. In each case the scattered light was analysed and the intensities of the H component with the electric vector in the plane of scattering and the V component with electric vector normal to the plane of scattering were determined mainly over the range of angles of scattering from 8° to 50°. The intensities of the different components may be denoted here by H_H, V_H, V_V and H_V, the respective subscripts H or V being used to denote that the incident electric vector is in the plane of scattering or normal to it. In his studies Chatelain made use of oriented specimens corresponding to two cases, wherein the optic axis of the

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medium was lying (i) normal to the plane of scattering and (ii) in the plane of scattering.

A striking angular dissymmetry in the intensities of the scattered light, analogous to that encountered with colloidal scattering was observed with regard to all the components. Further, at small angles it was observed that the intensity V_H was several times greater than H_H. Falgueirettes(3) who studied the intensity V_H for various angles of scattering in the case of nematic parabutyloxybenzoic acid, found the intensity to be large at small angles.

A theory of scattering of light in nematic liquid crystals was proposed by Chatelain(4) on the basis of the following assumptions. The intensity of scattering due to fluctuations in orientation (anisotropic scattering) is large compared to that arising from density fluctuations so that the latter part (isotropic scattering) may be neglected. The molecules are arranged with their long axes parallel to one another in the form of " paquets "-bundles which are spherical volume elements whose size is small compared to the wavelength of light, and phase correlation exists between the scattered waves from the molecules within a volume element. The different volume elements in the medium have different orientations for their optic axes and the orientation distribution function is assumed to be of the form $e^{-\beta\vartheta^2}$, where θ is the angle between the orientation axis of a volume element and the optic axis of the medium. Also the values of θ are restricted so that $0 \leqslant \theta \leqslant \theta_0$. Besides, Chatelain has also considered the case where the molecules may not form " paquets " but have an orientation distribution given by $e^{-\beta\theta^2}$. The results of the theory proposed by him gave the right order of magnitude for the depolarisation factors at small angles. However, detailed comparison of the intensities of scattering for different angles, from the standpoints of theory and experiment have not been made.

Chatelain has dealt with only the case corresponding to the optic axis of the medium lying normal to the plane of scattering. In the following, we theoretically consider, on the basis of an approach similar to his, but without using any specific distribution function, three cases of interest viz., where the optic axis of the medium lies (i) normal to the plane of scattering, (ii) along the direction of the incident light and (iii) in the plane of scattering and in a direction perpendicular to that of the incident light. An analysis of the intensity data of Chatelain is also carried out in this paper with the aid of the results of the theory, and in conjunction with a simple empirical relation to represent some of the effects which it is not possible to treat theoretically.

2. Theoretical

We consider the medium to be composed of spherical volume elements of average radius R, each volume element containing on an average l molecules which are arranged parallel to one another. The size of the volume element may be considered as equivalent to an average value of the persistent length for the orientational order in the medium, although one cannot altogether rule out correlations in the orientations between neighbouring volume elements. For the case where the orientations of the different volume elements are independent of one another, the average intensity of anisotropic scattering per unit volume is given by

$$I = \tfrac{1}{2}\nu[\overline{A_i^2} - (\bar{A}_i)^2] \tag{1}$$

where ν is the number of volume elements per unit volume, A_i is the amplitude of the scattering from the ith volume element and $\overline{A_i^2}$ and $\bar{A}_i$ are the mean values of A_i^2 and A_i, averaged over the different volume elements (see, for example, Cabannes$^{(5)}$). Since the molecules in any particular spherical volume element are aligned parallel to one another, the phase correlation between the scattered waves from them may be taken into account by assuming that the average propagation characteristics of the incident and scattered waves in the volume elements, are defined by the extraordinary and ordinary indices n_e and n_0 of the medium (see, for example, Rocard,$^{(6)}$ Chatelain$^{(4)}$).

If r is the distance of the detector of the scattered light from the scattering volume, $\mathbf{p}_i$ the electric moment induced in the molecule at the centre of the volume element, l the number of molecules in the volume element and $\mathbf{0}$ the unit vector along the direction of the electric vector of the scattered component in which we are interested, we have,

$$A_i = \frac{4\pi^2 l}{\lambda^2 r}(\mathbf{p}_i \cdot \mathbf{0})G_{ii} \tag{2}$$

where $$G_u = \frac{3/u^3}{\sin u - u\cos u} \quad \text{and} \quad u = \frac{2\pi R/\lambda}{|\,n_1\mathbf{s} - n_2\mathbf{s}_0\,|}.$$

Here λ is the wavelength of light, R is the radius of the volume element, $\mathbf{s}_0$ and $\mathbf{s}$ are unit vectors along the incident and scattered directions and n_1 and n_2 the appropriate refractive indices for the scattered and incident waves. For the various cases to be discussed, the expressions for u are shown in Table 1.

