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# Light Scattering in Binary Liquid Mixtures. II. Anisotropic Scattering

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Anisotropic light scattering in liquid mixtures of small nonelectrolyte molecules was measured at the wavelengths 546 and 436 nm. The mixtures of cyclohexane, *n*-heptane and carbon tetrachloride (component 1) with benzene and carbon disulfide (component 2) were examined. The optical anisotropy terms were determined from experimental data and their concentration dependence was analysed. So was validity of the additivity principle of optical anisotropy. It has been concluded that deviation from linearity of the effective molecular anisotropy plots indicates changes in the orientational correlations of molecules in mixtures. By analysing the excess thermodynamic functions of the same mixtures it has been concluded that such plots describe molecular interactions and their changes in dependence of concentration. Existing theoretical formulae in which orientational correlations effects have been considered, are discussed. It is emphasized that the parameters needed are concentration dependent and that explanation of their physical meaning is not possible at present. In testing methods for determining molecular anisotropies of isolated molecules based on the determination at infinite dilution it has been found that the intermolecular interactions between solute and solvent molecules, if the molecules are of comparable size, are always so strong that the anisotropy of isolated molecules cannot be determined by such methods.

## INTRODUCTION

In a review article written three years ago[1] it was stated that there is no satisfactory theory explaining the anisotropic part of the light scattering in multicomponent systems. The main difficulty is the lack of useful theoretical models for internal fields influencing the polarizabilities of different molecules in multicomponent dense systems.

The development of the theory of anisotropic scattering in liquid mixtures is mainly based on the experimental finding that the optical anisotropies of molecules show a tendency to be additive[2,3]. Shakhparonov[4] proposed a general formula resulting from calculations of fluctuations in the orientation of molecules in dense media.

The assumed additivity principle was applied by Bothorel and collaborators[5] when developing a method for studying the optical anisotropy of separate molecules. They have used it extensively in a series of papers concerned with the structure of molecules and the interactions between different types of molecules.

As shown by the light scattering theory in dense media, there exist strong intermolecular interactions which cause the appearance of an orientational correlation factor $G$ which in most cases is different from unity[1].

In several papers[6,7,8] describing experiments on various binary mixtures the results suggest that deviations from the additivity principle are found to be the rule. Shakhparonov[9] tried to discuss these deviations as a consequence of the appearance of molecular complexes in liquid mixtures. In a recent paper Kielich[10] discusses the problem of effective optical anisotropies in liquid mixtures and arrives to general expressions valid in liquid mixtures and dilute solutions. The latest experimental evidence[11-14] supports the theoretical assumptions, but no final conclusions on the role of orientational correlations in liquid mixtures have been drawn.

In this paper our own experimental results on the anisotropic light scattering in binary liquid mixtures are examined in view of a possible influence of the correlation factor $G$ in the analysis of the optical anisotropy of small molecules in liquid mixtures.

## THEORETICAL PART

The anisotropic part of the scattered light can be determined directly by measuring one of the partial Rayleigh ratios $H_v$ or $V_h$ which are identical by the Krishnan rule. The following equation holds[1]:

$$H_v = V_h = (\pi^2/5\,\lambda_0^4)\,3\,F_{anis} \tag{1}$$

Here the anisotropic molecular scattering factor $F_{anis}$ arising from orientational fluctuations can be expressed in terms of physical constants:

$$F_{anis} = (\delta^2 G/N)\,(N\partial\varepsilon/\partial N)^2, \tag{2}$$

where $\varepsilon = n^2$ is the dielectric constant measured at optical frequencies, $n$ is the refractive index of the dense medium, $N$ is the number density of the molecules, $\delta^2$ is the optical anisotropy of isolated molecules defined as in Ref. 1, and $G$ is the orientational correlation factor consisting of an integral function[1] $J_A$ containing the orientational correlation function[15].

