Dispersion of refractive properties of solvents: Chloroform, toluene, benzene, and carbon disulfide in ultraviolet, visible, and near-infrared

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Dispersion of refractive properties of solvents: Chloroform, toluene, benzene, and carbon disulfide in ultraviolet, visible, and near-infrared

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Refractive index dispersion formulas have been derived for chloroform, toluene, benzene, and carbon disulfide from a broad range of the experimental refractive index data at 20 °C. The data were examined with the linear least-squares method. The dispersion equations allow one to calculate the values of refractive index required for analysis of nonlinear optical measurements in the UV, visible, and near-IR wavelength range (0.3–2.5 μm) in these liquids and solutions. The indices were compared to those estimated from quantum chemical calculations. A survey of the experimental data revealed that the measurement results published recently [Opt. Mater. 20, 81 (2002); Rev. Sci. Instrum. 65, 2056 (1994); 66, 38 (1995); 69, 1243 (1998)] were significantly different from other data reported in the literature. © 2003 American Institute of Physics. [DOI: 10.1063/1.1615294]

I. INTRODUCTION

A wealth of experimental values of refractive index at 20 °C (n20) of four important liquids: chloroform (CHCl₃), toluene (C₆H₅CH₃), benzene (C₆H₆), and carbon disulfide (CS₂) in a broad wavelength range (about 0.3–2.5 μm) are accessible.¹⁻¹³ This critical review of the values of linear refractive indices of the above liquids has been motivated by the fact that they are often used in the studies of nonlinear optical (NLO) effects in the near-infrared region (0.7–2.5 μm). Many NLO experiments are carried at around 800 nm using femtosecond pulses from a Ti:sapphire solid state laser, however, the availability of optical parametric amplifiers (OPA) operating at longer wavelengths allows one to measure nonlinear responses from solids and solutions in the telecommunication wavelength range, 1.2–1.6 μm. The linear refractive indices are needed for determination of the third-order nonlinear optical properties (nonlinear refractive index, n₂, the third-order susceptibility, χ⁽³⁾) of solvents and solutes in solutions of organic materials.¹⁴⁻²° The NLO measurements can be performed on films of neat solids or solutions using, for example, degenerate four-wave mixing (DFWM) and Z-scan techniques with picosecond or femtosecond pulses, however, the procedure of measurements of solutions is quite convenient provided sufficient solubility of a compound is present. Refractive indices of a solvent, a solute, and of solutions are required to calculate the local field factor (the Lorentz factor, which relates local and external fields) in the derivation of the molecular nonlinearity, the second hyperpolarizability, γ, of molecules from the χ⁽³⁾ measurements. Also, an interest in the development of laser light sources and an increasing number of optoelectronic applications creates a need for the knowledge of the fundamental optical properties of materials in the telecommunication wavelength range. Solvents play an important role in the design of dye lasers; a cross section for stimulated emission depends on the refractive index of the active medium (the refractive index of a dilute solution is determined mainly by the index of the solvent).

The objective of the present work is to evaluate refractive indices of the solvents at longer wavelengths. They could be found either from measurements or from the interpolation of the experimental data provided a proper dispersion equation was available. In this article precise constants for the Cauchy’s dispersion equations of linear refractive indices at 20 °C are derived from available literature data for benzene, carbon disulfide, chloroform, and toluene in the UV-visible-near-infrared range.