TABLE 1

Orientation of the optic axis of the medium	Scattered component	Expressions for u
Case I: Normal to the plane of scattering	V_H	$\frac{2\pi R}{\lambda}(n_e^2+n_0^2-2n_en_0\cos\theta_s)^{1/2}$
	H_H	$\frac{4\pi R}{\lambda}n_0\sin(\theta_s/2)$
	V_V	$\frac{4\pi R}{\lambda}n_e\sin(\theta_s/2)$
	H_V	$\frac{2\pi R}{\lambda}(n_e^2+n_0^2-2n_en_0\cos\theta_s)^{1/2}$
Case II: along the direction of incident light	V_H	$\frac{4\pi R}{\lambda}n_0\sin(\theta_s/2)$
	H_H	$\frac{2\pi R}{\lambda}(n^2+n_0^2-2nn_0\cos\theta_s)^{1/2}$
	V_V	$\frac{4\pi R}{\lambda}n_0\sin(\theta_s/2)$
	H_V	$\frac{2\pi R}{\lambda}(n^2+n_0^2-2nn_0\cos\theta_s)^{1/2}$
Case III: In the scattering plane and perpendicular to the direction of incident light.	V_H	$\frac{2\pi R}{\lambda}(n_e^2+n_0^2-2n_en_0\cos\theta_s)^{1/2}$
	H_H	$\frac{2\pi R}{\lambda}(n^2+n_e^2-2nn_e\cos\theta_s)^{1/2}$
	V_V	$\frac{4\pi R}{\lambda}n_0\sin(\theta_s/2)$
	H_V	$\frac{2\pi R}{\lambda}(n^2+n_0^2-2nn_0\cos\theta_s)^{1/2}$

NOTE: In the above n is the extraordinary index for the scattered wave along θ_s and is given by $n^2 = n_0^2n_e^2(n_0^2\sin^2\theta_0+n_e^2\cos^2\theta_0)^{-1}$, where θ_0 is the angle between the scattering direction and the optic axis of the medium.

To calculate the induced moment $\mathbf{p}_i$, we assume that the molecules have two principal polarizabilities $\alpha_\parallel$ and $\alpha_\perp$ respectively parallel and perpendicular to the long axis of the molecules. The direction of the long axis of the molecule may be denoted by the unit vector $\mathbf{a}_i$, which also corresponds to the orientation axis of the volume element. For *p*-azoxyanisole we assume $\alpha_\parallel = C$ and $\alpha_\perp = (A+B)/2$ where A, B, C are the principal polarizabilities. If the incident electric vector $\mathbf{E}$ is represented by $E_0\mathbf{b}$ where $\mathbf{b}$ is the unit vector along $\mathbf{E}$ we have, $\mathbf{p}_i = E_0\{\alpha_\parallel(\mathbf{b}\cdot\mathbf{a}_i)\mathbf{a}_i + \alpha_\perp[\mathbf{b} - (\mathbf{b}\cdot\mathbf{a}_i)\mathbf{a}_i]\}$ and

$$\mathbf{p}_i\cdot\mathbf{0} = E_0\{\delta(\mathbf{b}\cdot\mathbf{a}_i)(\mathbf{a}_i\cdot\mathbf{0}) + (\alpha_0 - \delta/3)(\mathbf{b}\cdot\mathbf{0})\} \tag{3}$$

where $\delta = \alpha_\parallel - \alpha_\perp$ and $\alpha_0 = (\alpha_\parallel + 2\alpha_\perp)/3$. Using Eqs. (1), (2) and (3) the average intensity of anisotropic scattering per unit volume can be shown to be given by

$$I = KG_u^2\,\delta^2\{\overline{(\mathbf{b}\cdot\mathbf{a}_i)^2(\mathbf{a}_i\cdot\mathbf{0})^2} - [\overline{(\mathbf{b}\cdot\mathbf{a}_i)(\mathbf{a}_i\cdot\mathbf{0})}]^2\} \tag{4}$$

where K is a proportionality constant and the factor within the braces represents averages taken over all the volume elements. In arriving at Eq. (4), the terms involving $(\alpha_0 - \delta/3)$ and $2\,\delta(\alpha_0 - \delta/3)$ vanish owing to $(\mathbf{b}\cdot\mathbf{0})$ being a constant for a given angle of scattering and not related to the orientation of the volume elements.

The factor within the braces in Eq. (4) can be more explicitly written for the various cases by employing a Cartesian coordinate system defined by unit vectors $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$. The optic axis of the medium is taken as the direction $\mathbf{k}$. The vibration direction of the scattered light which is defined by $\mathbf{0}$ is then expressible in terms of the unit vectors $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ and the angle of scattering θ_s and Table 2 gives the details regarding the directions of $\mathbf{b}$ and $\mathbf{0}$ for the various cases in terms of $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$. We denote the direction cosines $(\mathbf{a}_i\cdot\mathbf{i})$, $(\mathbf{a}_i\cdot\mathbf{j})$, $(\mathbf{a}_i\cdot\mathbf{k})$ by α, β, γ and recognize that for the nematic phase which is uniaxial, $\overline{\alpha^2} = \overline{\beta^2} \neq \overline{\gamma^2}$; $\overline{\alpha^2\gamma^2} = \overline{\beta^2\gamma^2} \neq \overline{\alpha^2\beta^2}$ and $\overline{\alpha^4} = \overline{\beta^4} \neq \overline{\gamma^4}$. Making use of Table 2 and the above relations, the intensity expressions obtained for the various cases are given below. The constant of proportionality K involves the square of the effective electric field inside the medium. It was shown by Chandrasekhar and Madhusudana⁽⁷⁾ that in the case of nematic liquid crystals the polarization field is satisfactorily represented by a new and simple formula proposed by Vuks.⁽⁸⁾ Accordingly, the effective field here would be $(\overline{n^2}+2)/3$ times that of the external field, $\overline{n^2}$ being equal to $(n_e^2 + 2n_0^2)/3$. Hence, in the following the constant of proportionality K is the same for all cases.

