INFLUENCE OF INTERACTION BETWEEN NON-DIPOLE SOLVENT AND DIPOLE SOLUTE MOLECULES ON ANISOTROPIC LIGHT SCATTERING

BY S. WOŹNIAK AND S. KIELICH

Institute of Physics, A. Mickiewicz University, Poznań*

For the solutions $CCl_4 + CHCl_3$ and $CCl_4 + CH_3CN$, the influence of two-molecule radial, dispersional, and induced dipole-permanent dipole interactions between molecules of the solvent and those of the solute on the H_v-component of anisotropic light scattering and moreover, for $CCl_4 + CH_3CN$, that of induced dipole-quadrupole interaction, is calculated. The contribution from binary radial interactions is found to exceed decidedly that of the non-central interactions. If three-molecule radial interactions between molecules of CCl_4 and those of $CHCl_3$ and CH_3CN giving a negative contribution to anisotropic scattering are also taken into account, good agreement between the theory and experimental results is obtained.

1. Introduction

Anisotropic light scattering is an optical effect highly sensitive to intermolecular interactions and the internal structure of the scattering medium [1–3]. Studies of the effect in rarefied systems (gases under low pressure) enable us to determine quantities characterizing the optical properties of the isolated molecule; if carried out in dense systems (gases under higher pressure, liquids, and liquid solutions), they permit to draw conclusions concerning the interactions existing between the molecules. Of especial interest are solutions where, in general, we deal with interactions between molecules of the same species as well as between those of the solvent and those of the solute, all the more so as such two-component systems can be studied maintaining the one component constant and varying the other.

2. Fundamentals of the theory

We consider a dense system of volume V, containing $N = \sum_i N_i$ different molecules, N_i — being the number of those of the species i. We assume vertically line-polarized light of intensity I, with electric vector E vibrating parallel to the Z-axis, to be incident

---

* Address: Zakład Optyki Nieliniowej, Instytut Fizyki, Uniwersytet A. Mickiewicza, Grunwaldzka 6, 60-780 Poznań, Poland.

on the medium along the Y-direction. We are concerned with the light scattered in the X-direction or rather with the intensity of the so-called small i-component of scattered light with horizontal vibrations (along Y). This reduces to discussing the magnitude of H_v, given by [4]

$$H_v = \frac{16\pi^4}{15\lambda^4}\left(\frac{n^2+2}{3}\right)^2 \varrho \Gamma^2 \tag{1}$$

with λ — the incident light wavelength, n — the refractive index for λ, $\varrho = N/V$ — the number density of molecules, and Γ^2 — the effective optical anisotropy. For many--component systems, Γ^2 is given as

$$\Gamma^2 = \frac{3}{2N}\sum_{ij}\left\langle\sum_{p=1}^{N_i}\sum_{q=1}^{N_j} D_{pi} : D_{qj}\right\rangle, \tag{2}$$

where the symbol $\langle\ \rangle$ denotes statistical averaging in the presence of molecular correlations, whereas the deviator D_{pi} of molecule p of the component i is defined as follows in terms of the optical polarizability tensor A_{pi} of the molecule immersed in the medium, i.e. subject to the action of all the other molecules

$$D_{pi} = A_{pi} - \tfrac{1}{3} I(A_{pi} : I), \tag{3}$$

where I is the unit tensor.

Applying classical perturbation calculus, the effective polarizability of the molecule in the medium can be expressed in the form of the expansion

$$A_{pi} = A_{pi}^{(0)} + A_{pi}^{(1)} + A_{pi}^{(2)} + \ldots = \sum_{n=0} A_{pi}^{(n)}, \tag{4}$$

where $A_{pi}^{(0)} = a_{pi}$ is the tensor of linear polarizability of the isolated molecule whereas the other terms of (4) contain the influence of translational fluctuations, translational--orientational fluctuations, and fluctuations of the molecular electric fields. Restricting ourselves to the dipole approximation, we have [2]

$$A_{pi}^{(n)} = a_{pi} \cdot (-\sum_{j}\sum_{q=1}^{N_j} T_{piqj} \cdot a_{qj})^n, \tag{5}$$

where

$$T_{piqj} = -r_{piqj}^{-5}(3r_{piqj}r_{piqj} - r_{piqj}^2 I) \tag{6}$$

is the tensor of dipole-dipole interaction between a molecule p of the species i and a molecule q of the species j.