A severe discrepancy exists between results of interferometric measurements recently reported in Refs. 1–4 and the refractive index values already published in the literature on the same materials. A paper¹ entitled “Study of refractive properties of laser dye solvents: toluene, carbon disulfide, chloroform, and benzene” gave confusing values of refractive indices measured at two laser wavelengths, namely λ = 514.5 and λ = 632.8 nm. These indices were partially reported in a series of papers,²⁻⁴ where they were used in the derivation of the constants of optical dispersion (dn/dλ) at 600 nm, optical permittivity (ε = n²), the dielectric dispersion (de/dλ), and molecular constants: polarizability, molar refraction, molecular radius, etc. The wavelength dependence of the refractive index was described by a two parameter Cauchy’s dispersion equation in the range 400–800 nm.¹

The refractive index data and the temperature gradient (dn/dT) published in Refs. 1–4 were measured with the Mach–Zehnder laser interferometer developed in an earlier work,⁶ where the accuracy of 1 × 10⁻⁵ was reported. A parallel plate sample cell was inserted in the one arm of the interferometer and rotated against the incident laser beam. Refractive index and thickness were determined from the relationship between a number of fringes shifted and the rotation angle of the sample.²⁻³ Measurements of optical constants in the liquids at 514.5 nm were described in Ref. 4. All these papers underlined an advantage of using an interfero-
metric technique over other techniques for measuring refractive indices of liquids. It is known that the accuracy of interferometric measurements can be as high as to six decimal places. Such accuracy cannot be achieved with other optical methods, like the minimum angle of deviation or the Abbe refractometer, based on the effect of total reflection, which gives refractive index within the accuracy not better than 0.0001.23 However, as shown below, the values of refractive index calculated at the wavelength 400–800 nm using dispersion constants derived in Ref. 1 are in disagreement with experimental values published in the reference sources 5–10 accessible but were elegantly summarized by Nikogosyan.7 Not many data were available for common laser radiation and other spectral lines of the hydrogen discharge or mercury arc. The index data were usually given for the Fraunhofer lines: C 656.3 nm, D (589.3 nm), F (486.1 nm), G’ (434.1 nm), and other spectral lines of the hydrogen discharge or mercury arc. Not many data were available for common laser radiation sources.

II. EXPERIMENTAL DATA AND NUMERICAL DISPERSION RESULTS

This examination of the dependence of the refractive index n20 on wavelength in four neat liquids was based on the experimental values published in the reference sources5–10 and in original papers.11–13 Some data were obtained from the handbooks and sources, which were rather not easily accessible but were elegantly summarized by Nikogosyan.7 The index data were usually given for the Fraunhofer lines: C (656.3 nm), D (589.3 nm), F (486.1 nm), G’ (434.1 nm), and other spectral lines of the hydrogen discharge or mercury arc. Not many data were available for common laser radiation sources.

Tables I–IV contain information on the available refractive indices of four liquids in the ultraviolet, visible, and near-infrared region. Table I shows the data for chloroform in the wavelength range from 265.5 to 2480 nm, Table II for toluene (404.66–830 nm), Table III for benzene (276.3–2190 nm), and Table IV for carbon disulfide (340.4–2430 nm).

The dependence of refractive indices on the wavelength λ was approximated using the linear least-squares method for a function described with a formula

\[ y = m_1 \lambda_1 + m_2 \lambda_2 + m_3 \lambda_3 + \ldots + b. \]

The dependent y value was taken as a function of a range of multiple independent \( x_i \) variables \( \lambda = \lambda_i \pm 2\lambda_i \), where \( \lambda \) is the wavelength, and \( i \) is an integer), \( b \) was a constant. The regression allowed us to calculate the \( m_i \) coefficient (we use symbols \( A_i, B_i, C_i \) later on). Additional regression statistics were applied to determine the standard error values for the \( m_i \) coefficients, the standard error for the constant \( b \), the coefficient of determination \( r^2 \), and the standard error \( s \) for the dependent y.

