Angular Dependence of the Light Scattering in Pure Liquids

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A review of equations for the calculation of all possible Rayleigh ratios, polarization ratios and apparent optical anisotropy is given. It is shown that all these quantities can be derived from physical constants characteristic for a dense medium, provided the statistical theory of the fluctuations in density and orientation is applied. Angular light scattering measurements were performed using the Oster-Aminco photometer at wavelengths of 546 and 436 mµ. The results show a good agreement between theory and experiment.

The light scattering of liquids has been the subject of numerous theoretical and experimental studies. The light scattering method appears to be a useful tool for the investigations of several important properties of molecules, such as molecular polarizability and anisotropy, or correlation effects between molecules in dense systems. Although the number of experimental data for Rayleigh ratios of pure liquids at a scattering angle of 90° is considerable, studies of the angular distribution of scattered intensities are rather scarce.

Martin,1 King,2 and Cabannes3 were the first to give relationships for the angular dependence of the scattered intensity and polarization ratio, and Martin1 was able to present some experimental evidence for the relationships. Since then several workers4-7 have shown that the expressions, primarily developed for independent particles or molecules, hold also for liquids. These studies, however, were more or less a part of the studies on the calibration of light scattering apparatus and do not serve as contributions to the problem of molecular scattering itself.

Recently a more thorough study of the angular dependence of light scattering in liquids was published by Leite et al.8 They used a gas laser as a light source and measured the angular dependence of the relative intensities of light scattered from carbon tetrachloride, benzene and toluene. Since they used a plane — polarized incident beam, their data were restricted to the four possible combinations of intensities, depending on the orientation of the electric vectors of the incident and scattered beam to the scattering plane. Although the study of Leite et al.8 proved the applicability of theoretical equations to the angular variation of scattering in liquids, we feel that it still might be worth-while to report our own measurements carried out on a simple angular light scattering photometer with a mercury lamp as a light source. In addition, we

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tried to compare our experimental results with the values calculated from the physical constants of liquids, i.e. to relate the angular scattering in dense systems with the results of the statistical theory of fluctuations.

THEORETICAL PART

In the fluctuation theory of light scattering in molecular systems it is customary to define some light scattering quantities characteristic of these systems. If an assembly of N molecules per unit volume is irradiated by an unpolarized light beam of intensity $J_0$, then the so-called Rayleigh ratio at the scattering angle $\theta$ can be expressed as

$$R (\theta) = J (\theta) r^2/J_0 V.$$  \hspace{1cm} (1)

Here $J(\theta)$ is the intensity of light scattered by a volume $V$ at an angle $\theta$, and $r$ the distance between the particles and the observer. Thus the Rayleigh ratio is physically the scattered intensity of light per unit volume, per unit solid angle, and per unit incident intensity. The dimension of the Rayleigh ratio is [length$^{-1}$].

If the molecules are optically anisotropic, the total Rayleigh ratio, $R(\theta)$, can be expressed as a sum of both the isotropic and anisotropic part:

$$R (\theta) = R_{is} (\theta) + R_{anis} (\theta).$$  \hspace{1cm} (2)

According to the fluctuation theory, the isotropic part can be regarded as resulting from the fluctuations in density, and the anisotropic part from the fluctuations in orientation. As a result of statistical calculations,$^9$-$^{12}$ eqn. (2) can be expressed in a form which contains only physical constants.$^{13}$ The expression for $\theta = 90^\circ$ is as follows:

$$R (90) = (\pi^2/2 \lambda_0^4) (N \partial \varepsilon_{opt}/\partial N) \lambda^2 (kT x_T + 13 \delta^2 G/5 N).$$  \hspace{1cm} (3)

Here $\lambda_0$ is the wavelength of light in vacuo, $\varepsilon_{opt}$ the dielectric constant of the liquid measured at the optical frequencies ($\varepsilon_{opt} = n^2$, $n$ being the refractive index of the liquid), $T$ the absolute temperature, $k$ the Boltzmann's constant, $x_T$ the isothermal compressibility and $\delta$ the optical anisotropy of single molecules. The factor $G$ accounts for the orientational correlations between the molecules, having the same form as a factor discussed by several authors.$^{10}$-$^{19}$ All these factors are experimentally accessible quantities. ($N \partial \varepsilon_{opt}/\partial N)_T$ can be evaluated from the $(\partial n/\partial p)_T$ values$^{19}$ and $\delta^2$ from measurements of polarization ratios of molecules in the gaseous state. In the special case of nonpolar uniaxial molecules $G$ can be evaluated from Kerr constants or polarization ratios in the liquid state.$^{13}$ The first term in the binomial of eqn. (3) belongs to the isotropic part, the second to the anisotropic part.