Since it has been shown[16] that the refractive index increment $(N\partial\varepsilon/\partial N)$ is proportional to the effective polarizability $\alpha'$ of the molecules in the dense medium,

$$N\partial\varepsilon/\partial N = 4\pi N\alpha'\,[(n^2+2)/3], \tag{3}$$

and assuming that the optical anisotropy $\delta^2$ can be expressed by the effective molecular anisotropy $\gamma'^2$ of the molecules in the dense medium *via* the relation[16]

$$\delta^2 = \gamma'^2/9\alpha'^2, \tag{4}$$

it follows:

$$F_{anis} = (16\,\pi^2/9)\,N\gamma'^2\,G\,[(n^2+2)/3]^2. \tag{5}$$

By inserting (5) into (1) one obtains

$$H_v = (16\,\pi^4/15\,\lambda_0^4)N\gamma'^2\,G[(n^2+2)/3]^2. \tag{6}$$

Some authors express anisotropic scattering by the anisotropic Rayleigh ratio $R_{anis}$. This factor is related to $H_v$ by the expression

$$R_{anis} = 13H_v/6. \tag{7}$$

All equations given here are valid in multicomponent mixtures, but the physical constants for mixed media have to be inserted. In the case of binary mixtures the quantities $\delta^2 G$ and $\gamma'^2 G$ are the respective effective values of the optical anisotropy and molecular anisotropy of the mixture.

In the special case of binary mixtures two approaches have been suggested recently. The first was formulated by Kielich[10,17] by the expression (in our notation):

$$\gamma'^2 G = x_1\gamma_1^2 + x_2\gamma_2^2 + x_1^2\gamma_1^2 J_{11}^A + 2x_1x_2\gamma_1\gamma_2 J_{12}^A + x_2^2\gamma_2^2 J_{22}^A, \tag{8}$$

where $\gamma_1^2$ and $\gamma_2^2$ are the optical anisotropies of the isolated molecules of components (1) and (2), $x_1$ and $x_2$ the respective mole fractions. Quantities $J_{11}^A$ and $J_{22}^A$ are angular correlation integrals[15] between similar molecules, and $J_{12}^A$ is such an integral between unlike molecules. The second was proposed by Shakhparonov[9] and expressed by:

$$\gamma'^2 G = [x_1\gamma_1^2 + x_2\gamma_2^2 + P(x)]\,[(n^2+2)/3]^2, \tag{9}$$

where $P(x)$ is defined as

$$P(x) = Ax_1 + Bx_1x_2 + Cx_2 \tag{10}$$

with coefficients $A$, $B$, and $C$ depending on the correlations between like or unlike molecules.

It is obvious that both approaches make use of parameters describing orientational correlations and suggesting a second-order dependence of the effective optical anisotropy on the mole fraction. Both Kielich's and Shakhparonov's equations are based on the assumption that the anisotropic scattering is partially an additive function of the molecular anisotropies $\gamma_1^2$ of the isolated molecules, and partially influenced by intermolecular orientational correlations.

## EXPERIMENTAL

Details of the light scattering measurements were the same as described in Part I of this vork[24]. Measurements were performed with the following binary mixtures: cyclohexane-benzene, $n$-heptane-benzene, carbon tetrachloride-benzene, cyclohexane-carbon disulfide, $n$-heptane-carbon disulfide, and carbon tetrachloride-carbon disulfide.

## RESULTS

The values of $\delta^2 G$ for all six binary liquid mixtures as related to the mole fraction $x_2$ of component (2) are shown in Figs. 1 and 2. The quantity $\delta^2 G$ was calculated from the expression

$$\partial^2 G = (5\,\lambda_0^4/3\,\pi^2)\,[NH_V/(N\partial\varepsilon/\partial N)^2] \tag{11}$$

obtained by combining Eqs. (1) and (2). The values of the partial Rayleigh ratio $H_V$, number density $N$ of the mixtures, and the increment $N\partial\varepsilon/\partial N$ are listed in Table I. The ratios $H_V$ were determined directly by measurement of the light scattering. The values of $N$ were obtained from density data (see Part I) from the expression

$$N = N_A\varrho/M \tag{12}$$

where $N_A$ is the Avogadro number, $\varrho$ is the density of the mixture and $M = M_1 + (M_2 - M_1)\,x_2$ is the average molecular weight of the mixture. The quantity $N\partial\varepsilon/\partial N$ was determined from the expression (see Part I)

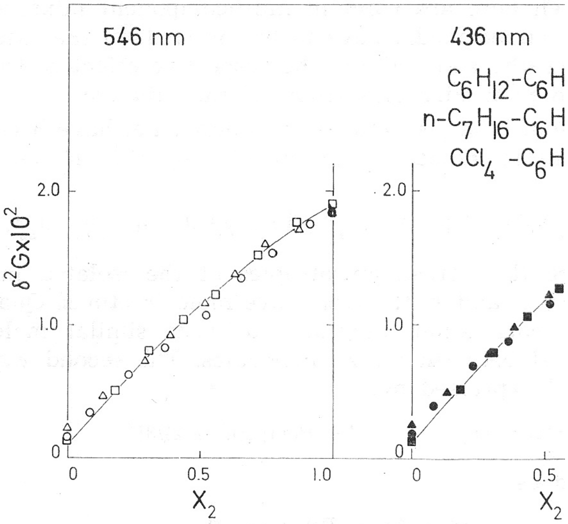

Fig. 1. The real optical anisotropy term $\delta^2G$ at wavelengths 546 and 436
fraction $x_2$ for liquid mixtures containing benzene as the sec