The refractive index spectrum can be described with various dispersion equations6,24 among them the Sellmeier, and the Cauchy equations are the most useful. Equation (1) represents the Sellmeier’s formula:

\[ n^2 = 1 + \sum_j \frac{s_j \lambda^2}{\lambda^2 - \lambda_0^2}, \]

where \( \lambda_0 \) is the wavelength of a corresponding characteris-

### Table I. Experimental values of linear refractive index of liquid chloroform at 20 °C.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data from Ref. 1</td>
<td>514.5</td>
<td>1.456661</td>
<td>434.0</td>
<td>1.4582</td>
<td>265.5</td>
<td>1.5051</td>
<td>589.3</td>
</tr>
<tr>
<td>Data from Ref. 6</td>
<td>632.8</td>
<td>1.44145</td>
<td>434.0</td>
<td>1.4570</td>
<td>289.4</td>
<td>1.4911</td>
<td>589.3</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>396.8</td>
<td>1.463</td>
<td>486.1</td>
<td>1.4529</td>
<td>313.1</td>
<td>1.4806</td>
<td>656.28</td>
</tr>
<tr>
<td>Data from Ref. 7</td>
<td>454.1</td>
<td>1.458</td>
<td>589.3</td>
<td>1.4467</td>
<td>365.0</td>
<td>1.4661</td>
<td>Data from Ref. 11</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>486.1</td>
<td>1.4530</td>
<td>589.3</td>
<td>1.4461</td>
<td>830</td>
<td>1.4855</td>
<td></td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>589.3</td>
<td>1.4467</td>
<td>656.3</td>
<td>1.4435</td>
<td>830</td>
<td>1.4855</td>
<td></td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>656.3</td>
<td>1.4443</td>
<td>656.3</td>
<td>1.4435</td>
<td>830</td>
<td>1.4855</td>
<td></td>
</tr>
</tbody>
</table>

### Table II. Experimental values of linear refractive index of liquid toluene at 20 °C.

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
<th>( \lambda ) (nm)</th>
<th>( n^{20} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Data from Ref. 1</td>
<td>514.5</td>
<td>1.498921</td>
<td>404.66</td>
<td>1.526120</td>
<td>632.8</td>
<td>1.493680</td>
<td>435.6</td>
</tr>
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<td>Data from Ref. 7</td>
<td>632.8</td>
<td>1.495612</td>
<td>435.84</td>
<td>1.517830</td>
<td>643.85</td>
<td>1.493005</td>
<td>486.1</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>434.1</td>
<td>1.5170</td>
<td>479.9</td>
<td>1.509285</td>
<td>656.28</td>
<td>1.49243</td>
<td>501.6</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>486.1</td>
<td>1.5070</td>
<td>486.13</td>
<td>1.508315</td>
<td>656.28</td>
<td>1.492285</td>
<td>546.1</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>589.3</td>
<td>1.4955</td>
<td>546.07</td>
<td>1.500715</td>
<td>706.52</td>
<td>1.489795</td>
<td>589.3</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>656.3</td>
<td>1.4911</td>
<td>587.56</td>
<td>1.496920</td>
<td>476.5</td>
<td>1.51008</td>
<td>667.8</td>
</tr>
<tr>
<td>Data from Ref. 6</td>
<td>589.0</td>
<td>1.496800</td>
<td>488.0</td>
<td>1.50826</td>
<td>656.3</td>
<td>1.49243</td>
<td>Data from Ref. 13</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>434.0</td>
<td>1.5174</td>
<td>589.3</td>
<td>1.49693</td>
<td>496.5</td>
<td>1.50701</td>
<td>830</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>486.1</td>
<td>1.5082</td>
<td>589.3</td>
<td>1.4969</td>
<td>514.5</td>
<td>1.50456</td>
<td>514.5</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
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<td>1.4970</td>
<td>589.3</td>
<td>1.49691</td>
<td>632.8</td>
<td>1.49390</td>
<td>589.3</td>
</tr>
<tr>
<td>Data from Ref. 5</td>
<td>656.3</td>
<td>1.4912</td>
<td>589.59</td>
<td>1.496755</td>
<td>632.8</td>
<td>1.49390</td>
<td>589.3</td>
</tr>
</tbody>
</table>

### Notes

* The data for chloroform in the source (Ref. 5) were obtained from Ref. 28.
* The data in the source (Ref. 7) were listed after Refs. 29–32.

