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Liquid Crystals

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To cite this Article Yakovenko, S. Ye.(1991) 'Refractometric studies of mesogenic molecules in isotropic solutions', Liquid Crystals, 10: 6, 741 — 750

To link to this Article: DOI: 10.1080/02678299108036449

URL: http://dx.doi.org/10.1080/02678299108036449

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LIQUID CRYSTALS, 1991, VOL. 10, NO. 6, 741–750

Refractometric studies of mesogenic molecules in isotropic solutions

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(*Received 16 April 1991; accepted 7 June 1991*)

The Lorenz–Lorentz equation for binary isotropic mixtures, consisting of anisotropic molecules, has been derived using the point-dipole approximation taking into account only pair molecular correlations. This permits the calculation of the effect of molecular correlations on the refractive index. Special attention has been paid to the case of infinite dilution in the solvents consisting of isotropic molecules, where an experimental check of the equations is possible. The specific refraction of some solutes with different molecular polarizability anisotropy and polarity has been studied in various solvents. It has been shown, that the main theoretically predicted features are observed in these experiments, but for a quantitative comparison information on the two-particle distribution function is needed.

1. Introduction

The derivation of the Lorenz–Lorentz equation is based on two main suppositions first the point polarizability approximation and secondly the neglect of molecular correlations [1]. In consequence this equation is strictly valid only for ideal cubic lattices, i.e. it is more or less valid for cubic crystals. Even for isotropic liquids, consisting either of spherically symmetric molecules, or of molecules with other symmetry, there are corrections to this equation originating from the local ordering [2, 3]. These corrections increase with the lowering of the molecular symmetry and make it necessary even to change the Lorenz local field correction by a more general one when the deviations from isotropic distribution become long range, i.e. for the case of the solid or liquid-crystalline state [4].

The validity of the Lorenz–Lorentz equation for the relation between the polarizability of a molecule and the refractive index (or dielectric constant in the high frequency limit) of dense liquids has been the subject of many experimental and theoretical investigations. The detailed statistical mechanical theory was formulated originally by Kirkwood [5] and Yvon [6]. They obtained the generalized Lorenz–Lorentz equation as a virial expansion and that is why it is not satisfactory at high densities. Later several attempts have been made to resume this series expansion in order to improve its clustering properties and to generalize it to the case of anisotropic molecules [3, 7–11]. It was also shown, that this theory can be reformulated to avoid the point polarizability approximation [12] for molecules or to include the contribution of higher multipoles [13] and the effect of molecular interactions on the molecular polarizability [14], which is considered constant in the classical theory.

Experimentally deviations from the Lorenz–Lorentz equation were observed even for noble gases, such as argon, at high pressures [15]. It could be supposed, that for elongated molecules, for example mesogenic ones, these corrections must be substantially larger and the only question is whether it is possible to analyse their contribution without a precise knowledge of the distribution function. In order to extract these corrections from the bulk value of the refractive index, here it is proposed to study the concentration dependence of the specific refraction of mesogens in solvents, consisting of globular molecules. In contrast to the isotropic phase of the mesogen, in such dilute solutions the corrections to the Lorenz–Lorentz equation are minimized.

The plan of the paper is as follows. In the second section the generalized Lorenz–Lorentz equation is derived for a binary mixture and special attention is paid to the limit of infinite dilution. Experimental details are described in the third section. In the last section after the outlining of the analysis of the experimental data, the variation of the specific refraction of some mesogens in different solvents is considered and compared with the predictions of the theory.

2. Theoretical background

The generalized Lorenz–Lorentz equation for an isotropic liquid consisting of anisotropic molecules lacking permanent dipoles in the point polarizability approximation and taking into account only pair molecular correlations may be written according to [3] as

$$\frac{\varepsilon-1}{\varepsilon+2}=\tfrac{4}{3}[\langle\alpha(\mathbf{r})\rangle+K], \tag{1}$$

where

$$K=\int d\mathbf{r}'\langle\delta\alpha(\mathbf{r})T(\mathbf{r}-\mathbf{r}')\delta\alpha(\mathbf{r}')\rangle. \tag{2}$$