Kielich$^{11}$ divided both $R_{is}$ and $R_{anis}$ into two parts; one part independent of angle and a function of physical constants only, denoted as $F_{is}$ and $F_{anis}$ respectively, the other part an angular function. In the terms of fluctuation theory, Kielich’s angular expression can be written in the form:

$$R_{is} (\theta) = (\pi^2/10 \lambda_0^4) [5 (1 + \cos^2 \theta) F_{is} + (13 + \cos^2 \theta) F_{anis}].$$  \hspace{1cm} (4)

Here the functions $F_{is}$ and $F_{anis}$ are different in some factors from Kielich’s original functions, and are defined as:
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\[ F_{is} = kT \kappa_T (N \partial \varepsilon_{opt}/\partial N)_{T^2}, \]

\[ F_{anis} = (\delta^2 G/N) (N \partial \varepsilon_{opt}/\partial N)_{T^2}. \]

Let us call them scattering factors.

The isotropic and anisotropic parts of the Rayleigh ratio are:

\[ R_{is}(\theta) = (\pi^2/10\lambda_\theta^4) (1 + \cos^2 \theta) \cdot 5F_{is}, \]  
\[ R_{anis}(\theta) = (\pi^2/10\lambda_\theta^4) (13 + \cos^2 \theta) \cdot F_{anis}. \]

The ratio

\[ F_{anis}/F_{is} = \delta^2 G/kT \kappa_T N = \Lambda^2 \]

is called the apparent optical anisotropy of the molecules. This is actually the optical anisotropy of strongly interacting molecules. As the medium approaches the ideal gas state, \( G \rightarrow 1, kT \kappa_T N \rightarrow 1, \) and \( \Lambda^2 \rightarrow \delta^2. \)

In light scattering experiments only \( R(\theta) \) is a directly measurable quantity. \( R_{is}(\theta) \) and \( R_{anis}(\theta) \) should be derived from a combination of polarizers in both the incident and scattered beams.

Regarding the incident intensity of an unpolarized beam as a sum of the intensities of vertically and horizontally polarized light (with respect to the scattering plane), the total Rayleigh ratio, \( R(\theta) \), can be represented as a sum of partial Rayleigh ratios:

\[ R(\theta) = [V_v(\theta) + V_h(\theta) + H_h(\theta) + H_v(\theta)]/2. \]

Here the indices \( v \) and \( h \) denote the vertically and horizontally polarized component of the incident beam, respectively. The capital letters \( V \) and \( H \) stand for the vertically and horizontally polarized components of the scattered beam, respectively.

These quantities are defined by the equations:

\[ V_v(\theta) = (\pi^2/5\lambda_\theta^4) (5F_{is} + 4F_{anis}), \]
\[ V_h(\theta) = H_v(\theta) = (\pi^2/5\lambda_\theta^4) \cdot 3F_{anis}, \]
\[ H_h(\theta) = (\pi^2/5\lambda_\theta^4) [5F_{is} \cos^2 \theta + (3 + \cos^2 \theta) F_{anis}]. \]

In addition, four other quantities can be measured (the index \( u \) denoting the unpolarized incident beam, the capital letter \( R \) denoting that no polarizer is placed in the scattered beam):

\[ V_u(\theta) = R_v(\theta) = V_v(\theta) + V_h(\theta) = (\pi^2/5\lambda_\theta^4) (5F_{is} + 7F_{anis}), \]
\[ H_u(\theta) = R_h(\theta) = H_v(\theta) + H_v(\theta) = (\pi^2/5\lambda_\theta^4) [5F_{is} \cos^2 \theta + (6 + \cos^2 \theta) F_{anis}]. \]