With regard to (3) and (4), we can write the effective optical anisotropy Γ^2 in the form of the following series:

$$\Gamma^2 = {}^{(0)}\Gamma^2 + {}^{(1)}\Gamma^2 + {}^{(2)}\Gamma^2 + \ldots \tag{7}$$

the successive terms of which are given by [2]

$$^{(0)}\Gamma^2 = \sum_i x_i {}^{(0)}\Gamma_i^2 + \sum_{ij} x_i x_j {}^{(0)}\Gamma_{ij}^2, \tag{8}$$

$$^{(1)}\Gamma^2 = \sum_{ij} x_i x_j {}^{(1)}\Gamma_{ij}^2 + \sum_{ijk} x_i x_j x_k {}^{(1)}\Gamma_{ijk}^2, \tag{9}$$

$$^{(2)}\Gamma^2 = \sum_{ij} x_i x_j {}^{(2)}\Gamma_{ij}^2 + \sum_{ijk} x_i x_j x_k {}^{(2)}\Gamma_{ijk}^2 + \sum_{ijkl} x_i x_j x_k x_l {}^{(2)}\Gamma_{ijkl}^2. \tag{10}$$

Above, $x_i = \dfrac{N_i}{N}$ is the molar fraction of the component i, whereas $^{(n)}\Gamma_{ij}^2$ is the contribution to $^{(n)}\Gamma^2$ from two-molecule interactions between molecules of the components i and j, $^{(n)}\Gamma_{ijk}^2$ — that from three-molecule interaction between molecules of the components i, j and k and $^{(0)}\Gamma_i^2$ is the contribution to $^{(0)}\Gamma^2$ in the approximation of non-interacting molecules.

On restricting the problem to two-component systems and neglecting four-molecule interactions we have, by (7)—(10)

$$\Gamma^2 = x_1 \gamma_1^2 + x_2 \gamma_2^2 + x_1^2 \Gamma_{11}^2 + 2x_1 x_2 \Gamma_{12}^2 + x_2^2 \Gamma_{22}^2$$

$$+ x_1^3 \Gamma_{111}^2 + 3x_1^2 x_2 \Gamma_{112}^2 + 3x_1 x_2^2 \Gamma_{122}^2 + x_2^3 \Gamma_{222}^2, \tag{11}$$

with γ denoting the polarizability anisotropy of the isolated molecule.

In the present work, we are concerned with the influence exerted by interactions between different molecules of the binary system on the effective optical anisotropy, i.e. on the terms accounting for two-molecular (Γ_{12}^2) and three-molecular (Γ_{112}^2, Γ_{122}^2) interactions (involving, in each case, molecules of the solvent *and* solute). Moreover, we shall be considering the case when the molecules of one of the two components of the system are isotropic (CCl_4) and those of the other component are axially-symmetric ($CHCl_3$, CH_3CN).

3. Discussion of the influence of binary interactions

By methods of statistical physics and classical mechanics we arrive at the following expressions for Γ_{12}^2 of Eq. (11) [2, 5]

$$\Gamma_{12}^2 = B_1^{(3,1)} J_{12}^{RA} + B_2 J_{12}^{R} + B_3^{(6,1)} J_{12}^{RA} + B_4^{(6,2)} J_{12}^{RA}, \tag{12}$$

where the constants $B_1, \ldots, B_4$ depend on the mean polarizabilities a of the isolated molecules and the anisotropies γ, and are given in the form

$$B_1 = 2a_1 \gamma_2 (3a_2 + \gamma_2),$$

$$B_2 = 9a_1^2 a_2^2 + \tfrac{4}{5} a_1^2 \gamma_2^2 + 2a_1 \gamma_2^2 (a_2 + \tfrac{1}{6} \gamma_2),$$

$$B_3 = a_1 \gamma_2 [2\gamma_2^2 + 2a_1 (6a_1 - \gamma_2) + (3a_2 - \gamma_2)(a_1 + a_2 + \gamma_2)], \tag{13}$$

$$B_4 = 4a_1^2 \gamma_2^2.$$

The parameters

$$^{(n,m)}J_{12}^{RA} = \frac{\varrho}{2V} \iint [(3\cos^2\theta_{q_2}-1)^m + c_m]r_{p_1q_2}^{-n} g_{12}^{(2)}(\tau_{p_1}, \tau_{q_2})d\tau_{p_1}d\tau_{q_2} \qquad (14)$$