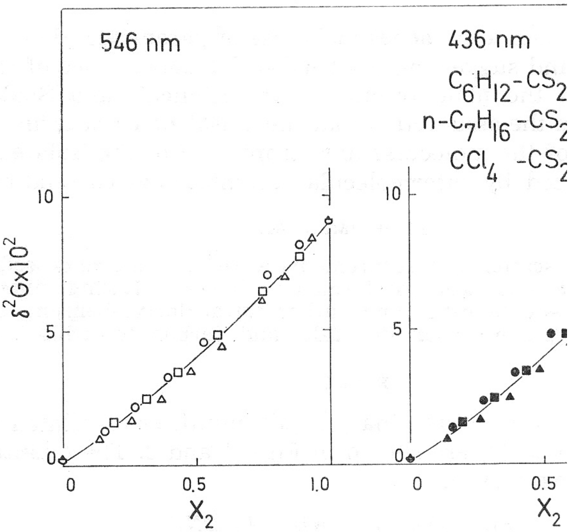

Fig. 2. The real optical anisotropy term $\delta^2G$ at wavelengths 546 and 436 n
fraction $x_2$ for liquid mixtures containing carbon disulfide as the

$$(N\partial\varepsilon/\partial N) = 0.304\,(n^2 - 1)\,(n^2 + 2),$$

where $n$ is the refractive index of the mixture. Only $H_v$
further analysis since it has been found that the $V_h$ rat
within the experimental error which can be estimated to
depending on the absolute intensities measured.

From data in Table I the values $\gamma'^2G$ can be determi
graphical presentation of the dependence of $\gamma'^2G$ on $x_2$ is gi

TABLE I

*Number Densities N, Partial Rayleigh Ratios $H_v$ and Increment $N\partial\varepsilon/\partial N$ in Dependence of Mole Fraction $x_2$ of Component (2) and Wavelenght $\lambda_0$ for Various Liquid Mixtures*