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tic resonance frequency (a position of an absorption band). The Sellmeier dispersion equation can be used to calculate refractive indices in the spectral region of the normal and anomalous dispersion.  

In the case of colorless transparent substances the variation of refractive index with wavelength, given by Eq. (1), can be replaced with simpler formulas. In an absorption-free range, at a considerable distance to the absorption band, Eq. (1) expanded into power series with respect to \( \lambda \) yields Cauchy’s equations,\(^6\,\)\(^24\) that can be represented by the formulas (2) and (3) (up to the fifth term of expansion):

\[
\lambda (\text{nm}) \quad n^{20} \quad \lambda (\text{nm}) \quad n^{20} \quad \lambda (\text{nm}) \quad n^{20} \quad \lambda (\text{nm}) \quad n^{20} \\
\hline
\text{Data from Ref. 1} \quad \text{Data from Ref. 7} \quad \text{Data from Ref. 8} \quad \text{Data from Ref. 9} \\
514.5 \quad 1.636019 \quad 560.8 \quad 1.6333 \quad 546.1 \quad 1.63608 \quad 435.9 \quad 1.67377 \\
632.8 \quad 1.623977 \quad 578 \quad 1.6298 \quad 587.6 \quad 1.62804 \quad 447.2 \quad 1.66805 \\
\text{Data from Ref. 5} \quad 587.56 \quad 1.6278 \quad 589.3 \quad 1.62774 \quad 542.1 \quad 1.65771 \\
434.1 \quad 1.6748 \quad 589.3 \quad 1.62774 \quad 656.3 \quad 1.61838 \quad 501.6 \quad 1.64742 \\
486.1 \quad 1.6523 \quad 589.3 \quad 1.62777 \quad 658.4 \quad 1.66080 \quad 546.1 \quad 1.63610 \\
656.3 \quad 1.6182 \quad 589.3 \quad 1.6276 \quad 583.6 \quad 1.63706 \quad 579.1 \quad 1.62961 \\
\text{Data from Ref. 6} \quad 589.3 \quad 1.627 \quad 3944 \quad 1.7018 \quad 587.6 \quad 1.62801 \\
434.0 \quad 1.6752 \quad 610.4 \quad 1.6243 \quad 441.6 \quad 1.67135 \quad 589.0 \quad 1.6276 \\
486.1 \quad 1.6527 \quad 643.85 \quad 1.61966 \quad 647.8 \quad 1.65923 \quad 568.3 \quad 1.6266 \\
656.3 \quad 1.6185 \quad 656.28 \quad 1.6182 \quad 489.0 \quad 1.65466 \quad 667.8 \quad 1.61686 \\
\text{Data from Ref. 7} \quad 670.8 \quad 1.6168 \quad 508.6 \quad 1.61441 \quad 597.0 \quad 1.69940 \\
404.66 \quad 1.6934 \quad 768.20 \quad 1.6080 \quad 533.9 \quad 1.63877 \quad 434.0 \quad 1.67480 \\
434.05 \quad 1.6750 \quad \text{Data from Refs. 7 and 11} \quad 589.3 \quad 1.62761 \quad 486.0 \quad 1.65230 \\
435.83 \quad 1.6742 \quad 2030 \quad 1.585 \quad 340.4 \quad 1.77580 \quad 589.0 \quad 1.62760 \\
460.2 \quad 1.6618 \quad 2200 \quad 1.584 \quad 344.4 \quad 1.76850 \quad 565.6 \quad 1.61620 \\
479.99 \quad 1.6544 \quad 2430 \quad 1.583 \quad 346.7 \quad 1.76440 \quad 589.0 \quad 1.62760 \\
486.13 \quad 1.65234 \quad \text{Data from Ref. 8} \quad 3612 \quad 1.73950 \quad 777.0 \quad 1.66720 \\
486.13 \quad 1.6525 \quad 589.0 \quad 1.62800 \quad 366.4 \quad 1.73250 \quad 873.0 \quad 1.66700 \\
497.2 \quad 1.6488 \quad 404.6 \quad 1.69340 \quad 388.9 \quad 1.70609 \quad 999.0 \quad 1.59680 \\
508.6 \quad 1.6455 \quad 430.4 \quad 1.67500 \quad 396.5 \quad 1.69960 \quad 1164 \quad 1.59280 \\
527 \quad 1.6405 \quad 435.8 \quad 1.67420 \quad 402.6 \quad 1.69478 \quad 1396 \quad 1.58910 \\
546.07 \quad 1.6308 \quad 480.0 \quad 1.65460 \quad 407.8 \quad 1.69105 \quad 1745 \quad 1.58560 \\
546.07 \quad 1.6360 \quad 486.1 \quad 1.65225 \quad 412.1 \quad 1.68797 \quad 1998 \quad 1.58400 \\
\hline
\text{Data for CS}_2 \quad \text{in the source (Ref. 5) were obtained from Ref. 28.} \\
\text{The data in the source (Ref. 7) were derived from Refs. 30–34, 36, 39–41.} \\
\text{The source (Ref. 8) contains results from Refs. 45–50.}
\]
A careful inspection of the graphs made of the form, 138 nm for toluene, 146 nm for benzene, and 183 nm was necessary to consider all possible representations given experimental points formed a curvature, and the value of the one-term Sellmeier Eq. 3 was obtained from Eqs. 2 and 3, respectively. The wavelength dependence of the refractive indices of these liquids is expected if the dispersion of optical permittivity \( \varepsilon \) is derived for Eq. (1). There are several resonances that should be taken into consideration to describe the refractive index dispersion in any of these liquids. Therefore we analyzed the experimental data from Tables I–IV using the Cauchy equations (2)–(4).