describe the angular-radial correlations, and

$$J_{12}^R = \frac{2\varrho}{V} \iint r_{p_1q_2}^{-6} g_{12}^{(2)}(\tau_{p_1}, \tau_{q_2})d\tau_{p_1}d\tau_{q_2} \qquad (15)$$

is the radial correlation parameter. θ_{q_2} is the angle between the symmetry axis of molecule q of species 2 and the radius-vector connecting it with molecule p of species 1; $g_{12}^2(\tau_{p_1}, \tau_{q_2})$ is the correlation function for two molecules at the configurations τ_{p_1} and τ_{q_2}, respectively, and the constant c_m is given as the following isotropic average:

$$c_m = -\overline{(3\cos^2\theta_{q_2}-1)^m}. \qquad (16)$$

The energy of interaction between a molecule of the species 1 and one of the species 2 consists of a central and non-central part

$$U_{12}(r, \omega) = U_{12}(r) + V_{12}(r, \omega). \qquad (17)$$

In the present case, when the component 1 is CCl_4 and the component 2 is CH_3CN or $CHCl_3$, we have the following interaction energies [6]:

$$V_{12} = V_{12}^{disp} + V_{12}^{\alpha-\mu} + V_{12}^{\alpha-\Theta}, \qquad (18)$$

(V^{disp} — dispersional, $V^{\alpha-\mu}$ — induced dipole α — dipole μ; $V^{\alpha-\Theta}$ — induced dipole α — quadrupole Θ).

With the interactions (18), the parameters (14) and (15) become

$$^{(3,1)}J_{12}^{disp} = C_1(\langle r_{12}^{-9}\rangle + \tfrac{5}{7}C_1\langle r_{12}^{-15}\rangle),$$

$$^{(6,1)}J_{12}^{disp} = C_1(\langle r_{12}^{-12}\rangle + \tfrac{5}{7}C_1\langle r_{12}^{-18}\rangle),$$

$$^{(6,2)}J_{12}^{disp} = \tfrac{4}{7}C_1(\langle r_{12}^{-12}\rangle + 2C_1\langle r_{12}^{-18}\rangle), \qquad (19)$$

$$^{(3,1)}J_{12}^{\alpha-\mu} = C_2[\langle r_{12}^{-9}\rangle + \tfrac{5}{7}(8C_2+9C_1)\langle r_{12}^{-15}\rangle];$$

$$^{(6,1)}J_{12}^{\alpha-\mu} = C_2[\langle r_{12}^{-12}\rangle + \tfrac{5}{7}(8C_2+9C_1)\langle r_{12}^{-18}\rangle],$$

$$^{(6,2)}J^{\alpha-\mu} = \tfrac{4}{7}C_2[\langle r_{12}^{-12}\rangle + (7C_2+9C_1)\langle r_{12}^{-18}\rangle], \qquad (20)$$

$$^{(3,1)}J_{12}^{\alpha-\Theta} = C_3(\langle r_{12}^{-11}\rangle + \tfrac{5 \cdot 5}{8}C_1\langle r_{12}^{-17}\rangle + \tfrac{70}{99}C_3\langle r_{12}^{-19}\rangle),$$

$$^{(6,1)}J_{12}^{\alpha-\Theta} = C_3(\langle r_{12}^{-14}\rangle + \tfrac{5 \cdot 5}{8}C_1\langle r_{12}^{-20}\rangle + \tfrac{70}{99}C_3\langle r_{22}^{-22}\rangle),$$

$$^{(6,2)}J_{12}^{\alpha-\Theta} = C_3(\langle r_{12}^{-14}\rangle + \tfrac{131}{22}C_1\langle r_{12}^{-20}\rangle + \tfrac{721}{104}C_3\langle r_{12}^{-20}\rangle), \qquad (21)$$

$$J_{12}^R = 2\langle r_{12}^{-6}\rangle, \qquad (22)$$

where

$$C_1 = \tfrac{1}{10}\frac{h}{kT}\frac{\nu_1\nu_2}{\nu_1+\nu_2}\,a_1\gamma_2, \quad C_2 = \tfrac{1}{5}\,a_1\frac{\mu_2^2}{kT}, \quad C_3 = \tfrac{12}{35}\,a_1\frac{\Theta_2^2}{kT}, \tag{23}$$

whereas the parameters $\langle r_{12}^{-n}\rangle$ are of the form

$$\langle r_{12}^{-n}\rangle = \frac{\varrho}{V}\iint r_{p_1 q_2}^{-n} g_{12}(r_{p_1 q_2})\,dr_{p_1}dr_{q_2}. \tag{24}$$