| | | $\lambda_0 = 546$ nm | | $\lambda_0 = 436$ nm | |
|---|---|---|---|---|---|
| $x_2$ | $N \times 10^{-21}$ (cm$^{-3}$) | $H_V \times 10^6$ (cm$^{-1}$) | $N\,\partial\varepsilon/\partial N$ | $H_V \times 10^6$ (cm$^{-1}$) | $N\,\partial\varepsilon/\partial N$ |
| Cyclohexane (1) — Benzene (2) | | | | | |
| 0.000 | 5.54 | 0.264 | 1.278 | 0.859 | 1.314 |
| 0.083 | 5.64 | 0.684 | 1.298 | 2.08 | 1.340 |
| 0.230 | 5.78 | 1.32 | 1.335 | 3.88 | 1.381 |
| 0.368 | 5.93 | 1.77 | 1.365 | 5.00 | 1.416 |
| 0.521 | 6.10 | 2.39 | 1.408 | 6.94 | 1.465 |
| 0.650 | 6.38 | 3.06 | 1.450 | 8.65 | 1.512 |
| 0.777 | 6.43 | 3.66 | 1.496 | 9.72 | 1.565 |
| 0.912 | 6.70 | 4.42 | 1.566 | 12.3 | 1.646 |
| 1.000 | 6.78 | 4.95 | 1.628 | 13.9 | 1.716 |
| *n*-Heptane (1) — Benzene (2) | | | | | |
| 0.000 | 4.08 | 0.457 | 1.116 | 1.28 | 1.144 |
| 0.137 | 4.29 | 0.974 | 1.147 | 2.70 | 1.180 |
| 0.295 | 4.58 | 1.58 | 1.197 | 4.44 | 1.237 |
| 0.388 | 4.78 | 2.01 | 1.230 | 5.63 | 1.272 |
| 0.518 | 5.10 | 2.56 | 1.279 | 7.16 | 1.326 |
| 0.637 | 5.43 | 3.16 | 1.345 | 8.98 | 1.402 |
| 0.751 | 5.79 | 3.82 | 1.418 | 10.7 | 1.483 |
| 0.869 | 6.20 | 4.40 | 1.506 | 12.5 | 1.582 |
| 1.000 | 6.72 | 5.08 | 1.639 | 14.5 | 1.728 |
| Carbon Tetrachloride (1) — Benzene (2) | | | | | |
| 0.000 | 6.20 | 0.270 | 1.419 | 0.696 | 1.465 |
| 0.177 | 6.26 | 1.16 | 1.454 | 3.13 | 1.508 |
| 0.307 | 6.35 | 1.89 | 1.480 | 4.98 | 1.539 |
| 0.437 | 6.42 | 2.54 | 1.508 | 6.90 | 1.572 |
| 0.556 | 6.48 | 3.04 | 1.532 | 8.49 | 1.602 |
| 0.719 | 6.57 | 3.89 | 1.564 | 10.9 | 1.641 |
| 0.865 | 6.64 | 4.62 | 1.595 | 12.8 | 1.678 |
| 1.000 | 6.73 | 5.11 | 1.625 | 14.1 | 1.715 |
| Cyclohexane (1) — Carbon Disulfide (2) | | | | | |
| 0.000 | 5.54 | 0.269 | 1.264 | 0.825 | 1.297 |
| 0.157 | 5.88 | 2.66 | 1.339 | 7.58 | 1.384 |
| 0.272 | 6.21 | 4.73 | 1.403 | 13.5 | 1.458 |
| 0.394 | 6.63 | 7.53 | 1.491 | 21.0 | 1.562 |
| 0.530 | 7.17 | 11.3 | 1.609 | 32.9 | 1.700 |
| 0.769 | 8.41 | 20.9 | 1.897 | 61.1 | 2.040 |
| 0.889 | 9.12 | 27.4 | 2.106 | 79.3 | 2.285 |
| 1.000 | 9.90 | 35.3 | 2.364 | 102.2 | 2.596 |

TABLE I (Continued)

| | | $\lambda_0 = 546$ nm | | $\lambda_0 = 436$ nm | |
|---|---|---|---|---|---|
| $x_2$ | $N \times 10^{-21}$ (cm$^{-3}$) | $H_V \times 10^6$ (cm$^{-1}$) | $N\partial\varepsilon/\partial N$ | $H_V \times 10^6$ (cm$^{-1}$) | $N\partial\varepsilon/\partial N$ |
| *n*-Heptane (1) — Carbon Disulfide (2) | | | | | |
| 0.000 | 4.08 | 0.446 | 1.094 | 1.22 | 1.135 |
| 0.139 | 4.40 | 1.96 | 1.150 | 5.16 | 1.183 |
| 0.259 | 4.75 | 3.51 | 1.211 | 9.40 | 1.254 |
| 0.371 | 5.20 | 5.28 | 1.281 | 14.3 | 1.333 |
| 0.482 | 5.65 | 7.76 | 1.366 | 21.3 | 1.431 |
| 0.600 | 6.33 | 10.3 | 1.473 | 28.9 | 1.555 |
| 0.753 | 7.30 | 16.8 | 1.696 | 46.9 | 1.814 |
| 0.834 | 8.10 | 19.9 | 1.825 | 58.7 | 1.966 |
| 0.938 | 9.10 | 28.8 | 2.127 | 82.7 | 2.316 |
| 1.000 | 9.94 | 35.4 | 2.357 | 101.9 | 2.589 |
| Carbon Tetrachloride (1) — Carbon Disulfide (2) | | | | | |
| 0.000 | 6.20 | 0.288 | 1.418 | 0.673 | 1.466 |
| 0.196 | 6.68 | 3.65 | 1.515 | 9.92 | 1.578 |
| 0.312 | 7.00 | 5.91 | 1.583 | 16.2 | 1.657 |
| 0.433 | 7.37 | 8.87 | 1.663 | 24.5 | 1.754 |
| 0.583 | 7.90 | 13.5 | 1.794 | 37.8 | 1.910 |
| 0.757 | 8.62 | 20.1 | 1.978 | 57.5 | 2.130 |
| 0.888 | 9.28 | 27.1 | 2.168 | 77.3 | 2.357 |
| 1.000 | 9.96 | 35.4 | 2.363 | 101.5 | 2.596 |