Here

$$\alpha(\mathbf{r})=\sum_{i}^{N}\alpha_i\delta(\mathbf{r}-\mathbf{r}_i), \tag{3}$$

is the unaveraged, fluctuating polarizability density, and $\delta\alpha$ is its fluctuating part. ε is the dielectric permittivity of the liquid, and the averaging is performed in thermal equilibrium (the trace of all tensorial properties is implied). For uniform liquids, consisting only of one sort of symmetric top molecules

$$\langle\alpha(\mathbf{r})\rangle=\alpha\rho, \tag{4}$$

where α and ρ are the average the polarizability and the number density, respectively. The correction to the Lorenz–Lorentz equation [3] is

$$K=\tfrac{4}{15}\rho^2[\alpha\Delta\alpha\tau_{20}-\tfrac{1}{30}(\Delta\alpha)^2\tau_{22}], \tag{5}$$

where

$$\alpha=\tfrac{1}{3}(\alpha_{zz}+2\alpha_{xx}),\qquad \Delta\alpha=\alpha_{zz}-\alpha_{xx},$$

and

$$\tau_{20}=\int\frac{4\pi r dr}{r}g_{200}(r), \tag{6}$$

$$\tau_{22}=\int\frac{4\pi r dr}{r}[2g_{222}(r)+g_{221}(r)-g_{220}(r)]. \tag{7}$$

Here $g_{LMN}(r) = g_{LNO,MNO}(r)$ are the coefficients of the expansion of the pair distribution function in an infinite series of Wigner rotation matrices

$$g(r_{12}, \Omega_1, \Omega_2) = \sum_{N(1)} \sum_{N(2)} g_{N(1),N(2)}(r_{12}) D_{N(1)}(\Omega_1) D_{N(2)}(\Omega_2), \qquad (8)$$

where Ω_i indicates the orientation of the ith molecule and $r = |\mathbf{r}|$.

Equations (2)–(7) give the corrections to the Lorenz–Lorentz equation only to second order of density. For spherically symmetric molecules the polarizability anisotropy equals zero and, as can be seen from equation (5), K vanishes. In this case the non-vanishing corrections to the Lorenz–Lorentz equation are of order $(\alpha\rho)^3$ [2]. Taking into account that for ordinary liquids $\alpha\rho \ll 1$ we can suppose that for spherically symmetric molecules the corrections are much smaller than for symmetric top molecules and we shall neglect them.

A similar approach can be used to obtain the generalized Lorenz–Lorentz equation for mixtures. We start from equations (1) and (2), because during the derivation of them no assumptions have been made about the composition of the liquid. For mixtures consisting of S components equation (3) for the polarizability density must be rewritten in the form

$$\alpha(\mathbf{r}) = \sum_{s=1}^{S} \sum_{i=1}^{Ns} \alpha_i^s \delta(\mathbf{r} - \mathbf{r}_i), \qquad (9)$$

where $\Sigma N_s = N$. To evaluate the averaged polarizability density and correction K we integrate equations (2) and (3) over $\mathbf{r}$ with the substitution of equation (9) and divide them by V. Since the equilibrium average for uniform liquids is independent of $\mathbf{r}$, the result is

$$\langle \alpha(r) \rangle = \sum_{s=1}^{S} \alpha^s \rho^s = \rho \sum_{s=1}^{S} \alpha^s C_s, \qquad (10)$$

$$K = \frac{1}{V} \sum_{s=1}^{S} \sum_{i=1}^{Ns} \sum_{p=1}^{P} \sum_{j=1}^{Np} \langle \delta\alpha_i^s T_{ij} \delta\alpha_j^p \rangle, \qquad (11)$$

where C_s is molar concentration. For two component systems in the limit of dilute solutions ($C_2 \to 0$) when solute–solute interactions are not taken into account expression (11) reduces to

$$K = \frac{1}{V} N(N-1)[C_2 C_1 \langle \delta\alpha_1^1 T_{12} \delta\alpha_2^2 \rangle + C_1^2 \langle \delta\alpha_1^1 T_{12} \delta\alpha_2^1 \rangle]. \qquad (12)$$

When the solvent consists of spherically symmetric molecules the last term in the brackets is zero (in all other cases it complicates concentrational dependence of the refractive index substantially). In this case the Lorenz–Lorentz equation takes the form