The latter are calculated for distribution functions in the form

$$g(r) = g_0(r) + \varrho g_1(r) + \varrho^2 g_2(r), \tag{25}$$

where $g_0(r) = \exp[-U(r)/kT]$, and $U(r)$ is the Lennard–Jones potential (18—6), whereas g_1 and g_2 are successive approximations to the distribution function for rigid spheres.
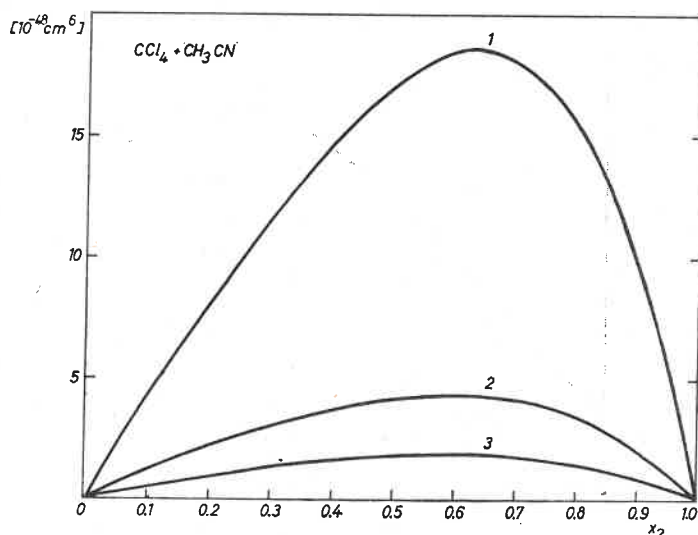

Fig. 1. The influence of two-molecule interactions on the effective optical anisotropy versus the molar fraction x_2: curve 1 — that of radial interactions ($^{\mathrm{rad}}\tilde{\Gamma}_{12}^2$); 2 — dispersional contribution ($10 \cdot {}^{\mathrm{disp}}\tilde{\Gamma}_{12}^2$); 3 — induced dipole-permanent dipole contribution ($^{\alpha-\mu}\tilde{\Gamma}_{12}^2$)

The contributions to Γ^2 from the various interactions in the entire range of concentrations of solutions CCl_4+CH_3CN and CCl_4+CHCl_3 are shown in graphs 1 and 2, whereas graphs 3 and 4 give the joint contribution of all the types of interaction, with the notation: ${}^{\mathrm{disp}}\tilde{\Gamma}_{12}^2 = 2x_1x_2\,{}^{\mathrm{disp}}\Gamma_{12}^2$, $\tilde{\Gamma}_{12}^2 = 2x_1x_2\Gamma_{12}^2$, etc.