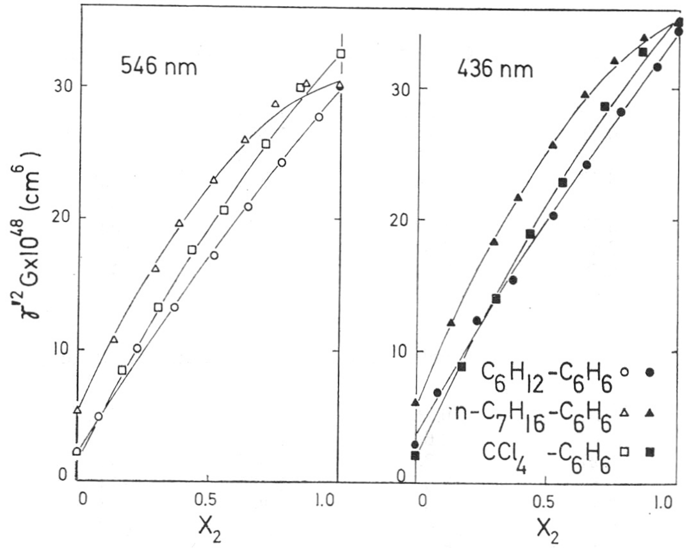

Fig. 3. The effective molecular anisotropy term $\gamma'^2 G$ at wavelengths 546 and 436 nm in dependence of mole fraction $x_2$ for liquid mixtures containing benzene as the second component.

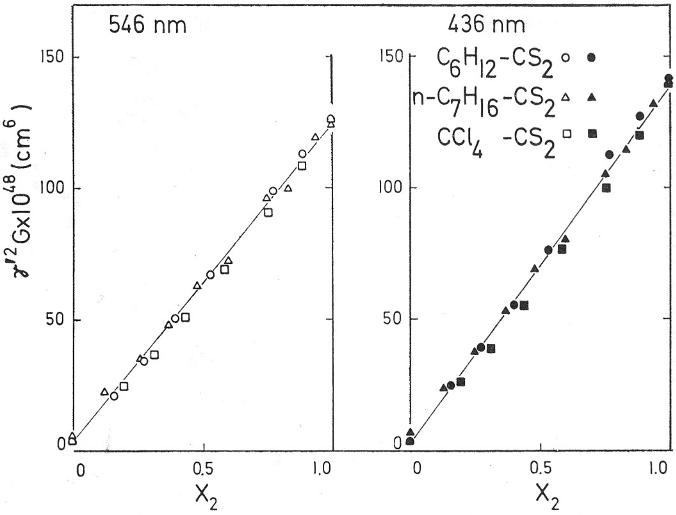

Fig. 4. The effective molecular anisotropy term $\gamma'^2G$ at wavelengths 546 and 436 nm in dependence of mole fraction $x_2$ for liquid mixtures containing carbon disulfide as the second component.

In order to examine the concentration dependence of Shakhparonov's $\gamma'^2G/[(n^2+2)/3]^2$ values on the mole fraction, the $\gamma'^2G/[(n^2+2)/3]^2$ values were calculated from Eq. (9) and plotted against $x_2$ in Figs. 5 and 6.

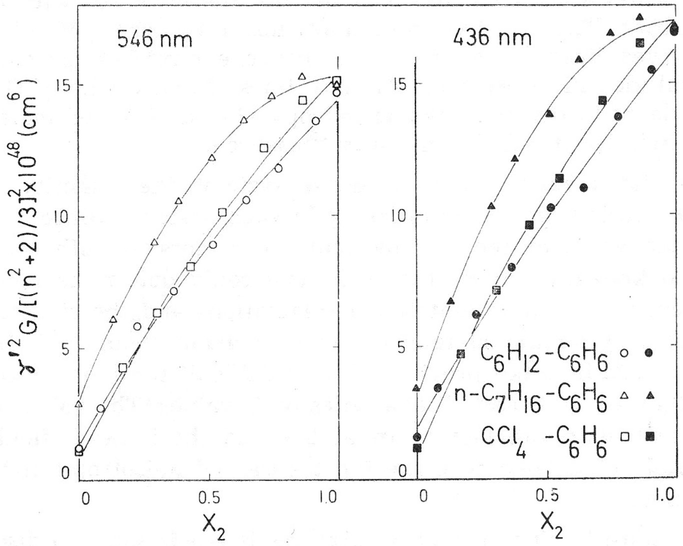

Fig. 5. The anisotropy term $\gamma'^2G/[(n^2+2)/3]^2$ at wavelengths 546 and 436 nm in dependence of mole fraction $x_2$ for liquid mixtures containing benzene as the second component.