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3} [\rho\alpha_1 C_1 + (\rho\alpha_2 + C_1 K^{(2)}) C_2], \qquad (13)$$

and the concentration independent $K^{(2)}$ term can be evaluated by introducing the molecular two particle density, distribution and correlation functions in order to deal with fluctuating values

$$\langle \ldots \rangle = \frac{1}{N^2} \int dR_1 dR_2 (\ldots) \rho^{(2)}(R_1, R_2), \qquad (14)$$

$$g(R_1, R_2) = \frac{\Omega^2}{\rho^2} \rho^{(2)}(R_1, R_2), \tag{15}$$

$$h(R_1, R_2) = g(R_1, R_2) - 1, \tag{16}$$

$$K^{(2)} = \frac{\rho^2}{V(8\pi^2)^2} \int dR_1 dR_2 h(R_1, R_2)[\alpha_1\alpha_2(T_{12}^{zz}) + \alpha_1(T_{12}\Delta\alpha_2)^{zz}], \tag{17}$$

where $R_i = \{\mathbf{r}_i, \Omega_i\}$, and Ω_i is the set of three Euler angles, so that in the general case

$$\Omega = \int d\Omega_i = 8\pi^2.$$

Expanding the distribution and correlation functions in an infinite series of Wigner rotation matrices we can perform almost all of the integrations in equation (17) in the same way as for the one component case in [3]; this gives

$$K^{(2)} = \tfrac{2}{15}\alpha_1 \rho^2 \Delta\alpha_2 \tau_{20}. \tag{18}$$

During the integration the normalization properties of the Wigner rotation matrices are used. The first term in the brackets of equation (17) vanishes after integration due to the isotropy of the sample.

For elongated molecules the polarizability anisotropy is usually positive and τ_{20} is negative [3]. As a result the correction to the Lorenz–Lorentz equation in this case reduces the apparent molecular polarizability which can be determined experimentally.

3. Experimental

The refractive index of liquid mixtures has been measured with an Abbe refractometer IRF-454B with an accuracy of ±0·0003. Density measurements were performed with a self-constructed pycnometer, calibrated with distilled water taking into account the thermal expansion of the pycnometer itself. Special precautions have been made to prevent evaporation of the mixtures. The relative error was ±0·0005. The concentration was determined by weight measurements with an accuracy ±0·1 per cent. This was the main source of error in the specific refraction calculations, especially at low concentrations. Most of the studies were performed with 4-*n*-pentyl-4′-cyanobiphenyl (5CB) produced by Reachim without further purification as well as cyclohexene, hexylbenzene and benzonitrile. Tetrachloromethane and benzene were dried additionally. 4-*n*-Pentyl-4′-cyanophenylcyclohexyl (5PCH), supplied by Merck, and 4-*n*-pentyl-4′-methylbiphenyl (51B), supplied privately by a chemical group, were used without further purification. The refractive indices and densities at some temperatures of the substances under investigation are summarized in the table. The data for cyclohexane, tetrachloromethane, benzene, 5CB and 5PCH agree with that accessible in the literature [16].

4. Results and discussion

In order to analyse the effect of the corrections to the Lorenz–Lorentz equation we have calculated the specific refraction for the set of elongated molecules in solvents consisting of spherical symmetrical molecules at different concentrations

$$R_2 = \frac{1}{P_2}(R_{\text{solution}} - P_1 R_1), \tag{19}$$

Refractometric and volumetric data of the studied substances.

Compound	$T/°C$	$d/10^3\,kg\,m^{-3}$	n
Cyclohexane	16·5	0·7819	1·4280
Cyclohexane	21	0·8175	1·4471
Tetrachloromethane	21	1·5914	1·4601
Benzene	16	0·8826	1·5031
Hexylbenzene	17	0·8624	1·4893
Benzonitrile	16	1·0040	1·5298
51B	56	0·9352	1·5523
5CB	40	1·0056	1·5839
5PCH	59·7	0·9325	1·5083

