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Determination of Effective Anisotropy of the Optical Polarizability for the Two-component Solutions by using the He-Ne Laser Light Beam

In this paper the H_v-component parallel to the scattered light has been measured for the solutions: toluene-benzene, toluene-cyclohexane, m-, p-xylene-cyclohexane, o-, m-, p-xylene-benzene, by using the perpendicularly polarized incident light. On the base of these measurements the squares of the effective anisotropy of optical polarizability have been calculated for two-component solutions, and the influence of the interactions between the molecules of the solvent and the dissolved substance on the effective optical anisotropy has been determined.

1. Introduction

Interesting information concerning the correlations between the molecules of different and of the same kind may be obtained by investigating the anisotropic scattering of light in solutions. In the solutions containing anisotropic molecules a great part (besides translational fluctuations) is played by translational-orientational fluctuations and the fluctuations of the molecular fields. The optical anisotropy of the molecules may, among others, be determined from the measurements of the anisotropic component of the scattered light intensity.

2. A formula for effective optical anisotropy

For the two-component solutions the effective anisotropy of the optical polarizability may be represented in the following way [1–3]

$$\Gamma^2 = f_1\gamma_1^2 + f_2\gamma_2^2 + f_1^2\Gamma_{11}^2 + 2f_1f_2\Gamma_{12}^2 + f_{22}\Gamma_{22}^2, \quad (1)$$

where f_1 and f_2 are the molar fractions of the first and second components, respectively, γ_1 and γ_2 are the anisotropics of the linear polarizability of isolated molecules of the first and second components, Γ_{11}^2 — presents an interaction between the molecules of the first component, Γ_{22}^2 — presents an interaction between the molecules of the second component, and Γ_{12}^2 — gives the interaction between the molecules of the first and second components. The terms Γ_{12}^2 depend, in general, on the radial, angular and radial-angular interactions [2].

The effective optical anisotropy of the i-th component of the solution may be expressed by the relation

$$\Gamma_i^2 = \gamma_i^2 + \Gamma_{ii}^2, \quad (2)$$

where Γ_{ii}^2 — represents the two-molecule interaction. In accordance with the chosen model of interactions the theoretical calculations, giving a satisfactory consistence with the experiment, indicate that this magnitude is proportional to the number of molecules in a unity volumne.

$$\Gamma_{ii}^2 = A_iN_i, \quad (3)$$

where $A_i = A_i\,(T, \alpha_i, \gamma_i, M_i, \ldots, V_i, \delta_i, \varepsilon_i)$ is function of temperature T and depends on parameters determining the properties of molecules of i-th component, such as mean linear polarizability α_i, anisotropy of linear polarizability γ_i, electric multipole moments M_i and the frequency of vibration V_i which influences dispersive interactions of the Lennard-Jones potential constants δ_i and ε_i. By taking account of (2) and (3) the equation (1) applied to two-component solution takes the form

$$\Gamma^2 = f_1\gamma_1^2 + f_2\gamma_2^2 + 2f_1f_2\Gamma_{12}^2 + (f_1^2A_1 + f_2^2A_2)N_{12}, \quad (4)$$

where N_{12} is a number of molecules in a unity volume of the solution composed of the components 1 and 2 given in concentrations f_1 and f_2, respectively. From the equation (4) and the relations (2) and (3) we determine the contribution to the effective anisotropy from the interactions between the molecules of com-

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ponents 4 and 2

$$\tilde{\Gamma}_{12}^2 = \Gamma^2 - f_1\gamma_1^2 - f_2\gamma_2^2 - \left(f_1\frac{\Gamma_1^2-\gamma_1^2}{N_1} + f_2\frac{\Gamma_2^2-\gamma_2^2}{N_2}\right)N_{12}, \quad (5)$$

where $\Gamma_{12}^2 = 2f_1f_2\Gamma_{12}^2$.

As it may be seen from (5) the influence of interactions between the molecules of components 1 and 2 on the effective anisotropy (and thus also the participation of these interactions in the anisotropic scattering of light by the solutions) may be determined experimentally for an arbitrary concentration by calculating the

Γ^2 — effective optical anisotropy of the solution under given concentration,

Γ_1^2 — effective optical anisotropy of pure component 1 ($f_1 = 1, f_2 = 0$),

Γ_2^2 — effective optical anisotropy of pure component 2 ($f_1 = 0$, $f_2 = 1$), provided that linear polarizability anisotropy (γ_1, γ_2) of isolated molecules of components 1 and 2, and the number of molecules in a unity volume of solution are known.