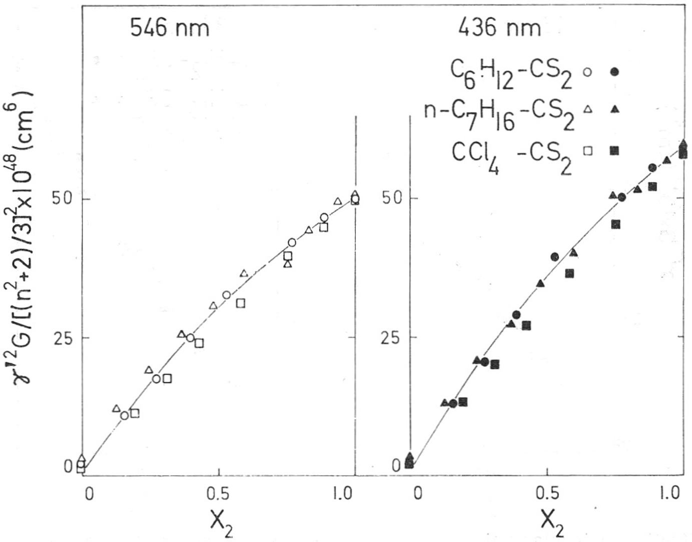

Fig. 6. The anisotropy term $\gamma'^2G/[(n^2 + 2)/3]^2$ at wavelengths 546 and 436 nm in dependence of mole fraction $x_2$ for liquid mixtures containing carbon disulfide as the second component.

## DISCUSSION

In investigating the validity of the additivity principle of optical anisotropy in molecular systems one is interested to check which of the anisotropy quantities used in Figs. 1—6, *i. e.* $\delta^2G$, $\gamma'^2G$ or $\gamma'^2G/[(n^2 + 2)/3]^2$ satisfies this principle.

The real optical anisotropy term $\delta^2G$ (being related to the apparent optical anisotropy[18] $\Delta^2$ by the Ornstein-Zernike integral[19] $kT\varkappa_TN$, where $k$ is the Boltzmann constant, $T$ the absolute temperature and $\varkappa_T$ the isothermal compressibility) shows a deviation from linearity in both the mixtures with benzene and carbon disulfide. The effective molecular anisotropy term $\gamma'^2G$ plotted against $x_2$ gives curved lines for all the three benzene mixtures measured, but the carbon disulfide mixtures give straight lines. Finally, the $\gamma'^2G/[(n^2 + 2)/3]^2$ quantity, related to the moleculer anisotropy $\gamma^2$ of an isolated molecule[16], deviates from linearity in all the mixtures measured.

It was stated earlier[1] that in dense systems the quantity $\delta^2G$ is very useful in discussing molecular ordering in such systems. Since in our case $\delta^2$ is an average value of the two molecular constants of both components $\delta_1{}^2$ and $\delta_2{}^2$, and knowing the mixture rule, one could determine factor $G$ which gives an insight into the orientational correlations and the structure of liquid mixtures. A very similar statement could be made about $\gamma'^2G$. However, for reasons discussed in detail previously[1], it is difficult to draw far-reaching conclusions either about $\delta^2$ and $\gamma'^2$ quantities or $G$ values. The values of $\delta^2$ and $\gamma'^2$ are not known with satisfactory reliability and the internal field effects are not adequately elucidated to make the theories of anisotropic light scattering more complete.

Like in pure liquids, in binary mixtures it is advisable to discuss changes in $\delta^2G$ or $\gamma'^2G$ values, in the pertinent case in dependence of $x_2$.

If in the $\delta^2 G$ plots the mixture rule of the type $\delta^2 = \delta_1^2 x_1 + \delta_2^2 x_2$ is supposed to be valid, then the benzene mixtures show a positive deviation, *i. e.* the values of $G$ seem to increase toward the central part of the curve. Since for pure benzene $G$ amounted to about 0.5, this increase would mean a disordering of perpendicularly oriented molecules. For carbon disulfide mixtures the negative deviation would suggest a decrease in $G$, meaning a perpendicular ordering of carbon disulfide molecules.

To $\gamma'^2 G$ plots similar reasoning may be applied. Here again for benzene mixtures $G$ seems to rise towards the central part of the plot, but straight lines for carbon disulfide mixtures suggest constant $G$ values.