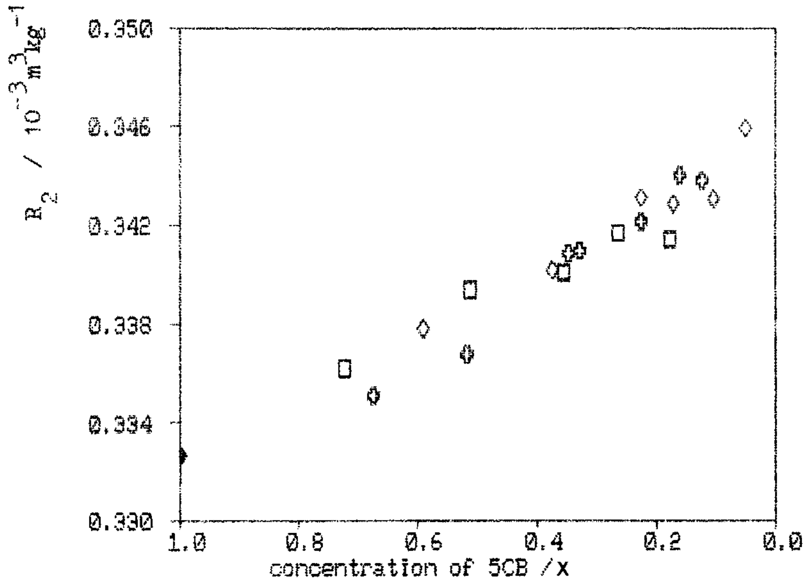

Figure 1. Concentration dependence of the specific refraction of 5CB in various solvents consisting of globular molecules: (+) CCl_4, (◇) cyclohexane, (□) cyclohexene. The concentration of 5CB is represented by the weight fraction (x).

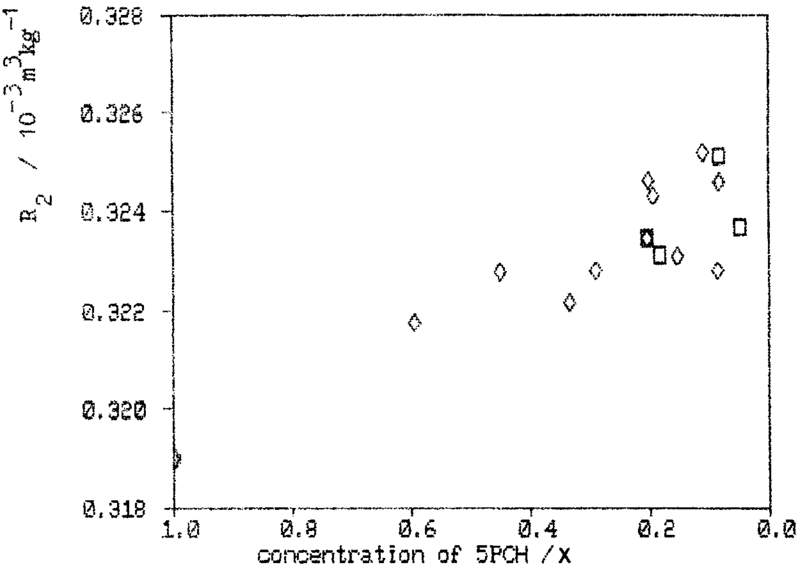

Figure 2. Concentration dependence of the specific refraction of 5PCH in various solvents consisting of globular molecules: (□) CCl_4, (◇) cyclohexane. The concentration of 5PCH is represented by the weight fraction (*x*).

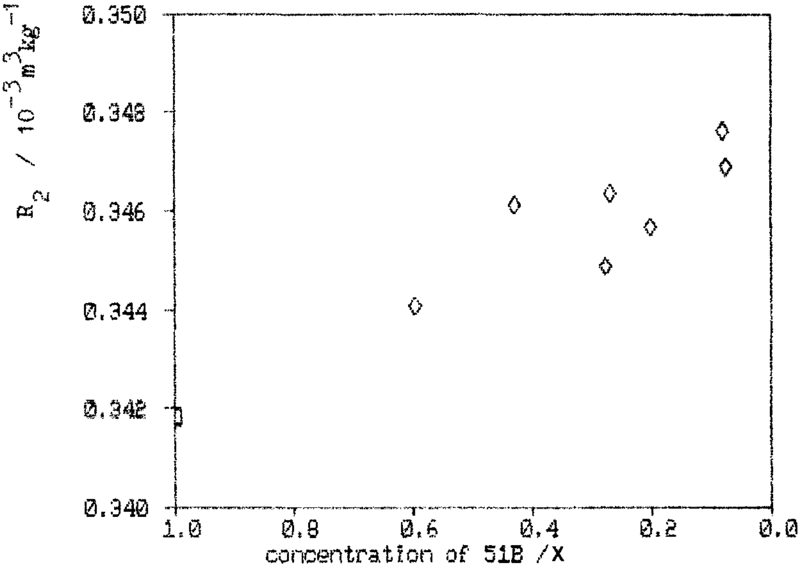

Figure 3. Concentration dependence of the specific refraction of 51B in cyclohexane. The concentration of 51B is represented by the weight fraction (*x*).