Case I. Optic axis normal to the plane of scattering

$$\mathrm{V_H} = KG_u^2\,\delta^2\overline{(\alpha^2\gamma^2)} \tag{5}$$

$$\mathrm{H_H} = KG_u^2\,\delta^2\{[\overline{\alpha^4} - (\overline{\alpha^2})^2]\cos^2\theta_s + \overline{(\alpha^2\beta^2)}\sin^2\theta_s\} \tag{6}$$

$$\mathrm{V_V} = KG_u^2\,\delta^2[\overline{\gamma^4} - (\overline{\gamma^2})^2] \tag{7}$$

$$\mathrm{H_V} = KG_u^2\,\delta^2\overline{(\alpha^2\gamma^2)} \tag{8}$$

Case II. Optic axis along the direction of the incident light

$$\mathrm{V_H} = KG_u^2\,\delta^2\overline{(\alpha^2\beta^2)} \tag{9}$$

$$\mathrm{H_H} = KG_u^2\,\delta^2\{[\overline{\alpha^4} - (\overline{\alpha^2})^2]\cos^2\theta_s + \overline{(\alpha^2\gamma^2)}\sin^2\theta_s\} \tag{10}$$

$$\mathrm{V_V} = KG_u^2\,\delta^2[\overline{\alpha^4} - (\overline{\alpha^2})^2] \tag{11}$$

$$\mathrm{H_V} = KG_u^2\,\delta^2[\overline{(\alpha^2\beta^2)}\cos^2\theta_s + \overline{(\alpha^2\gamma^2)}\sin^2\theta_s] \tag{12}$$

Case III. Optic axis lying in the plane of scattering and perpendicular to incident direction

$$\mathrm{V_H} = KG_u^2\,\delta^2\overline{(\alpha^2\gamma^2)} \tag{13}$$

$$\mathrm{H_H} = KG_u^2\,\delta^2\{[\overline{\gamma^4} - (\overline{\gamma^2})^2]\cos^2\theta_s + \overline{(\alpha^2\gamma^2)}\sin^2\theta_s\} \tag{14}$$

$$\mathrm{V_V} = KG_u^2\,\delta^2[\overline{\alpha^4} - (\overline{\alpha^2})^2] \tag{15}$$

$$\mathrm{H_V} = KG_u^2\,\delta^2[\overline{(\alpha^2\gamma^2)}\cos^2\theta_s + \overline{(\alpha^2\beta^2)}\sin^2\theta_s] \tag{16}$$

Chatelain(4) gives the expressions for only Case I. In his paper the averages are represented by integrals involving the orientation distribution function. In the above, the u values to be used in G_u^2 for the various cases are those tabulated in Table 1. It may be noted that $\mathrm{V_H} = \mathrm{H_V}$ is satisfied only for Case I as is to be expected. Making use of the fact that $\overline{\alpha^2} + \overline{\beta^2} + \overline{\gamma^2} = 1$ and that $\overline{(\alpha^2 + \beta^2 + \gamma^2)^2} = 1$ and also that in the nematic phase any orientation distribution would be a function of only θ ($= \cos^{-1}\gamma$), it can be shown that in the above expressions,

$$\overline{\alpha^4} = 3\overline{\alpha^2\beta^2}; \qquad \overline{\alpha^2\beta^2} = \tfrac{1}{8}(1 - 2\overline{\gamma^2} + \overline{\gamma^4})$$

and
$$\overline{\alpha^2\gamma^2} = \tfrac{1}{2}(\overline{\gamma^2} - \overline{\gamma^4}). \tag{17}$$

Hence, the intensity expressions involve only the averages $\overline{\gamma^2}$ and $\overline{\gamma^4}$. Further, it may be noted that $\overline{\gamma^2}$ is obtainable from the order para-

TABLE 2

Orientation of the optic axis of the medium: **k**	Direction of incident light	Scattered component	**b**	**0**
Case I Normal to the plane of scattering	**i**	V_H	**j**	**k**
	i	H_H	**j**	**j** $\cos\theta_s$ − **i** $\sin\theta_s$
	i	V_V	**k**	**k**
	i	H_V	**k**	**j** $\cos\theta_s$ − **i** $\sin\theta_s$
Case II Along the direction of the incident light	**k**	V_H	**j**	**i**
	k	H_H	**j**	**j** $\cos\theta_s$ + **k** $\sin\theta_s$
	k	V_V	**i**	**i**
	k	H_V	**i**	**j** $\cos\theta_s$ + **k** $\sin\theta_s$
Case III In the scattering plane and perpendicular to the direction of incident light	**i**	V_H	**k**	**j**
	i	H_H	**k**	**k** $\cos\theta_s$ + **i** $\sin\theta_s$
	i	V_V	**j**	**j**
	i	H_V	**j**	**k** $\cos\theta_s$ + **i** $\sin\theta_s$

meter S calculable from the birefringence of the medium using the well-known relation that $\overline{\gamma^2} = (2S+1)/3$.

3. Analysis of the Experimental Data

In our calculations we make use of the values of $n_e = 1.819$ and $n_0 = 1.568$ obtained from the measurements of Chatelain and Germain(9) for p-azoxyanisole. Calculations of the S factors for p-azoxyanisole at various temperatures were made by Chandrasekhar and Madhusudana(7) using the Vuk's formula.(8) At 125 °C the values of S and $\overline{\gamma^2}$ are respectively 0.4618 and 0.6412. The relative intensities V_H, H_H, etc., for cases I and II as reported by Chatelain are shown in Table 3. Case III has not so far been experimentally investigated. The values of V_H and H_H (for Case I) shown, are the revised values from Ref. 2. All the other values are from Ref. 1 and require a correction by a factor of $\cos\theta_s$ as pointed out by Chatelain in his later paper, Ref. 4. Accordingly, this correction will be made for purposes of the analysis of these data.