The expressions for the polarization ratios can be deduced from eqns. (11) to (15):

\[ D_u(\theta) = H_u(\theta)/V_u(\theta) = [5F_{is} \cos^2 \theta + (6 + \cos^2 \theta) F_{anis}]/(5F_{is} + 7F_{anis}); \]
\[ D_v(\theta) = H_v(\theta)/V_v(\theta) = 3F_{anis}/(5F_{is} + 4F_{anis}), \]
\[ D_h(\theta) = V_h(\theta)/H_h(\theta) = 3F_{anis}/[5F_{is} \cos^2 \theta + (3 + \cos^2 \theta) F_{anis}]. \]
All these expressions can be given in a form more suitable for experimental verification by combining the Rayleigh and polarization ratios at 90°. The full set of equations, most of them already known from literature,1-7,11 is as follows:

\[ R(\theta) = R(90) \left[ 1 + \frac{1 - D_u(90)}{1 + D_u(90)} \cos^2 \theta \right] \]  
(19)

\[ V_u(\theta) = V_u(90) \]  
(20)

\[ H_u(\theta) = \frac{1}{2} H_u(90) \left[ 1 + \sin^2 \theta + \frac{1}{D_v(90)} \cos^2 \theta \right] \]  
(21)

\[ V_v(\theta) = V_v(90) \]  
(22)

\[ V_h(\theta) = H_v(\theta) = V_h(90) = H_v(90) \]  
(23)

\[ H_h(\theta) = H_h(90) \left[ \sin^2 \theta + \frac{1}{D_v(90)} \cos^2 \theta \right] \]  
(24)

\[ D_u(\theta) = D_u(90) \left[ 1 + \frac{1 - D_u(90)}{D_u(90)} \cos^2 \theta \right] \]  
(25)

\[ D_v(\theta) = D_v(90) \]  
(26)

\[ D_h(\theta) = D_h(90) \left[ \sin^2 \theta + \frac{1}{D_v(90)} \cos^2 \theta \right] \]  
(27)

Derived Rayleigh ratios \( R_{is} \) and \( R_{anis} \) can be deduced from measurable ones giving expressions:

\[ R_{is}(\theta) = \frac{1}{2} \left[ V_v(\theta) + H_h(\theta) - \frac{1}{3} V_h(\theta) (7 + \cos^2 \theta) \right] \]  
(28)

\[ R_{anis}(\theta) = \frac{1}{6} V_h(\theta) (13 + \cos^2 \theta) \]  
(29)

There is the useful relationship linking the polarization ratios

\[ D_u(\theta) = [1 + 1/D_h(\theta)]/[1 + 1/D_v(\theta)]. \]  
(30)

For the special case of \( \theta = 90^\circ \),

\[ D_h(90) = 1, \]  
(31)

\[ D_u(90) = 2 D_v(90)/[1 + D_v(90)]. \]  
(33)

All these equations, except eqns. (6) and (9), hold for media of arbitrary density, consisting of any molecules small compared with the wavelength of light. Equations (6) and (9) are restricted to the small, nonpolar, uniaxial molecules. For other types of molecules the equations for \( F_{is} \) and \( F_{anis} \) are more complicated and contain factors such as the hyperpolarizability and the anisotropy of hyperpolarizability11 which at present are not experimentally accessible.
Light scattering measurements were carried out with an Oster-Aminco photometer improved as described earlier. The measuring instrument was the Skalen-galvanometer manufactured by Zeiss, Jena, Germany. The apparatus was calibrated with benzene using values obtained on the basis of calibration with Ludox. These data belong to the group of most reliable values, as shown in a critical survey by Kratohvil et al. and are in perfect agreement with values recently obtained by Claesson and Ohman. The plane — polarized components were obtained by placing carefully adjusted polaroid discs in front of the cell or photomultiplier tube. All data were corrected for differences in refractive indices, resistors in the photometer circuit, and the different sensitivity of the photomultiplier tube to light beams polarized in different planes.

For measurements of absolute Rayleigh ratios semioctagonal cells made by Hellma GMBH, Müllheim/Baden, Germany, were used. Angular measurements were made with cylindrical cells, supplied by the American Instrument Company, Silver Spring, Maryland, U.S.A. Cells were always black painted on the back outer surface which proved to eliminate most of the stray reflections in the cell. All measurements were made at room temperatures (23-26°C).

The liquids were reagent grade chemicals. Benzene was distilled several times over sodium and collected directly into the cell. Carbon disulphide was shaken for some time with mercury and mercurous chloride. After shaking with distilled water the material was dried and fractionally distilled into the cell in the dark. Phosphorus pentoxide was used as a drying agent in both the drying and distillation processes. The final product had an ethereal odor.