Tables V–VIII contain values of the dispersion constants \( A_i, B_i, C_i \), their standard errors, the coefficient of determination \( r^2 \), and the standard error \( \sigma \) for the dependent fitting the experimental index data with different techniques. The dispersion of optical permittivity \( \varepsilon = n^2 \) of studied liquids is represented with constants of Eq. (2) as it is shown in Table V. Adding the term in \( 1/\lambda^6 \) to Eq. (2) gives identical values of calculated refractive indices.

RefRACTive properties of liquid chloroform were represented with 25 experimental values of in the range of frequently used lasers. The standard errors are rather large due to the scatter of the experimental data obtained from many authors and measured with different techniques. The dispersion of optical permittivity \( \varepsilon = n^2 \) is given in Table V. The wavelength dependence was characterized with three \( \lambda \)-dependent terms as it is shown in Table V. Adding the term in \( 1/\lambda^8 \) slightly improved the \( r^2 \) value from 0.99785 to 0.99791 when \( \varepsilon = n^2 \), or from 0.99781 to 0.99788 when \( \varepsilon = n \), but increased the standard error for the constants \( A_0 \) and \( B_0 \) thus we decided to limit the number of terms to three.

---

**Table V. Constants of Cauchy’s equations and calculated refractive indices of liquid chloroform at 20 °C.**

<table>
<thead>
<tr>
<th>Parameter ( A_i )</th>
<th>( y = n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6})^a )</th>
<th>Parameter ( B_i )</th>
<th>( y = n(\lambda^{-2},\lambda^{-4},\lambda^{-6})^b )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>( 2.048766\pm0.001728 )</td>
<td>( B_0 )</td>
<td>( 1.431364\pm0.000595 )</td>
</tr>
<tr>
<td>( A_1(10^9 \text{ nm}^2) )</td>
<td>( 16.1937\pm1.0373 )</td>
<td>( B_1(10^9 \text{ nm}^2) )</td>
<td>( 5.63241\pm0.35709 )</td>
</tr>
<tr>
<td>( A_2(10^{10} \text{ nm}^2) )</td>
<td>( -5.9111\pm1.8380 )</td>
<td>( B_2(10^{10} \text{ nm}^2) )</td>
<td>( -2.0805\pm0.6327 )</td>
</tr>
<tr>
<td>( A_3(10^{13} \text{ nm}^6) )</td>
<td>( 3.7538\pm0.8978 )</td>
<td>( B_3(10^{11} \text{ nm}^6) )</td>
<td>( 1.2613\pm0.3091 )</td>
</tr>
</tbody>
</table>