As seen from the graphs, the decisive role in both solutions belongs to two-molecule radial interactions. In CCl_4+CH_3CH, the contributions from induced dipole-permanent dipole interaction and dispersional interactions are, respectively, 10 and about 40 times smaller than that due to radial interaction; induced dipole-permanent quadrupole interaction contributes but weakly. At the concentration $x_2 = 0.5$ the radial contribution
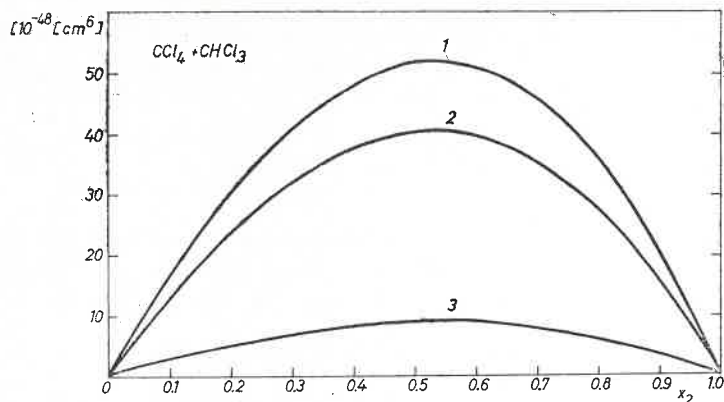
Fig. 2. The influence of two-molecule interactions on the effective optical anisotropy versus the molar fraction x_2: curve 1 — that of radial interactions ($^{rad}\tilde{\Gamma}^2_{12}$); 2 — dispersional contribution ($100 \cdot {}^{disp}\tilde{\Gamma}^2_{12}$); 3 — induced dipole-permanent dipole contribution ($-100 \cdot {}^{\alpha-\mu}\tilde{\Gamma}^2_{12}$)
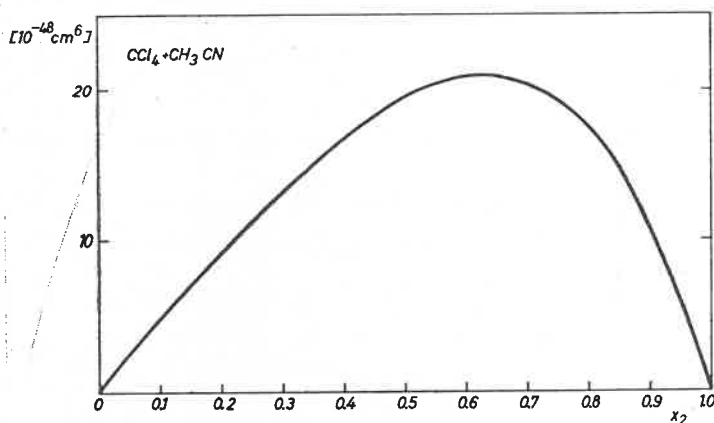

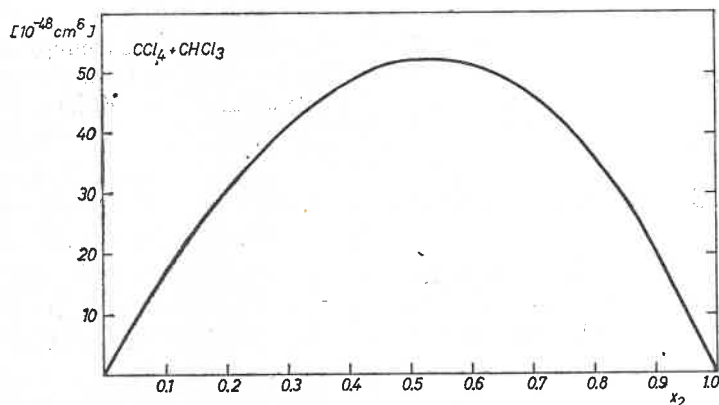Fig. 3. Total binary interaction effect on effective optical anisotropy, vs x_2

Fig.4. Total binary interaction effect on effective optical anisotropy, vs x_2

$^{rad}\tilde{\Gamma}_{12}^2$ amounts to 88.4% of $\tilde{\Gamma}_{12}^2$, the dispersional contribution $^{disp}\tilde{\Gamma}_{12}^2$ to 2.2%, and the induced dipole-permanent contribution to 9.4%. In $CCl_4 + CHCl_3$, radial interaction is strongly predominant; at $x_2 = 0.5$, $^{rad}\tilde{\Gamma}_{12}^2$ amounts to 99.4%, $^{disp}\tilde{\Gamma}_{12}^2$ to 0.81%, whereas $^{\alpha-\mu}\tilde{\Gamma}_{12}^2$ is negative, amounting to -0.2%.

4. Discussion of the role of three-molecule interaction

In dense media not only binary but moreover ternary interaction is appreciable. Taking into account ternary radial interactions we obtain the following expressions for the various contributions to Γ^2:

$$\Gamma_{112}^2 = 6a_1^2 a_2(2a_1 + a_2)J_{112}^R, \tag{26}$$

$$\Gamma_{122}^2 = 6a_1 a_2^2(a_1 + 2a_2)J_{122}^R. \tag{27}$$

The radial interaction parameters J_{112}^R, J_{112}^R are of the form:

$$J_{ijk}^R = 8\pi^2 \varrho^2 S(p_i, q_j, r_k) \int_0^\infty r_{p_i q_j} \exp\left[-U(r_{p_i q_j})/kT\right]dr_{p_i q_j} \int_0^\infty r_{q_j r_k} \exp\left[-U(r_{q_j r_k})/kT\right]dr_{q_j r_k}$$

$$\int_{|r_{p_i q_j} - r_{q_j r_k}|}^{r_{p_i q_j} + r_{q_j r_k}} r_{p_i r_k}\{\exp\left[-U(r_{p_i r_k})/kT\right] - 1\}(3\cos^2\theta - 1)r_{p_i q_j}^{-3} r_{q_j r_k}^{-3} dr_{p_i r_k}. \tag{28}$$

The operator $S(p_i, q_j, r_k)$ symmetrizes the expression following it with respect to the molecules p_i, q_j, r_k, whereas $\cos\theta = r_{p_i q_j} \cdot r_{q_j r_k}/r_{p_i q_j} r_{q_j r_k}$.