where R_1 and R_2 are the specific refractions of the solute and solvent, respectively and P_i is the weight concentration. Specific refractions of the solutions and the solvents were determined from the refractive index and density measurements

$$R=\frac{1}{d}\frac{n^2-1}{n^2+2}. \tag{20}$$

As we can see from the theoretical analysis, the specific refraction of elongated molecules in both the pure liquid and the limit of infinite dilution

$$R_2^p=\frac{4\pi}{3}\frac{\alpha^2}{m_2}\left[1+\frac{4}{15}\rho_2\Delta\alpha_2\tau_{20}-\frac{2\rho_2(\Delta\alpha)^2}{225\alpha}\tau_{22}\right], \tag{21}$$

$$R_2^d=\frac{4\pi}{3}\frac{\alpha^2}{m_2}\left[1+\frac{2}{15}\frac{\alpha_1\rho_1}{\alpha_2\rho_2}\rho_2\Delta\alpha_2\tau_{20}\right], \tag{22}$$

differs from the Lorentz result

$$R=\frac{4\pi}{3}\frac{\alpha}{m}, \tag{23}$$

where ρ_i is the number density of the solute and the solvent and m is the molecular mass. From equations (21) and (22) we can see, that after such determination all corrections due to orientational correlations (in solvents consisting of spherically symmetric molecules) are included in the specific refraction of the anisotropic molecules. In fact, from figures 1–3 we can see a nearly linear concentration dependence of the specific refraction for different elongated molecules in various spherical solvents.

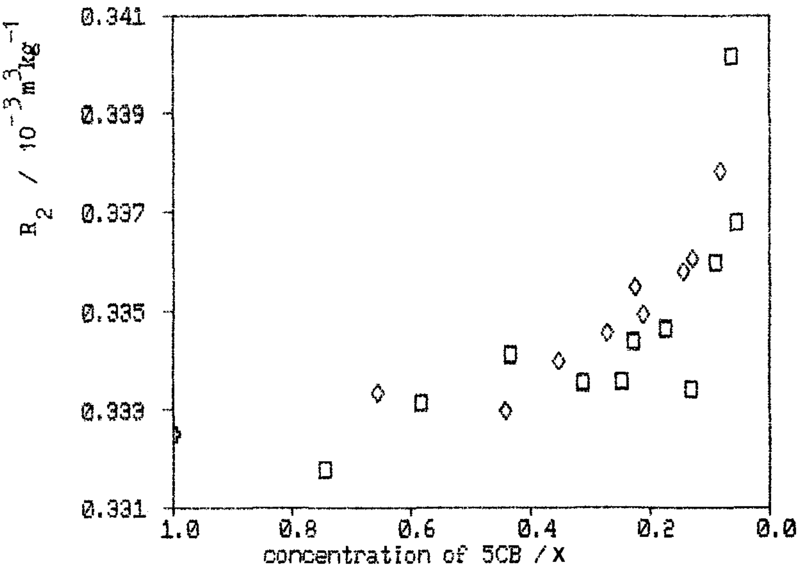

Figure 4. Concentration dependence of the specific refraction of 5CB in various solvents, consisting of weakly elongated molecules: (◇) benzonitrile, (□) *n*-hexylbenzene. The concentration of 5CB is represented by the weight fraction (*x*).

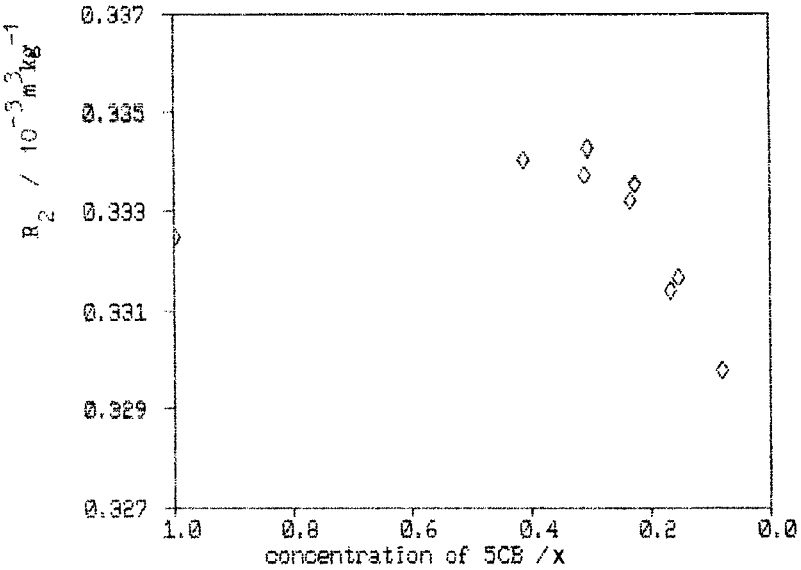

Figure 5. Concentration dependence of the specific refraction of 5CB in benzene. The concentration of 5CB is represented by the weight fraction (x).