Calculated values \( n_{\text{calc}} \) for CHCl3:

<table>
<thead>
<tr>
<th>( \lambda ) (nm)</th>
<th>( n_{\text{calc}} )</th>
<th>( \lambda ) (nm)</th>
<th>( n_{\text{calc}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>514.5</td>
<td>1.45035</td>
<td>514.5</td>
<td>1.45035</td>
</tr>
<tr>
<td>532</td>
<td>1.44922</td>
<td>532</td>
<td>1.44922</td>
</tr>
<tr>
<td>589.3</td>
<td>1.44616</td>
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<td>632.8</td>
<td>1.44433</td>
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<tr>
<td>800.0</td>
<td>1.43971</td>
<td>800.0</td>
<td>1.43970</td>
</tr>
<tr>
<td>1064</td>
<td>1.43619</td>
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<td>1.43619</td>
</tr>
<tr>
<td>1550</td>
<td>1.43367</td>
<td>1550</td>
<td>1.43367</td>
</tr>
</tbody>
</table>

\( n^2 = A_0 + \frac{A_1}{\lambda^2} + \frac{A_2}{\lambda^4} + \frac{A_3}{\lambda^6} + \frac{A_4}{\lambda^8}, \)

and

\( n = B_0 + \frac{B_1}{\lambda^2} + \frac{B_2}{\lambda^4} + \frac{B_3}{\lambda^6} + \frac{B_4}{\lambda^8}. \)

The constants \( A_0 \) and \( B_0 \), i.e., the zero terms \( i = 0 \) in the series \( 1/\lambda^{2i} \) in Eqs. (2) and (3), represent the refractive index \( n_2 \) and \( n_\infty \) for infinite wavelength \( \lambda \rightarrow 0 \), respectively.

The expression for the refractive indices of liquids in the UV-visible-near-IR range is expected if the dispersion is required, is considerably large, i.e., \( \lambda^2 \gg \lambda_0^2 \) in Eq. (1). A single value of the constant \( s \) (equal to \( A_0 \) in Eq. (2)) could satisfy this relation only if several values of \( \lambda_0 \) were taken into account proving that several resonances should be taken into consideration to describe the refractive index dispersion in any of these liquids. Therefore we analyzed the experimental data from Tables I–IV using the Cauchy equations (2)–(4).
A graphic representation of the experimental refractive indices of chloroform and these calculated from the fit with the three \( \lambda \)-dependent terms of Cauchy’s Eq. (3) using parameters from Table V in the wavelength range 250–2500 nm is shown as curve 1 in Fig. 1. This curve is compared to the dispersion curve 2 obtained for the range 400–800 nm from one \( \lambda \)-dependent term of the Cauchy equation of the type \( n = A + (B/\lambda^2) \), taking values of the constants \( A = 1.41167 \) and \( B = 11.9090909 \). The graph shows significantly different dispersion curves and values of refractive indices measured in Ref. 1 at the same wavelength, and those obtained from interpolation using Eq. (2) or Eq. (3). The differences become larger at 400 and 800 nm. Curve 1 in Fig. 1 shows a trend in the change of refractive index which cannot be experimentally verified due to a lack of data in the range 0.7–2 \( \mu \)m. The refractive index in the near-infrared region is almost constant. Here the tail of normal dispersion caused by the electronic absorption in UV overlaps with the high-energy tail of the anomalous dispersion caused by weaker vibrational absorption in the infrared. One may expect that the C–H overtones might impose a structure on the dispersion curve in the near-infrared wavelength range. The experimental evidence did not show the influence of overtones on refractive indices beyond the accuracy of the measurements using the Abbe refractometer (2 × 10^{-4}) because absorption of the higher-order overtones in the near infrared is very weak. The steep dependence of refractive index on wavelength in chloroform, given in Ref. 1 and shown by curve 2 in Fig. 1, does not appear to be justified.