RESULTS

In determinations of Rayleigh ratios it is very important to correct the galvanometer readings for differences in refractive indices of the scattering media. In the simplest case the detector does not «see» past the edges of the incident beam. For this case Hermans and Levinson derived the well-known \( n^2 \)-correction, which has been successfully applied to experimental work (for a discussion of this correction see Ref. 21). Recently it was claimed that the Aminco photometer does not fulfill the requirement for the \( n^2 \)-correction, as has previously been pointed out. Experience in this laboratory with the evidence following from simple geometric calculations, taking into account a certain divergence of the incident beam, has led to the same conclusion. We have now tried to prove this directly. A strip of Kodak Plus-X film was placed behind the receiver nosepiece and, having a semioctagonal cell filled with benzene or carbon disulphide and the goniometer at 90°, exposed for several hours to light of wavelength 546 µm. A dark spot suitable for densitometry developed after 5 hours exposure (with a AH-4 mercury lamp as light source) in the case of carbon disulphide, and 1 day in the case of benzene. The optical density of the film was measured with a single beam, selenium cell, spectrographic densitometer. The result of the measurement with carbon disulphide as the scattering medium is shown in Fig. 1. The nosepiece consisted of two equal rectangular slits 2.8 × 1.5 mm. separated by 15 mm. The edges of the slit are sharply marked on the film by the plateau in the broken lines of optical density measurements. It is obvious that the detector «sees» a scattering volume within the incident beam, because the scattered intensity decrease linearly in each direction from the edge of the slit.

* The measurements were made on the densitometric equipment of the Department of Forensic Medicine, Faculty of Medicine, University of Zagreb. We acknowledge Prof. K. Weber for making this equipment available.
Values of $F_{is}$ and $F_{anis}$ and the physical constants needed for their calculation are given in Table I. The constants are taken from a previous paper. Here the orientational correlation factor, $G$, is derived from both the Kerr constant and polarization ratio data.

**Table I**

Physical Constants and Scattering Factors for Benzene and Carbon Disulphide at 25°C

<table>
<thead>
<tr>
<th>$\lambda_0$ (m)</th>
<th>n</th>
<th>$(N \partial \varepsilon_{opt}/\partial N)_T$</th>
<th>$\delta^2 \times 10^2$</th>
<th>$F_{is} \times 10^{24}$ (cm.²)</th>
<th>$F_{anis} \times 10^{24}$ (cm.²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>546</td>
<td>1.502</td>
<td>1.624</td>
<td>3.2</td>
<td>10.5</td>
<td>6.7</td>
</tr>
<tr>
<td>436</td>
<td>1.519</td>
<td>1.712</td>
<td>3.4</td>
<td>11.6</td>
<td>7.8</td>
</tr>
<tr>
<td>benzene,</td>
<td>$\kappa_T = 9.65 \times 10^{-11}$ dyne cm.²,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) G = 0.53</td>
<td>(b) G = 0.58</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>546</td>
<td>1.632</td>
<td>2.36</td>
<td>13.2</td>
<td>21.9</td>
<td>53</td>
</tr>
<tr>
<td>436</td>
<td>1.663</td>
<td>2.59</td>
<td>14.6</td>
<td>26.4</td>
<td>71</td>
</tr>
<tr>
<td>carbon disulphide,</td>
<td>$\kappa_T = 9.58 \times 10^{-11}$ dyne cm.²,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) G = 0.72</td>
<td>(b) G = 0.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From these $F_{is}$ and $F_{anis}$ data values of the Rayleigh ratios, polarization ratios and apparent optical anisotropy were calculated by use of eqns. (4), (9), and (11) to (18). These values are collected in Tables II and III.
The experimental polarization ratios were calculated directly from the galvanometer deflections after correcting for the difference in sensitivity of the photomultiplier tube to light beams polarized in different planes. The total Rayleigh ratio, R, of carbon disulphide was evaluated on the basis of the previously determined values of benzene by applying the \( n^2 \)-correction. Other Rayleigh ratios were derived from the total ratios in the following way. From eqn. (10), (14) and (15) it is obvious that the calibration factors can be defined. Here factors \( C_1 \) and \( C_2 \) are different because by measuring \( V_u \) and \( H_u \) there is only one polaroid placed before the detector whereas in the case of measuring \( V_v \), \( V_h \), \( H_v \) and \( H_h \) there are two polaroids both in the incident and scattered beams. The primed quantities in eqns. (34) and (35) are galvanometer readings for a certain combination of polaroids. These factors were determined for both the semioctagonal and cylindrical cells for benzene and carbon disulphide. Average values for different wavelengths were used in further calculations. Partial Rayleigh ratios can be determined from expressions of the type:

\[
V_u = C_1 V'_u R / R'
\]
| TABLE III |

Rayleigh Ratios, Polarization Ratios and Apparent Optical Anisotropy of Carbon Disulphide at $\theta = 90^\circ$ and $25^\circ$ C