If the orientations of the spherical volume elements are mutually independent of one another it follows from Eq. (5) that the intensity V_H (Case I) should be proportional to G_u^2. Chatelain(4) has estimated

TABLE 3

Components	θ_s										
	8°	9°	11°	15°	20°	25°	30°	40°	50°	160°	172°
V_H†	137	100	75	46	27	—	13	—	5	5	3.5
H_H†	15	13	11	9	6.4	—	5.1	—	3.7	—	—
V_V†	18	16	13	10.5	7.5	6	5.8	4.9	4.9	—	—
V_H‡	86	73	53	32	20	14	11	8.5	8	4.2	3.5
H_H‡	22	19	16	11	8.5	8	7	6.8	6.7	—	—
V_V‡	14	12	10.5	7	5.2	4.5	4	3.3	3.1	—	—
H_V‡	67	58	43	24	15	10	8	5.5	5	3.9	4.2

† Optic axis normal to the plane of scattering.
‡ Optic axis along the incident direction.

from the ratio of the observed intensities of the scattering at θ_s and $(180-\theta_s)$ that the radius of the volume elements should be about 0.1μ. Four pairs of such ratios are reported by Chatelain and from these it was deduced by us that if R/λ, ($\lambda = 5893$ Å) were to lie between 0.18 and 0.13 the correct order of magnitude of the ratio would be obtained. However, it was found on calculation that no one particular value of R/λ when used for calculating G_u^2, would give a straight line plot for the data of the intensities V_H against G_u^2. In fact, the rapid increase of intensity in the nearly forward directions could not be accounted for, because of the slow variation of G_u^2 with θ_s. Evidently, the assumption made in the theory that the orientations of the neighbouring volume elements are independent of each other cannot be valid for a dense anisotropic medium. A large proportion of the variation of intensity with the angle of scattering probably arises due to the correlation between the orientations of the molecules in neighbouring volume elements. Debye(10) has discussed an analogous problem in the case of colloidal scattering by solutions which are neither too dilute nor too strong and shown that the intensity expression would involve an additional form factor—which is a function of θ_s—arising from the phase correlation in the scattering from the different particles. However, his formula cannot be used here owing to its validity being restricted to cases where the concentrations are not too high. In addition to the above effect, there is also the possibility of the enhancement of intensity by multiple scattering; this is a complex problem to treat theoretically, especially in the case of anisotropic media.

In the following, we show that the present theory enables us to analyse the experimental data and obtain the average value $\overline{\gamma^4}$. Let us consider a system of oriented spherical groups of molecules with correlation in their orientations. Let $\overline{\gamma^2}$ and $\overline{\gamma^4}$ be the averages for this system. The intensity of anisotropic scattering for this system may be denoted by I (dependent) $= f(\theta_s)$. Now, for a hypothetical system with the same averages $\overline{\gamma^2}$ and $\overline{\gamma^4}$, but in which there are no orientational correlations, the intensity of anisotropic scattering would be different. Let I_{ind} be equal to a function $g(\theta_s)$. The theory developed by us gives $g(\theta_s)$. We can write,

$$(I_{\text{dep}})/(I_{\text{ind}}) = f(\theta_s)/g(\theta_s) = h(\theta_s)$$

and $I_{\text{dep}} = f(\theta_s) = g(\theta_s)h(\theta_s)$. If the form of the function $(I_{\text{dep}})/g(\theta_s)$ could be obtained at least over a range of θ_s where there are no discontinuities in the functions, it would enable us to calculate the average value of $\overline{\gamma^4}$ appearing in $g(\theta_s)$.

Chatelain had earlier found that he could represent the various observed intensities by an empirical formula $I = A\ (\sin\theta_s)^x$ where A and x are constants, x being negative. The values of x for the different cases are in the range of -1 to -2. There are also other instances of correlated systems, where the function for the intensity takes this form. For example, it is well-known(11) that in the case of critical opalescence where strong correlations exist between the fluctuations of the neighbouring volume elements, the intensity formula involves a factor $kT/[\beta^{-1} + \{(2\pi g/\lambda')\sin\frac{1}{2}\theta_s\}^2]$ and β^{-1} tends to zero near the critical point. Another example which may be cited here is the case of medium density polyethylene wherein the orientational correlations between the crystallites give rise to very strong small angle scattering. We find that the data for the scattered intensity H_V reported by Stein(12) can be well represented by the function $(\sin\theta_s)^x$ with $x = -2.64$. Therefore it appeared that $h(\theta_s)$ itself could most probably be represented by $(\sin\theta_s)^x$.

We have analysed the data for V_H (case I) by plotting $\log\ (V_H/G_u^2)$ versus $\log\ (\sin\theta_s)$ for various values of (R/λ). It was found that a value of $(R/\lambda) = 0.141$ gave the best straight line fit, as shown in Fig. 1. The data for H_V (case I) are not reproduced here in a graphical plot since H_V is experimentally found to be equal to V_H. The data for V_H (case II) also gave a reasonable straight line fit as