Liquid toluene was characterized with 37 values of refractive index. All of them were measured within a relatively narrow wavelength range from 405 to 830 nm. The fitting parameters and the \( r^2 \) values in Table VI were obtained from Eqs. (2) and (3) based on two \( \lambda \)-dependent terms. Almost

### Table VI. Constants of Cauchy’s equations and calculated refractive indices of liquid toluene at 20 °C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( y = n^2(\lambda^{-a} \cdot \lambda^{-b} \cdot \lambda^{-c}) )</th>
<th>Parameter</th>
<th>( y = n(\lambda^{-a} \cdot \lambda^{-b} \cdot \lambda^{-c}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>2.175 132 ± 0.002 395</td>
<td>( B_0 )</td>
<td>1.474 775 ± 0.000 797</td>
</tr>
<tr>
<td>( A_1(10^4 \text{ nm}^2) )</td>
<td>20.4682 ± 1.3647</td>
<td>( B_1(10^4 \text{ nm}^2) )</td>
<td>6.990 31 ± 0.453 79</td>
</tr>
<tr>
<td>( A_2(10^4 \text{ nm}^2) )</td>
<td>7.3100 ± 1.8139</td>
<td>( B_2(10^4 \text{ nm}^2) )</td>
<td>2.177 63 ± 0.603 2</td>
</tr>
<tr>
<td>( r^2 )</td>
<td>0.997 64</td>
<td>( r^2 )</td>
<td>0.997 64</td>
</tr>
<tr>
<td>( \sigma \times 10^{-4} )</td>
<td>14.51</td>
<td>( \sigma \times 10^{-4} )</td>
<td>4.82</td>
</tr>
<tr>
<td>Calculated values ( n ) for ( C_8H_8 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.504 29</td>
<td>( n_{\text{calc}} )</td>
<td>1.504 29</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.502 19</td>
<td>( n_{\text{calc}} )</td>
<td>1.502 19</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.496 71</td>
<td>( n_{\text{calc}} )</td>
<td>1.496 71</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.493 59</td>
<td>( n_{\text{calc}} )</td>
<td>1.493 59</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.486 24</td>
<td>( n_{\text{calc}} )</td>
<td>1.486 23</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.481 12</td>
<td>( n_{\text{calc}} )</td>
<td>1.481 12</td>
</tr>
</tbody>
</table>