3. The measurement method

For the two-component solutions like: toluene-cyclohexane, m-xylene-cyclohexane, p-xylene-cyclohexane and toluene-benzene, o-, m-, p-xylene-benzene the parallel component H_v of the scattered radiation for the perpendicularly polarized incident light have been measured by using the apparatus presented in the Fig. 1.

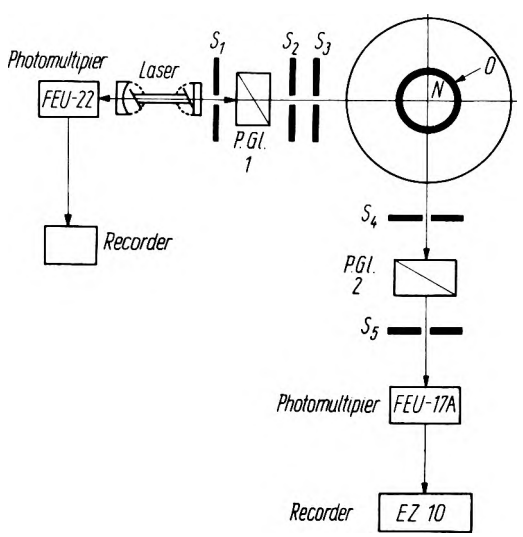

Fig. 1. Apparatus for measurements of the component H_v of solutions

An He—Ne laser used as a light source generated the wave radiation 632.8 μm 10 m power which operated in the principal mode. The laser applied to the measurements was composed of a capillary tube of 1.5 mm internal diameter and 1.5 m length, closed with the windows positioned under the Brewster's angle and of two dielectric mirrors that constituted a plane-convex optical resonator. The plane exit mirror exhibits 2.6 % transmission at the wavelength 632.8 nm, while the convex mirror of the 3.5 curveture radius was of 0 % transmission. In such resonator system the beam divergence did not exceed $0.5\text{–}10^{-4}$ rad. The laser beam power was controlled by a FEU-22 photomultiplier (after suitable reduction of the light flux) located on the side of 0 % transmission mirror, while the power run was registered on a recorder.

The measuring vessel was made of pyrex glasstube of 1 mm wall thickness and the external diameter amounting to 46 mm. It was closed with a ground glass plug.

The parasitic scattering on the vessel walls was negligible due to very small incident beam diameter (1 mm), vessel diameter being relatively great (46 mm), and to very carefully cleaned walls of the vessel. In the absence of fluid no signal was obtained in the measuring system. The measuring vessel was closed tightly in a metal housing blackened with a metal point. A rectangular slit S_4 of 2 mm width, which was inserted in the detecting system located at a distance of 35 mm from the centre of the scattering region, was tightly fastened to the metal housing of the measuring vessel. A polarizing Glan's prism P GL 2 is located on the way of the scattered beam which would be rotated with the accuracy of 1 min. of arc. Next, at the distance of 75 mm from the system centre a slit S_5 of 2 mm width was placed. The scattered signal was detected by a FEU-17A photomultiplier positioned at a distance of 150 mm from the centre of the scattering volume. The signal from the photomultiplier was transmitted to a d.c. recorder of FZ-10 type.

By using the setup described above the values of the anisotropic component have been determined; they are presented in Figs 2 and 3. The measurements of the H_{vsol} component allowed to calculate the square of the effective anisotropy of optical polarizability of the solutions examined as well as the change of this value in a function of the number of molecules, and to determine the influence of the interaction

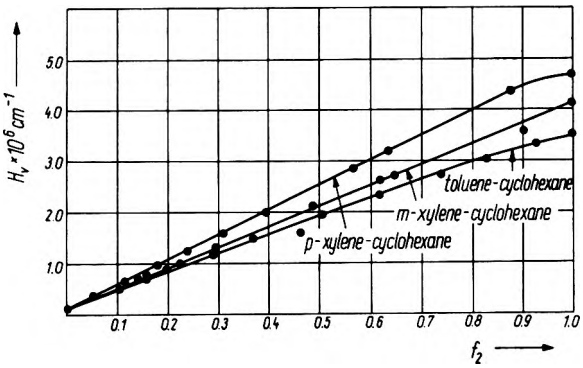

Fig. 2. The value of the component H_v vs. concentration of the solution

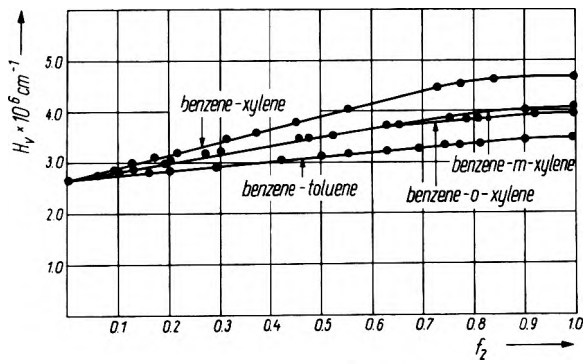

Fig. 3. Value of the component H_v vs. molar concentration of the solution

between the molecules of the solvent and the solved substance.