We can summarize the main features of the observed phenomenon as follows:

(i) the specific refraction variation is observed both in polar (5CB, 5PCH) and in non-polar (51B) substances, so it is evident, that it cannot be attributed to the existence of dimers or other aggregates in polar mesogens [17];

(ii) its behaviour, within the experimental accuracy, is independent of the solvent nature, and the size of the spherical molecules, so we can be sure that in our case specific interactions with the solvent do not effect the polarizability;

(iii) the slope of this concentration dependence correlates with the molecular polarizability anisotropies, evaluated in [18] (it is likely that the polarizability anisotropy of 51B is also smaller than that of 5CB); the proportionality of the correction term with τ_{20} to the polarizability anisotropy is predicted by equations (21) and (22) as well;

(iv) in solvents consisting of non-spherical molecules the concentration behaviour of the specific refraction is much more complex (see figures 4 and 5). After dilution in weakly anisometric solvents, such as benzonitrile and n-hexylbenzene we can observe a small increase of the 5CB specific refraction and its concentration dependence is strongly non-linear. In the benzene solution its behaviour at high concentrations is the same, but at low concentrations just the opposite. This fact can be understood by taking into account quasi-crystal local packing of the molecules in liquid benzene.

We can make a qualitative comparison of the corrections to the Lorenz–Lorentz equation for symmetric top molecules (see equations (1) and (5)) and for the case of their infinite dilution in a solvent of spherically symmetric molecules (see equations (1) and (18)). To do this we can neglect the second term in the brackets of equation (5), because in normal cases τ_{22} does not exceed τ_{20} [19] and the polarizability anisotropy does not exceed its average value. The product $\alpha\rho$ does not vary considerably in organic liquids and even τ_{20}, characterizing the anisotropy of the distribution of the centres of mass of all other molecules relative to the orientation of the sited molecule and determined by the shape of this molecule, must not depend strongly on the nature of the solvent. In fact the data for different solvents coincide within experimental accuracy (see figures 1 and 2). So we can conclude that for pure liquids the correction is approximately twice as large as that for the case of infinite dilution. The relative difference of the specific refractions in these cases, with an accuracy of a few per cent, equals

$$(R^p-R^d)/R^d=\tfrac{2}{15}\rho_2\Delta\alpha_2\tau_{20}\left[2-\frac{\alpha_1\rho_1}{\alpha_2\rho_2}\right]. \tag{24}$$

This relation can be used to evaluate τ_{20} for various substances. Using the values for the polarizability anisotropy from [18] and our refractometric data we have obtained the following estimates of this coefficient: $4{\cdot}1\pm0{\cdot}3$ and $4{\cdot}6\pm0{\cdot}2$ for 5PCH and 5CB, respectively. This is somewhat larger than the computer simulation estimates of this coefficient for a model diatomic fluid [20], as could be expected taking into account the larger anisometry of the mesogenic molecules. It should be mentioned, that some systematic errors, such as the neglect of all other terms excepting τ_{20}, can influence the values obtained here.

5. Conclusions

As we have seen, the concentration dependence of the specific refraction of mesogens in different solvents, can be explained by the influence of orientation–translational intermolecular correlations on the optical properties of dense fluids. We have shown that it is possible to describe all of the features experimentally observed in this paper, even with a rather simple model, neglecting many-particle correlations and the real distribution of the molecular electron density. Nevertheless the analysis of the experimental data, presented here should not be thought to be complete: encouraging qualitative agreement cannot replace quantitative estimates. Unfortunately, at present it is impossible to compare the change of the specific refraction obtained experimentally for 5PCH and 5CB with theoretical predictions (see equations (2), (5), (13), (18) or (24)). To do this it is necessary to evaluate τ_{2q}, which are determined by the anisotropy of the pair distribution function. In principle it is possible with the help of computer simulation experiments and such work is now in progress.

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