The most pronounced deviation from linearity is observed with $\gamma'^2 G/[(n^2 + 2)/3]^2$ *vs.* $x_2$ curves. Having in mind the remark made[20] it can be concluded that with this kind of plotting the optical anisotropy is corrected for an excess internal field factor $[(n^2 + 2)/3]^2$ as noted by Coumou[21].

To the question which of the three anisotropy factors should be used when discussing changes in $G$, no definite answer can be given at present owing to the unreliability of the physical constants needed and the inadequacy of present light scattering theories in dense media. It seems, however, that preference should be given to the $\gamma'^2 G$ *vs.* $x_2$ plots since the effective molecular anisotropy, in our case obtained from the partial Rayleigh ratio $H_v$ by assuming an internal field of the spherical Lorentz type, is almost completely corrected for internal field effects. The application of other forms of internal field factors, such as the Lorentz ellipsoidal, the Onsager spherical, or the Onsager-Sholte, would introduce minor changes in absolute values, but the picture would remain the same. Plots of $\delta^2 G$ *vs.* $x_2$ appear to be inferior since $\delta^2 G$ includes internal field effects.

If the results on the excess thermodynamic functions obtained with the same binary mixtures (Part I of this series) are taken into consideration, preference can again be given to $\gamma'^2 G$ plots. It has been noted that benzene mixtures show excess free energies above 60 cal/mol, whereas for carbon disulfide mixtures far lower values are reported. Increasing values of excess free energy can often be connected with the increasing values of excess entropy and may indicate the existence of clustering of molecules or any type of intermolecular interaction. If the curvilinear behavior of benzene mixtures plots and the linear behavior of carbon disulfide mixtures plots with $\gamma'^2 G$ are significant, this might indicate, in accordance with thermodynamic data, changes in the molecular orientation of benzene molecules in dependence of $x_2$ as well as almost no changes in the orientation of carbon disulfide molecules with dilution.

We tried to use Eqs. (8) and (9) in analysing the curves shown in Figs. 3 to 6. The second-order least-squares curves were evaluated in relation to $x_2$, but no definitive conclusions could be formulated. It can be assumed that all parameters taken as constants in these second-order equations are concentration dependent and that the analysis of the physical meaning of the equation constant is a task not solvable at present.

Finally the Bothorel method for determining the optical anisotropy of separate molecules by measuring $H_v$ in dilute solutions was examined in view of our results. Bothorel's method[5] consists in measuring the $H_v$ (he calls it depolarized scattered intensity) of the mixture and subtracting $H_{v,1}^0$, the partial Rayleigh ratio of pure solvent corrected for the actual presence of this component in the mixture by the weight fraction $w_1$. In our notation and rearranged to give $\gamma_2'^2 G$, Bothorel's equation reads:

$$\gamma_2'^2 G = (15\,\lambda_0^4/16\,\pi^4 N_2)\,\{H_V/[(n^2+2)/3]^2 - H_{V,1}^0\, w_1/[(n^2+2)/3]^2\} \qquad (14)$$

with $N_2$ being the number density of solute molecules. We used also a simplified version of this equation:

$$\gamma_2'^2 G = (15\,\lambda_0^4\, M_2/16\,\pi^4 N_A c_2)\,\{H_V/[(n^2+2)/3]^2 - H_{V,1}^0/[(n^2+2)/3]^2\} \qquad (15)$$

since it could be proved that both equations, within the range of experimental error, give equal results. In Eq. (15) $c_2$ is the concentration of the solute in grams per cm$^3$, and $M_2$ is the molecular weight of the solute. Fig. 7 gives an example for two mixtures: cyclohexane-benzene and cyclohexane-carbon disulfide. Bothorel assumed that the values of $\gamma_2'^2 G$ were constant in the range of lower solute concentrations, but the results shown in Fig. 7 and obtained with other mixtures suggest a concentration dependence of $\gamma_2'^2 G$. This could be expected from a simple examination of Figs. 1—6. Extrapolation to zero concentration leads to $(\gamma_2'^2 G)_0$ values differing from mixture to mixture. A summary of extrapolated values is given in Table II. At infinite dilution, if the solute molecules can be assumed to be isolated, $G \rightarrow 1$ and $(\gamma_2'^2 G)_0 = \gamma_2'^2$. However, from all the $(\gamma_2'^2 G)_0$ values no $\gamma^2$ values comparable with the literature values[22] for isolated molecules could be obtained. In performing extrapolations one would like to have measurements nearer to the zero concentration. Unfortunately, the experimental error at $x_2 < 0.1$ rises too much and does not allow reliable experimental determination of $\gamma_2'^2 G$ at very low concentrations. Although the reliability of the absolute amounts of the extrapolated values could be questioned, it is hardly believable that the general trend of the curves as well as