In Figs. 4 and 5 changes of the square of the effective anisotropy with the molar concentration are shown for the following seven solutions: toluene-cyclohexane, m-, p-xylene--cyclohexane and toluene-benzene, o-, m-, p-xylene-benzene.

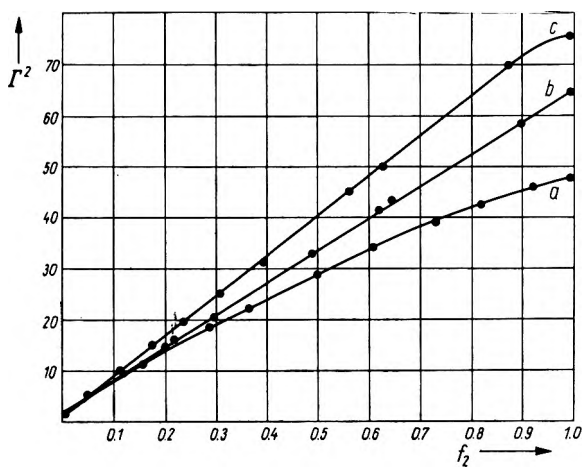

Fig. 4. Square of the effective anisotropy of optical polarizability vs. molar composition of the solution

a) toluene-cyclohexane
b) m-xylene-cyclohexane
c) p-xylene-cyclohexane

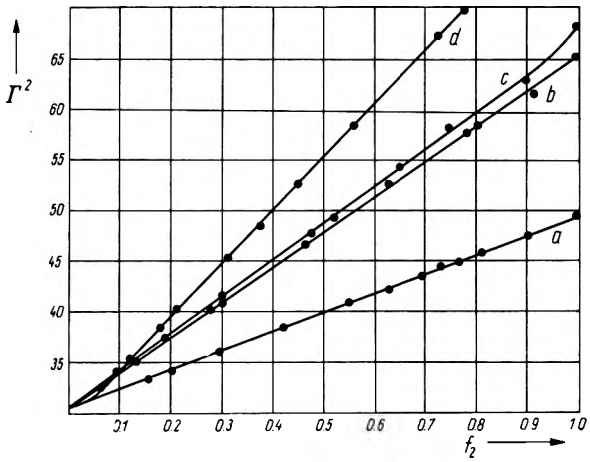

Fig. 5. Square of the effective anisotropy of optical polarizability vs. molar composition of the solution

a) toluene-benzene
b) o-xylene-benzene
c) m-xylene-benzene
d) p-xylene-benzene

The magnitude Γ^2 was calculated on the base of the measurement of the anisotropic component $(H_v)_{sol}$ according to formula (4)

$$\Gamma^2_{sol} = \frac{(H_v)_{sol}}{\frac{16\pi^4}{15\lambda^4}\left(\frac{n^2_{sol}+2}{3}\right)^2 N_{12}}. \qquad (6)$$

For given value of Γ^2 the value of $\tilde{\Gamma}^2_{12}$ was determined from the equation (4)

$$\tilde{\Gamma}^2_{12} = \Gamma^2_{sol} - f_1\gamma_1^2 - f_2\gamma_2^2 - (f_1^2 A_1 + f_2^2 A_2) N_{12}.$$

The results obtained from $\tilde{\Gamma}^2_{12}$ are given in the Figs 6, 7 and 8.

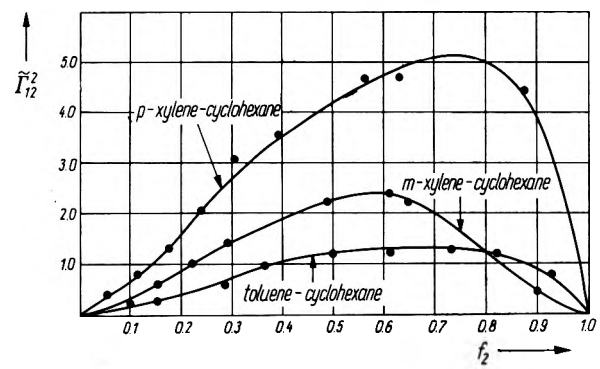

Fig. 6. $\tilde{\Gamma}^2_{12}$ vs. molar concentration of the solution

Some auxiliary measurements, made before the examinations of scattering for each given solution, allowed to determine the changes in the refractive index of the solution and in density depending on concentration.