The role of ternary non-central interactions is negligible.

Computation of the parameters (28) for rigid spheres leads to:

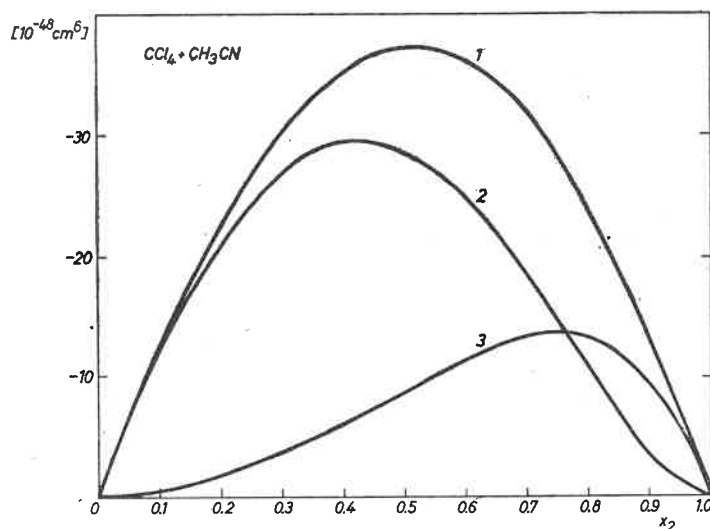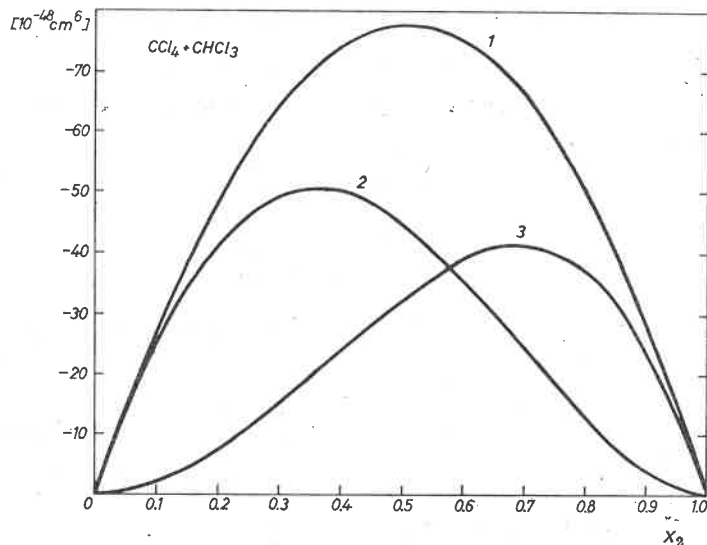$$J_{112}^R = J_{122}^R = -\tfrac{5}{3}\pi^2\varrho^2. \tag{29}$$

Fig. 5. Influence of three-molecule interactions on the effective optical birefringence: curve 1 — $\tilde{\Gamma}_{112}^2 + \tilde{\Gamma}_{122}^2$; curve 2 — $\tilde{\Gamma}_{112}^2$; curve 3 — $\tilde{\Gamma}_{122}^2$

The integral expression (28) depends but weakly on the radial interaction model assumed; when calculated with the Lennard–Jones potentials (15—6), (12—6) and (9—6), it differs by about 1% from its rigid sphere value [7].

The contribution from ternary interaction to the effective optical anisotropy Γ^2 is shown in graphs 5 and 6. All the contributions are negative.