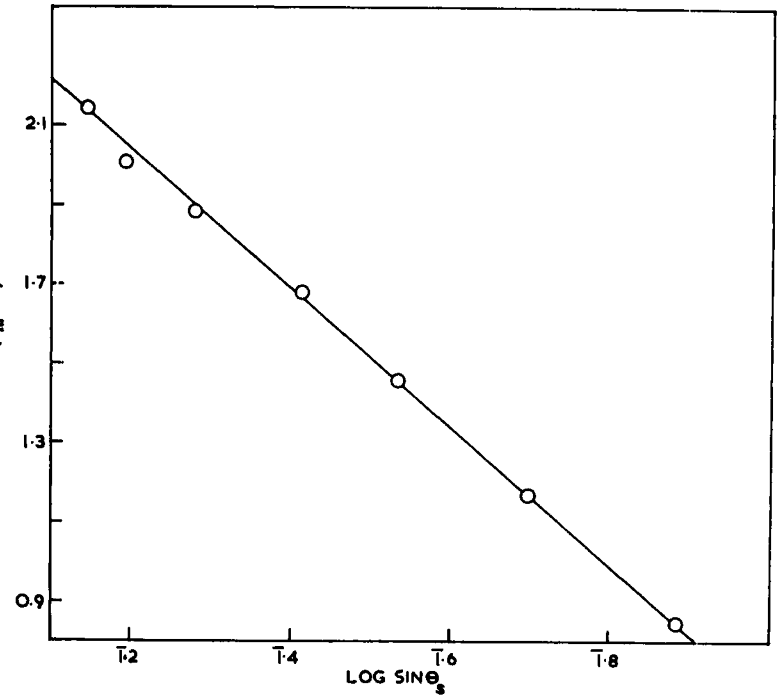

Figure 1.

shown in Fig. 2, again in confirmation of the choice of the factor as $(\sin \theta_s)^x$. We have adopted the same value of $(R/\lambda) = 0.141$ for calculating the G_u^2 appearing in all the cases analysed here. Further confirmation of the validity of our approach is obtained from the analysis of the data for H_H (cases I and II) and H_V (case II); for these cases the $g(\theta_s)$ itself is more complicated and involves also functions like $[\overline{(\alpha^2\beta^2)} \cos^2 \theta_s + \overline{(\alpha^2\gamma^2)} \sin^2 \theta_s]$ and these will have to be calculated for the different angles before the analysis is made.

The cases of V_V and H_H evidently involve also isotropic scattering, although conceivably it is a small value. The intensity of isotropic scattering, which arises due to density fluctuations, may be considered as proportional to α_0^2 where $\alpha_0 = (\alpha_\parallel + 2\alpha_\perp)/3$. For the intensities V_V (I and II cases) the isotropic scattering should be representable therefore by a constant C, so that the anisotropic part of scattering is $[V_V \text{ (obs)} - C]$. In the case of H_H on the other hand, the isotropic scattering which is dependent on θ_s should be repre-

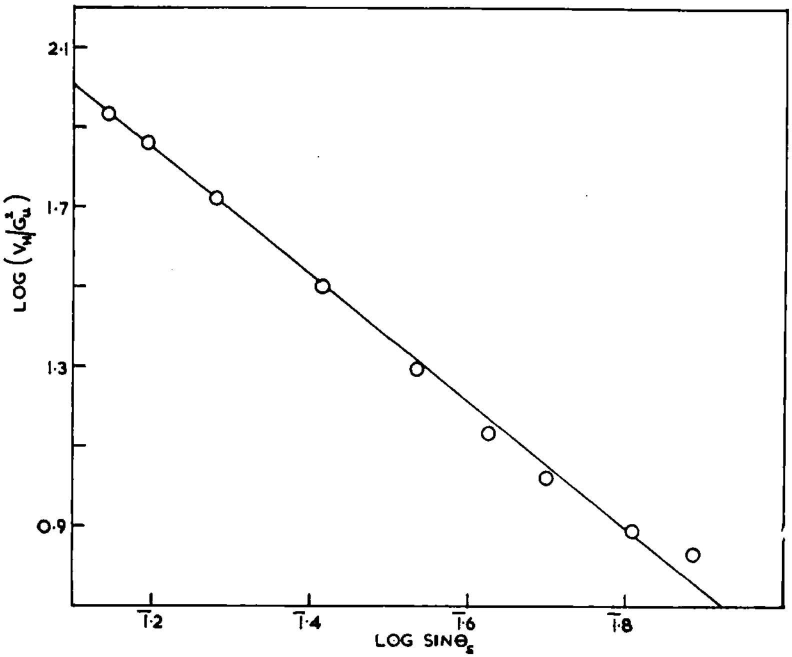

Figure 2.

sentable by $C\cos^2\theta_s$, so that the anisotropic part of the scattering becomes equal to $[\mathrm{H_H}\,(\mathrm{obs}) - C\cos^2\theta_s]$. On including the empirical factor, the observed values of the intensities may be expressed as follows:

Case I:
$$\mathrm{V_H} = \mathrm{H_V} = KG_u^2\,\delta^2(\overline{\alpha^2\gamma^2})(\sin\theta_s)^x \tag{18}$$

$$\left.\begin{aligned} \mathrm{H_H} - C\cos^2\theta_s &= KG_u^2\,\delta^2 F_1(\theta_s)(\sin\theta_s)^x \\ \text{where}\quad F_1(\theta_s) &= [\overline{\alpha^4} - (\overline{\alpha^2})^2]\cos^2\theta_s + \overline{\alpha^2\beta^2}\sin^2\theta_s \end{aligned}\right\} \tag{19}$$

$$(\mathrm{V_V} - C) = KG_u^2\,\delta^2[\overline{\gamma^4} - (\overline{\gamma^2})^2](\sin\theta_s)^x \tag{20}$$