<table>
<thead>
<tr>
<th>Calculated</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$G = 0.72$</td>
<td>$G = 0.64$</td>
</tr>
<tr>
<td>$\lambda_0 = 546\ \mu m$</td>
<td>$\lambda_0 = 436\ \mu m$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$\times 10^6$ (cm.$^{-1}$)</th>
<th>$\times 10^6$ (cm.$^{-1}$)</th>
<th>$\times 10^6$ (cm.$^{-1}$)</th>
<th>$\times 10^6$ (cm.$^{-1}$)</th>
<th>$\times 10^6$ (cm.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>$V_u$</td>
<td>$H_u$</td>
<td>$V_v$</td>
<td>$H_h$</td>
</tr>
<tr>
<td>89</td>
<td>304</td>
<td>282</td>
<td>282</td>
<td>282</td>
</tr>
<tr>
<td>81</td>
<td>313</td>
<td>306</td>
<td>306</td>
<td>306</td>
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<tr>
<td>36</td>
<td>32</td>
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<td>32</td>
<td>36</td>
<td>36</td>
<td>36</td>
<td>36</td>
</tr>
<tr>
<td>0.66</td>
<td>0.50</td>
<td>1.00</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>$\Delta^2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.4</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

by changing only $V_u$ and $V'_u$ by the desired symbols. $C_1$ should be used for the calculation of $V_u$ and $H_u$, and $C_2$ for the calculation of $V_v$, $V_h$, $H_v$ and $H_h$.

Experimental Rayleigh ratios for benzene and carbon disulphide at $\theta = 90^\circ$ are given in Tables II and III. For the sake of convenience, the designation of the scattering angle is left out. Quantities without indication of the angle always mean data at $\theta = 90^\circ$.

Adopting the experimental values of $R$ and $D_{tu}$ obtained from measurements in the semioctagonal cell, as the basis for all other data, it is possible to calculate all other ratios from these two quantities from the equations:

$$V_u = 2R/(1 + D_u),$$
$$H_n = 2RD_{tu}/(1 + D_u),$$
$$V_v = R(2 - D_u)/(1 + D_u),$$
$$V_h = H_v = H_h = D R_{tu}/(1 + D_u).$$

These data are given in column (3) of Tables II and III. The data in column (4) are obtained from equations of type (36). Data in column (5) are calculated in the same way, by using average galvanometer readings measured at nine different angles ranging from $35^\circ$ to $135^\circ$. These average readings were obtained from calculations of the normalized readings from eqns. (19) to (27). If neces-
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Fig. 2. Angular dependence of the Rayleigh ratios \( R(\theta) \), \( H_a(\theta) \) and \( H_b(\theta) \) of benzene at 25°C and 546 and 436 m\( \mu \). Points are experimental, curves theoretical (--- 546 m\( \mu \), ----- 436 m\( \mu \)).

sary, each galvanometer reading, after correcting for the changes in scattering volume by multiplying by \( \sin \theta \), was divided (or multiplied) by the factor in brackets. The standard errors (expressed as the percentage errors of one measurement) of the values in column (5) are given in column (6).

As an illustration of the angular dependence of Rayleigh and polarization ratios, the data for benzene are shown in Figs. 2, 3 and 4. Points are experimental values, solid and broken curves and lines are theoretical, calculated from eqns. (4) and (11) to (15). The data for carbon disulphide follow the same pattern.

DISCUSSION

If the data listed in Tables II and III are compared, it can be seen that the differences between the values in different columns (including calculated values) vary from 2 to 12\%/o. In general, the differences between Rayleigh ratios amount to 7%/o, and between polarization ratios to 6%/o. Since the polaroid discs used in these measurements cannot be regarded as fully reliable, and allow
results only of 5—10% accuracy, the overall experimental error of light scattering data in this paper can be estimated to be between the same limits. On the other hand, from the discussion of the precision of calculated data in a previous paper, it may be concluded that the error in these data is again 5—10%. The agreement, therefore, between the experimental and calculated data can be regarded as satisfactory.