Fig. 6. Influence of three-molecule interactions on the effective optical birefringence: curve $1 — \tilde{\Gamma}^2_{112} + \tilde{\Gamma}^2_{122}$; curve $2 — \tilde{\Gamma}^2_{112}$; curve $3 — \tilde{\Gamma}^2_{122}$

The difference in maximal values of the functions $\tilde{\Gamma}^2_{112}$ and $\tilde{\Gamma}^2_{122}$ ($\tilde{\Gamma}^2_{112} = 3x_1^2 x_2 \Gamma^2_{112}$, $\tilde{\Gamma}^2_{122} = 3x_1 x_2^2 \Gamma^2_{122}$) for a given solution is due to the different mean polarizabilities of the molecules of the two species; thus, for CCl_4 $a_1 = 10.5 \cdot 10^{-24}$ cm³, for CH_3CN $a_2 = 4.28 \cdot 10^{-24}$ cm³, whereas for $CHCl_3$ $a_2 = 8.23 \cdot 10^{-24}$ cm³. This is also the reason why $\tilde{\Gamma}^2_{112}$ and $\tilde{\Gamma}^2_{122}$ differ for the two solutions and the maximal value of $\tilde{\Gamma}^2_{112}$ is almost twice and that of $\tilde{\Gamma}^2_{122}$ three times larger in $CCl_4 + CHCl_3$ than in $CCl_4 + CH_3CN$.

The graph showing the joint contribution to Γ^2 from ternary interactions is similar for the two solutions studied; however, the values for $CCl_4 + CHCl_3$ are about twice larger than for $CCl_4 + CH_3CN$.

In graphs 7 and 8, curve I shows the effective optical anisotropy, calculated theoretically taking into account only interactions between molecules of the same species: $\tilde{\Gamma}^2_A + \tilde{\Gamma}^2_B$ (where A symbolizes CCl_4 and B stands for $CHCl_3$ or CH_3CN). Curve 2 shows the contribution $\tilde{\Gamma}^2_{AB}$ from binary and ternary solvent-solute interactions: $\tilde{\Gamma}^2_{AB} = \tilde{\Gamma}^2_{12} + \tilde{\Gamma}^2_{112} + \tilde{\Gamma}^2_{122}$. The value of $\tilde{\Gamma}^2_{AB}$ is negative throughout the entire concentration range and is zero for $x_2 = 0$, $x_1 = 1$. The sum of the curves I and 2 (in graphs 7 and 8) is plotted (continuous line) in graphs 9 and 10, where Γ^2 determined from anisotropic light scattering measurements [8] is given too. Graphs 9 and 10 point to excellent agreement between the theoretically calculated and experimentally determined value of Γ^2 in the entire range of concentrations.
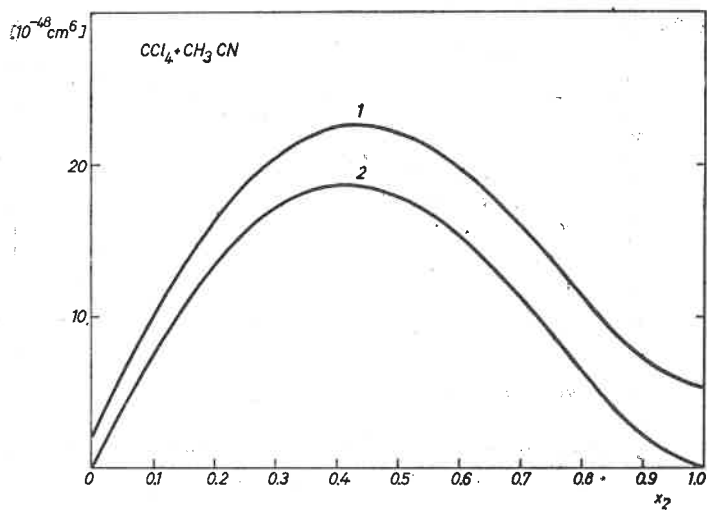
Fig. 7. Curve *1* — influence on Γ^2 of interaction between molecules of the same species; curve *2* — that of interaction between molecules of different species (negative values)