Case II:
$$\mathrm{V_H} = KG_u^2\,\delta^2(\overline{\alpha^2\beta^2})(\sin\theta_s)^x \tag{21}$$

$$\left.\begin{aligned} \mathrm{H_H} - C\cos^2\theta_s &= KG_u^2\,\delta^2 F_2(\theta_s)(\sin\theta_s)^x \\ \text{where}\quad F_2(\theta_s) &= [\overline{\alpha^4} - (\overline{\alpha^2})^2]\cos^2\theta_s + (\overline{\alpha^2\gamma^2})\sin^2\theta_s \end{aligned}\right\} \tag{22}$$

$$(\mathrm{V_V} - C) = KG_u^2\,\delta^2[\overline{\alpha^4} - (\overline{\alpha^2})^2](\sin\theta_s)^x \tag{23}$$

$$\left.\begin{aligned} \mathrm{H_V} &= KG_u^2\,\delta^2 F_3(\theta_s)(\sin\theta_s)^x \\ \text{where}\quad F_3(\theta_s) &= (\overline{\alpha^2\beta^2})\cos^2\theta_s + (\overline{\alpha^2\gamma^2})\sin^2\theta_s \end{aligned}\right\} \tag{24}$$

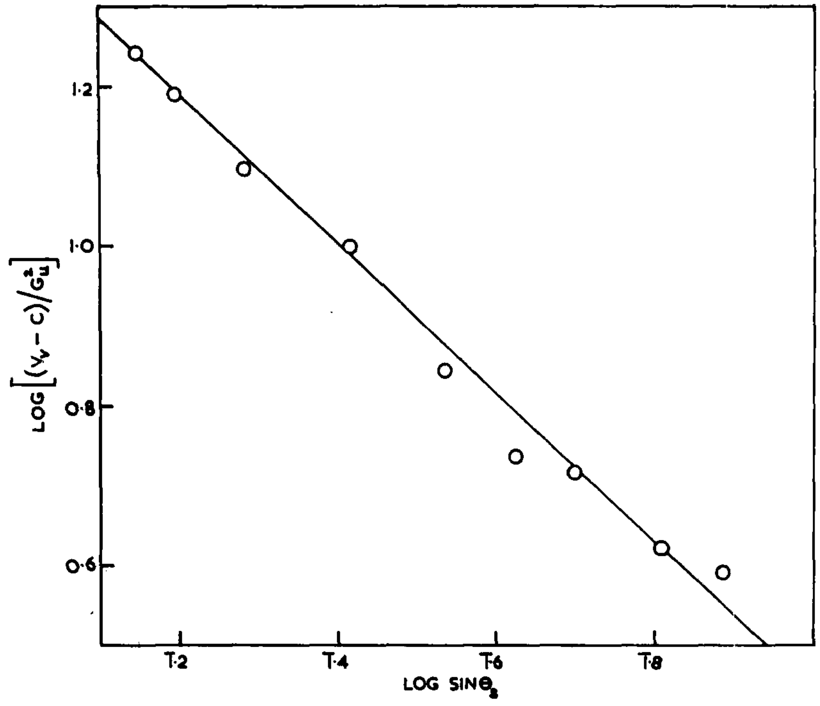

Figure 3.

In the above, the intensities V_H, H_H etc. are the observed intensities. As already mentioned, Eqs. (18) and (21) are verified from the graphical plots shown in Figs. 1 and 2. Graphical plots of $\log[(V_V - C)/G_u^2]$ versus $\log(\sin\theta_s)$ for Cases I and II were made and it was found that with $C = 0.5$, straight line plots were obtainable as shown in Figs. 3 and 4. Before proceeding to the other three cases which involve $F_1(\theta_s)$, $F_2(\theta_s)$, $F_3(\theta_s)$, a calculation of $\overline{\gamma^4}$ was made, using the graphical plots of Figs. 1, 3 and 4. If we write Eqs. (18), (20) and (23) in the form of $V_H/G_u^2 = A_1(\sin\theta_s)^{x_1}$, $(V_V - C)/G_u^2 = A_2(\sin\theta_s)^{x_2}$ and $(V_V - C)/G_u^2 = A_3\,(\sin\theta_s)^{x_3}$, the corresponding constants x and A can be determined from the slopes and intercepts of Figs. 1, 3 and 4. Then, we have from Eqs. (18), (20) and (23),

$$\frac{A_1}{A_2} = \frac{\overline{\alpha^2\gamma^2}}{\overline{\gamma^4} - (\overline{\gamma^2})^2} \tag{25}$$