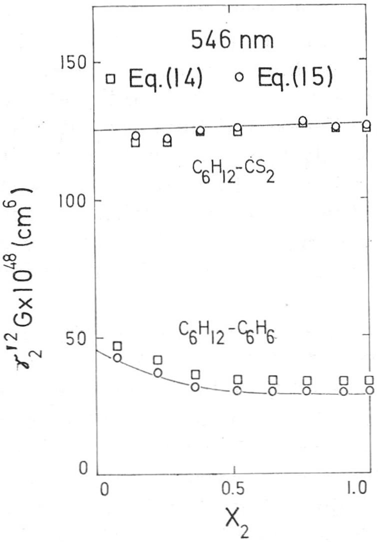

Fig. 7. The effective molecular anisotropy term $\gamma_2'^2 G$ of benzene and carbon disulfide dissolved in cyclohexane in dependence of the mole fraction of solute $x_2$. The quantity $\gamma_2'^2 G$ was evaluated by Eqs. (14) and (15) from light scattering data determined at the wavelength 546 nm.

TABLE II

*Extrapolated Values* $(\gamma_2'^2 G)_0$ *of Benzene and Carbon Disulfide in Various Solvents*

| Component (1) | Component (2) | $(\gamma_2'^2 G)_0 \times 10^{48}$ (cm$^6$) | |
|---|---|---|---|
| | | 546 nm | 436 nm |
| cyclohexane | benzene | 45.3 | 52.0 |
| *n*-heptane | benzene | 42.4 | 48.7 |
| carbon tetrachloride | benzene | 37.4 | 40.5 |
| cyclohexane | carbon disulfide | 115.3 | 136.0 |
| *n*-heptane | carbon disulfide | 125.0 | 148.2 |
| carbon tetrachloride | carbon disulfide | 128.7 | 150.0 |

the discrepansies between the $(\gamma_2'^2 G)_0$ and $\gamma^2$ values would be much changed. All this suggests that even at infinite dilution the intermolecular interactions between solute and solvent molecules are so strong that a distorsion of the molecular polarizability tensors takes place. In a recent paper by Bothorel and collaborators[23] this has been confirmed. By measuring a series of normal alcanes in different solvents they found differences in extrapolated values and concluded that this might be ascribed to the existence of orientational correlations between the alcane chains and the solvent molecules. Thus, the optical anisotropy of single molecules could not be determined by infinite dilution methods if the molecules of the solute and the solvent are of comparable size.

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## IZVOD

### Rasipanje svjetlosti u binarnim tekućim smjesama. II. Anizotropno rasipanje

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Anizotropno rasipanje svjetlosti u tekućim smjesama malih molekula neelektrolita mjereno je kod valnih dužina 546 i 436 nm. Ispitivane su smjese cikloheksana, *n*-heptana i ugljičnog tetraklorida (komponenta 1) s benzenom i ugljičnim disulfidom (komponenta 2). Iz eksperimentalnih podataka određeni su faktori optičke anizotropije te je proučavana njihova koncentracijska zavisnost. Analizirana je valjanost principa aditivnosti optičke anizotropije. Zaključeno je da odstupanje efektivne molekularne anizotropije od linearnosti ukazuje na promjenu u orjentacijskim korelacijama molekula u smjesama. Analizirajući dodatne termodinamičke funkcije istih smjesa zaključeno je da takve krivulje opisuju molekularne interakcije i njihove promjene u zavisnosti od koncentracije. Razmatrane su postojeće teorijske formule i istaknuto je da potrebni parametri zavise od koncentracije te da tumačenje njihova fizikalnog značenja za sada nije moguće. Ispitivane su metode za određivanje molekularnih anizotropija izoliranih molekula koje se zasnivaju na vrijednosti kod beskonačnog razrjeđenja. Nađeno je da su intermolekularne interakcije između molekula otapala i otopljene tvari, ako su molekule usporedive veličine, uvijek tako znatne da se takvim metodama ne može odrediti anizotropija izoliranih molekula.

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