Fig. 8. Curve *1* — influence on Γ^2 of interaction between molecules of the same species; curve *2* — that of interaction between molecules of different species (negative values)
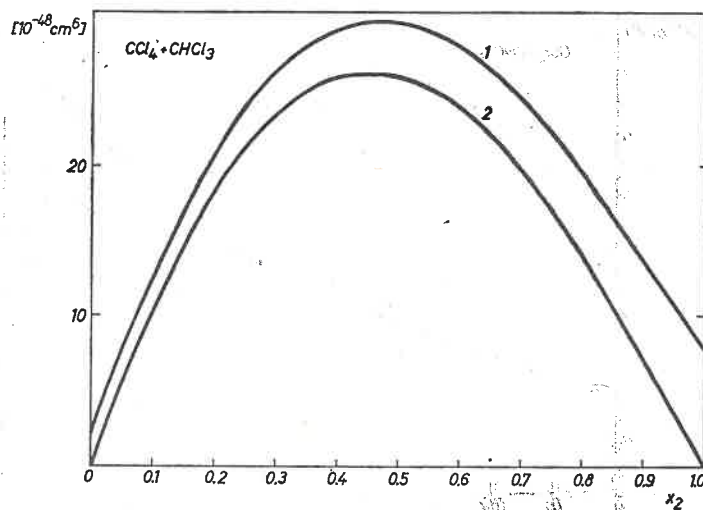
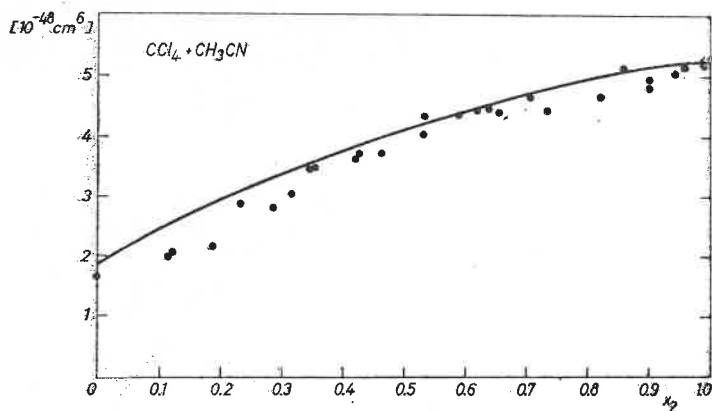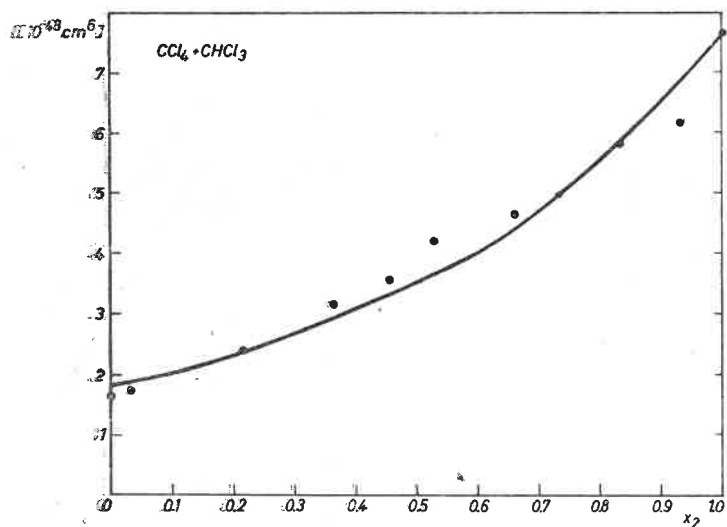**Fig. 9. Theoretical** concentration-dependence of Γ^{2} (continuous line), and the experimental values (dots) [8]

Fig. 10. Theoretical concentration-dependence of Γ^{2} (continuous line), and the experimental values (dots) [8]

REFERENCES

[1] S. Kielich, *J. Chem. Phys.* **46**, 4090 (1967).

[2] S. Kielich, S. Woźniak, *Acta Phys. Pol.* **A45**, 163 (1974).

[3] S. Woźniak, S. Kielich, *J. Phys.* (France) **36**, 1305 (1975).

[4] S. Kielich, *Chem. Phys. Lett.* **2**, 112 (1968).

[5] S. Woźniak, *Acta Phys. Pol.* **A45**, 981 (1974).

[6] S. Kielich, J. R. Lalanne, F. B. Martin, *J. Phys.* (France) **33**, C1-191 (1972).

[7] H. B. Levine, D. A. Mc Quarrie, *J. Chem. Phys.* **44**, 3500 (1966); Document No. **8807** deposited with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress.

[8] M. S. Malmberg, Thesis, University of Maryland, 1967; M. S. Malmberg, E. R. Lippincott, *J. Colloid Interface Sci.* **27**, 591 (1968).