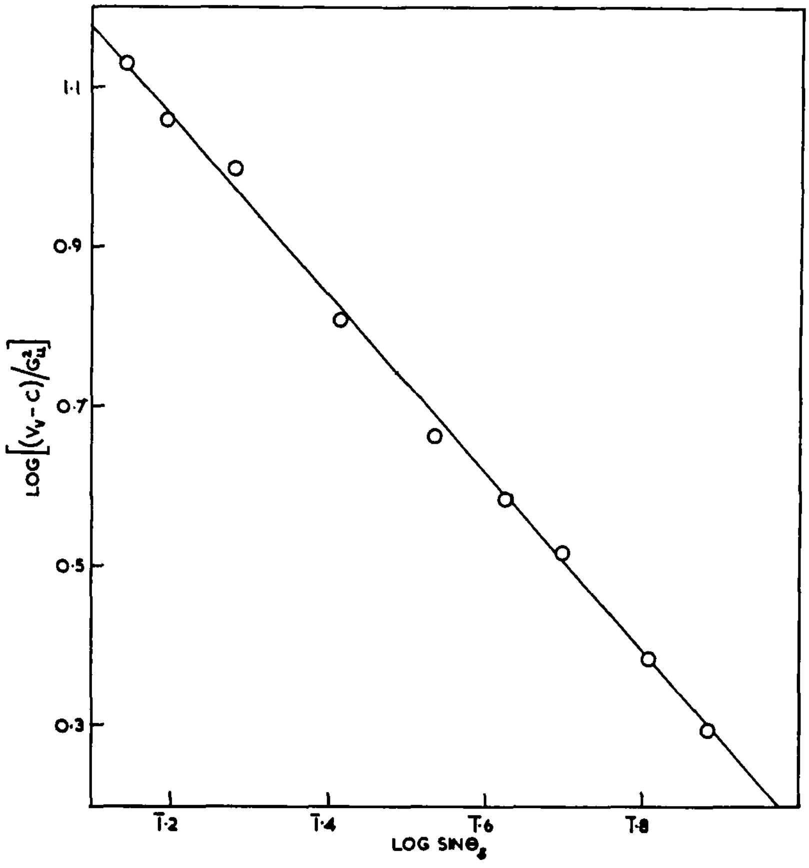

Figure 4.

and

$$\frac{A_1}{A_3} = \frac{\overline{\alpha^2\gamma^2}}{\overline{\alpha^4} - (\overline{\alpha^2})^2} \tag{26}$$

Using Eq. (17) and the value of $\overline{\gamma^2} = 0.6412$, two values for $(\overline{\gamma^4})$ were calculated and found to be 0.466 and 0.453 respectively. The values are in reasonable agreement, considering that the intensity data are accurate to about 10%. Similar calculations were made using Eqs. (18) and (21), but the value of $\overline{\gamma^4}$ turns out to be about 0.4. This discrepancy arises presumably because in the case of specimens used in Case II the orientation of the optic axis (parallel to the thickness of the specimen) was easily disturbed and the optic axis

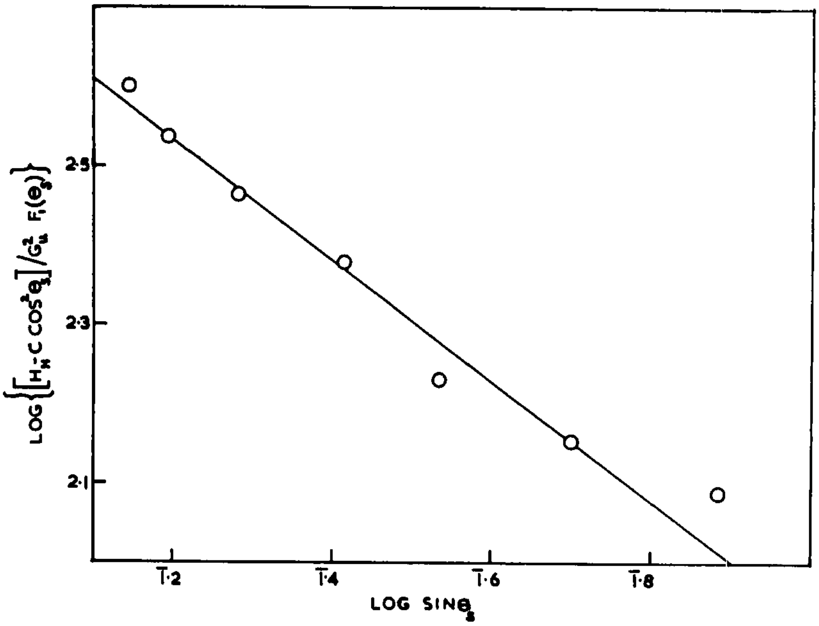

Figure 5.

was only approximately defined, as remarked by Chatelain.(1) Hence, we prefer to use the value of $\overline{\gamma^4} = 0.466$, calculated wholly from Case I, for purposes of our calculation of $F_1(\theta_s)$, $F_2(\theta_s)$ and $F_3(\theta_s)$ in the following.

It may be remarked here that the values of $\overline{\gamma^4}$ calculated from Eqs. (25) and (26) are in reasonable agreement with the value of 0.49 (at 125 °C) calculated by Chandrasekhar and Madhusudana,(13) in connection with the statistical theory of orientational order in nematic liquid crystals, proposed by them. We are thankful to them for providing this value which has not been included in their paper.

Graphical plots of

$$\log\,[(\mathrm{H_H} - C\cos^2\theta_s)/G_u^2F_1(\theta_s)],$$

$$\log\,[(\mathrm{H_H} - C\cos^2\theta_s)/G_u^2F_2(\theta_s)]$$

and $\log\,[\mathrm{H_V}/G_u^2F_3(\theta_s)]$ versus $\log(\sin\theta_s)$ verifying Eqs. (19), (22) and (24) are shown in Figs. 5, 6 and 7. The fit obtained in the above three cases shows again that the value of $\overline{\gamma^4}$ obtained from the analysis of the data is a reasonably good estimate.