The number of molecules in a unity volume of the solution has been determined from the following relation

$$N_{12} = \frac{N_A \varrho_{12}}{M_{12}},$$

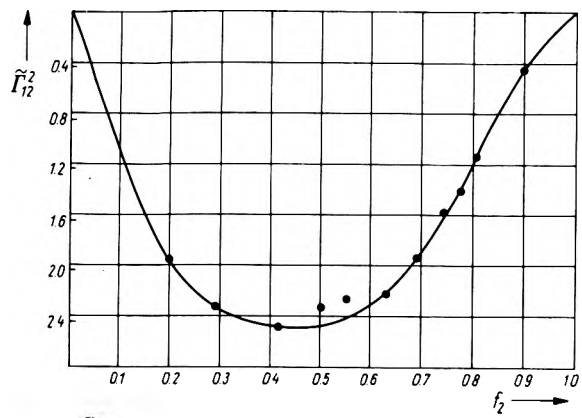

Fig. 7. $\tilde{\Gamma}^2_{12}$ vs. molar concentration of toluene-benzene solution

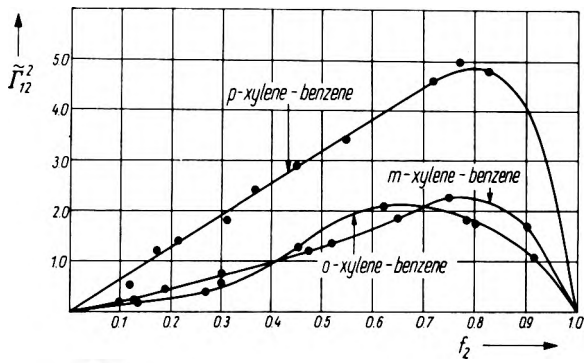

Fig. 8. $\tilde{\Gamma}^2_{12}$ vs. molar concentration of the solution

where, N_A — the Avogadro's number, ϱ_{12} — the solution density in g/cm^3, $M_{12} = f_1 M_1 + f_2 M_2$, f — molar concentration of the first component, f_2 — molar concentration of the second component, M_1 — molar mass of the first component, M_2 — molar mass of the second component.

4. Measurement results and conclusions

The analysis of the results obtained for the square of the effective anisotropy Γ_{sol} of the solution as dependent on the molar concentration indicates a linear dependence of this magnitude for the solutions: toluene-benzene, o-xylene-benzene, m-xylene-benzene, m-xylene-cyclohexane and for the solution p-xylene-cyclohexane and p-xylene-benzene. No distinct changes in the effective anisotropy of optical polarizability, which could be caused by the interaction of xylene with both the cyclohexane and benzene in the respective solutions, were observed in the examined solution with the increase of concentration. The dependence of this type allows to conclude that the interactions between the molecules of xylene and benzene as well as xylene and cyclohexane are weaker than those of xylene-xylene, cyclohexane-cyclohexane or benzene-benzene types.

The hypothesis that the influence of interaction of xylene and cyclohexane as well as that of xylene and benzene is low has been confirmed also by the values of $\tilde{\Gamma}^2_{12}$ calculated in this work.

The values of $\tilde{\Gamma}^2_{12}$ determined from (5) suggest that the contribution from the interaction between the molecules of different kinds to the effective optical anisotropy Γ^2 changes with the concentration and assumes the maximal percentage values for the following solutions:

toluene-cyclohexane 4.3 % for concentration $f_2 = 0.635$,

orto-xylene-benzene 3.9 % for concentration $f_2 = 0.625$,

meta-xylene-benzene 3.8 % for concentration $f_2 = 0.75$,

meta-xylene-cyxlohexane 7.1 % for concentration $f_2 = 0.713$,

para-xylene-benzene 7.2 % for concentration $f_2 = 0.770$,

para-xylene-cyxlohexane 12 % for concentration $f_2 = 0.635$.

The interaction between the components of the solutions grows with the increase of the concentration, while the maximum of the function $\tilde{\Gamma}_{12}$ is shifted toward higher concentrations of strongly interacting fluids.

In the case of toluene-benzene solution the negative values of $\tilde{\Gamma}^2_{12}$ shows a tendency of mutually perpendicular positioning of these molecules.

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Определение эффективной оптической анизотропии поляризуемости для бинарных растворов с применением светового пучка лазера He-Ne

Рассчитана составляющая H_v, параллельная рассеянному свету, для следующих растворов: толуол-бензол, толуол-циклогексан, р-ксилол-о-m-циклогексан, р-ксилол-бензол, причем применяли перпендикулярно поляризованный падающий свет. На основе произведенных измерений рассчитаны квадраты эффективной оптической поляризуемости для бинарных растворов и определено влияние взаимодействия молекул растворителя и растворенного вещества на оптическую анизотропию.

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