The absolute values of the total Rayleigh ratio of carbon disulphide are higher than those values listed in the literature, and, in general, it can be observed that the discrepancies amongst the data are greater than amongst data for other liquids. This might be caused by the difficulty in obtaining highly pure samples of carbon disulphide, and by the property of this compound to decompose with time, especially when exposed to light of shorter wavelengths. We tried to purify carbon disulphide with great care and to avoid any unnecessary exposure of the sample to light, but the results were reproducibly higher than the literature values. Older measurements, carried out several years ago in this laboratory, gave values of the total Rayleigh ratio of $85 \times 10^{-6}$ and

![Fig. 3. Angular dependence of the Rayleigh ratios $V_u(\theta)$, $V_v(\theta)$, $V_b(\theta)$ and $H(\theta)$ of benzene at 25°C and 546 and 436 mu. Points are experimental lines theoretical (--- 546 mu, ------ 436 mu).](image)
256 \times 10^{-6} \text{ cm}^{-1} \text{ for 546 and 436 m}_{\mu}, \text{ respectively, in good agreement with the present data. } D_u \text{ data of the same set of measurements were 0.65 and 0.67 for 546 and 436 m}_{\mu}, \text{ respectively. Some recent data of Coumou at al.}^{19} \text{ and Jennings and Jerrard}^{25} \text{ for 546 m}_{\mu} \text{ agree with these data, although Jennings and Jerrard's value for 436 m}_{\mu} \text{ is again much lower. On the other hand, the good agreement with the calculated data suggests that the older values for carbon disulphide may be too low. Although the discrepancy between theoretical data for carbon disulphide calculated with G from the Keer constant and from polarization ratios is remarkable (resulting from rather inaccurate values of}

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{benzene.png}
\caption{Angular dependence of the polarization ratios $D_u(\theta)$, $D_v(\theta)$ and $D_h(\theta)$ of benzene at 25°C and 546 and 436 m\textmu. Points are experimental, curves theoretical (--- 546 m\textmu, -------- 436 m\textmu).}
\end{figure}

physical constants used for calculations\textsuperscript{(d)}, all these data are still in reasonable agreement.

Moreover, recent data of Lundberg \textit{et al.}\textsuperscript{26} for $V_u(90)$ (they actually measured $R_v$ which is identical with $V_u$) of several liquids at 6937 Å confirm the theory. For benzene, Lundberg \textit{et al.} report $V_u(90) = 8.4 \times 10^{-6} \text{ cm}^{-1}$, the calculated value being $8.3 \times 10^{-6} \text{ cm}^{-1}$. For carbon disulphide the experimental value is
40 \times 10^{-6} \text{ cm}^{-1} \text{ and the calculated value } 36 \times 10^{-6} \text{ cm}^{-1} \text{ Constants } (N\delta_{\text{opt}}/\partial N)_T \text{ and } \delta^2 \text{ necessary for the calculation were evaluated as described previously.}^{13}

Figs. 2, 3 and 4 also show the close agreement between theory and experiment. Greater discrepancies in the case of D_h can be explained by the unreliability of the polaroids.

It may be concluded from these results that the theories derived for dense systems can be regarded as exact. The angular scattering equations of dense systems are formally the same as those of gases. It is possible to calculate all scattering data for all scattering angles from physical constants of the particular system. However, the lack of more accurate physical constants on the one hand, and a still low precision of absolute Rayleigh ratios on the other, does not allow better agreement than 5—10\%.

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REFERENCES

7. S. Claesson and J. Öhman, Arkiv kemii 23 (1964) 69.
IZVOD

Kutna zavisnost rasipanja svjetlosti u čistim tekućinama

Gj. Deželić i J. Vavra

U ovom radu navedene su jednadžbe za računanje svih mogućih Rayleighovih omjera, polarizacijskih omjera i prividne optičke anizotropicije. Pokazano je da se ove veličine mogu izvesti iz fizičkih konstanata, karakterističnih za neki gusti medij, uz primjenu statističke teorije fluktuacija u gustoći i orijentaciji. Izvršena su mjerenja kutne zavisnosti rasute svjetlosti valnih dužina 546 i 436 mÅ pomocu fotometra Oster-Aminco. Rezultati pokazuju dobro slaganje između teorije i eksperimenta.

ODIO ZA PRIMIJEJENU BIOKEMIJU
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ZAGREB