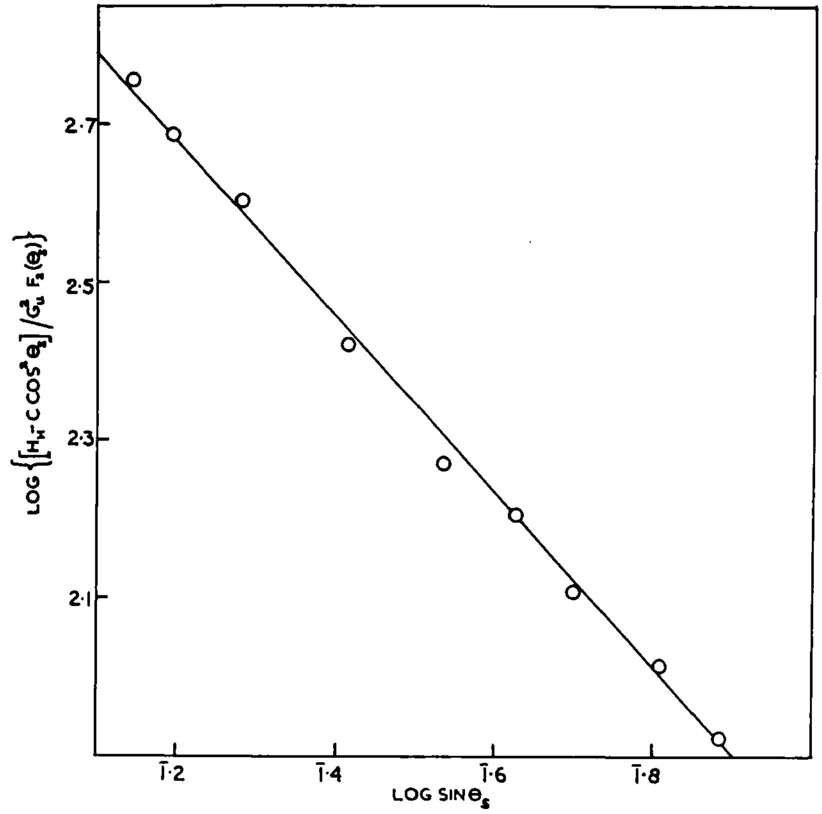

Figure 6.

It may be remarked here that the intensity data of V_H (Case I) for backward scattering(2) cannot be represented accurately using the same empirical factor $(\sin \theta_s)^x$, although the correct order of magnitude may be obtained at about $\theta_s = 165°$. This shows that the empirical factor would not be valid for large angles of scattering. However, we wish to stress that for all the seven cases analysed, the (R/λ) value used is the same, the same form of the empirical factor is used, and that the value of $\overline{\gamma^4}$ is in reasonable agreement with the value independently calculated by Chandrasekhar and Madhusudana. Besides, Gravatt and Brady(14) have recently reported from their studies on the small angle X-ray scattering with *p*-azoxyanisole, that the correlation length for molecular ordering, at the nematic–isotropic transition point, is about 1900 Å. This is in satisfactory

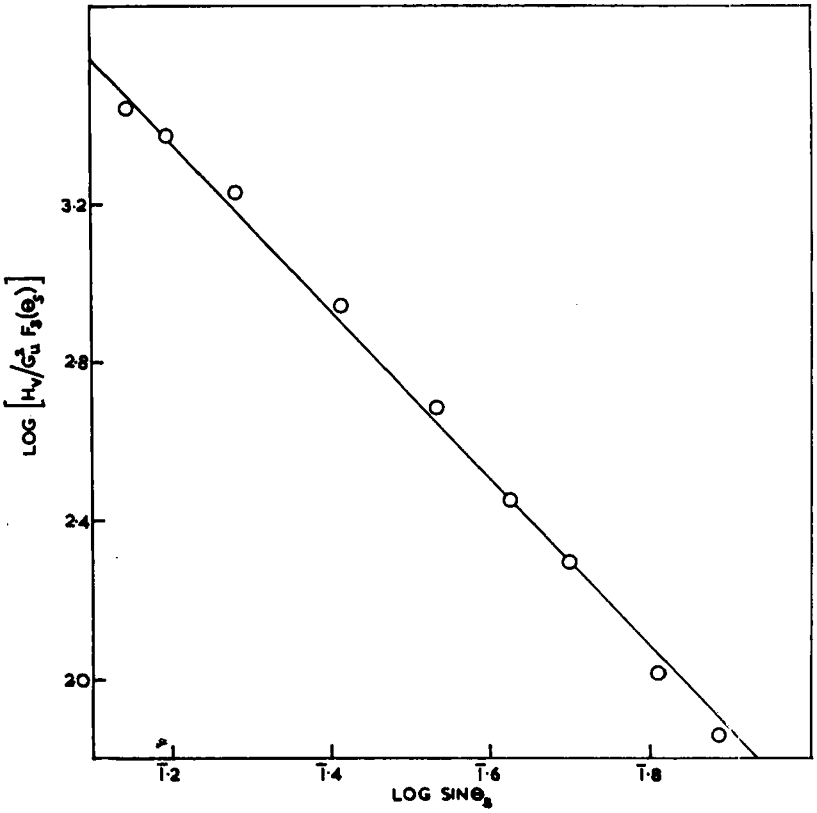

Figure 7.

agreement with the value of 1600 Å for the diameter of the spherical volume elements discussed in this paper. In the foregoing analysis we have not considered the effect of scattering by unattached molecules, as we presume that it is likely to be negligible and further because it would not give rise to strong dependence of the intensities on the angle of scattering. Although one can envisage the possibility of accounting for all the observed facts in terms of correlations between the orientations of the molecules, the use of correlation functions involves a number of constants and can be fruitful only if the intensities of scattering are available over a very wide range of angles for the different cases.

In the case of the nematic phase of parabutyloxybenzoic acid also the intensity data for V_H is available and it is possible to reasonably represent them by a graphical plot of log (V_H/G_u^2) versus log $(\sin \theta_s)$. But, in the absence of data with regard to the other components of intensities, we have not gone into that case in detail.

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