---

#### Table VII. Constants of Cauchy’s equations and calculated refractive indices of liquid benzene at 20 °C.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>( y = n^2(\lambda^{-a} \cdot \lambda^{-b} \cdot \lambda^{-c}) )</th>
<th>Parameter</th>
<th>( y = n(\lambda^{-a} \cdot \lambda^{-b} \cdot \lambda^{-c}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 \cdot B_0 \cdot C_0 )</td>
<td>2.178 271 ± 0.000 989</td>
<td>( B_0 \cdot C_0 )</td>
<td>1.475 922 ± 0.000 315</td>
</tr>
<tr>
<td>( A_1 \cdot B_1 \cdot C_1(10^4 \text{ nm}^2) )</td>
<td>28.7420 ± 1.1374</td>
<td>( B_1 \cdot C_1(10^4 \text{ nm}^2) )</td>
<td>9.671 57 ± 0.361 81</td>
</tr>
<tr>
<td>( A_2 \cdot B_2 \cdot C_2(10^4 \text{ nm}^2) )</td>
<td>−15.5591 ± 4.0503</td>
<td>( B_2 \cdot C_2(10^4 \text{ nm}^2) )</td>
<td>−5.2538 ± 1.2884</td>
</tr>
<tr>
<td>( A_3 \cdot B_3 \cdot C_3(10^4 \text{ nm}^2) )</td>
<td>26.1346 ± 5.0427</td>
<td>( B_3 \cdot C_3(10^4 \text{ nm}^2) )</td>
<td>8.5442 ± 1.6041</td>
</tr>
<tr>
<td>( A_4 \cdot B_4 \cdot C_4(10^4 \text{ nm}^2) )</td>
<td>−7.6948 ± 2.0083</td>
<td>( B_4 \cdot C_4(10^4 \text{ nm}^2) )</td>
<td>−2.6163 ± 0.6388</td>
</tr>
<tr>
<td>( C_5(10^{-10} \text{ nm}^2) )</td>
<td>0.999 603</td>
<td></td>
<td>4.8623 ± 2.7035</td>
</tr>
<tr>
<td>( r^2 )</td>
<td>21.40</td>
<td></td>
<td>6.69</td>
</tr>
<tr>
<td>Calculated values ( n ) for ( C_8H_8 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.509 03</td>
<td>( n_{\text{calc}} )</td>
<td>1.509 03</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.506 89</td>
<td>( n_{\text{calc}} )</td>
<td>1.506 90</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.501 28</td>
<td>( n_{\text{calc}} )</td>
<td>1.501 28</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.498 04</td>
<td>( n_{\text{calc}} )</td>
<td>1.498 06</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.490 08</td>
<td>( n_{\text{calc}} )</td>
<td>1.490 11</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.484 12</td>
<td>( n_{\text{calc}} )</td>
<td>1.483 51</td>
</tr>
<tr>
<td>( n_{\text{calc}} )</td>
<td>1.479 86</td>
<td>( n_{\text{calc}} )</td>
<td>1.479 35</td>
</tr>
</tbody>
</table>

---

^1 Equation (2).  
^2 Equation (3).  
^3 Equation (4).
TABLE VIII. Constants of Cauchy’s equations and calculated refractive indices of liquid CS₂ at 20 °C.

<table>
<thead>
<tr>
<th>Parametera,b,c</th>
<th>( y = n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8},\lambda^{-10})^a )</th>
<th>( y = n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})^b )</th>
<th>( y = n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8},\lambda^{-10})^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0, B_0, C_0 )</td>
<td>( 2.499 \times 10^{-3} \pm 0.000 \times 608 )</td>
<td>( 1.580 \times 10^{3} \pm 0.000 \times 178 )</td>
<td>( 1.582 \times 10^{4} \pm 0.000 \times 585 )</td>
</tr>
<tr>
<td>( A_1, B_1, C_1(10^9 \text{ nm}^{-3}) )</td>
<td>( 47.487 \times 10^{1} \pm 1.0077 )</td>
<td>( 15.289 \times 10^{2} \pm 0.2949 )</td>
<td>( 13.737 \times 10^{3} \pm 0.5910 )</td>
</tr>
<tr>
<td>( A_2, B_2, C_2(10^9 \text{ nm}^{-3}) )</td>
<td>( 22.644 \times 10^{1} \pm 4.987 )</td>
<td>( 4.8578 \times 10^{2} \pm 1.4596 )</td>
<td>( 10.0243 \times 10^{3} \pm 2.2686 )</td>
</tr>
<tr>
<td>( A_3, B_3, C_3(10^{11} \text{ nm}^{-3}) )</td>
<td>( -38.030 \times 10^{1} \pm 8.947 )</td>
<td>( -8.2863 \times 10^{2} \pm 2.6186 )</td>
<td>( -15.6572 \times 10^{3} \pm 3.5766 )</td>
</tr>
<tr>
<td>( A_4, B_4, C_4(10^{13} \text{ nm}^{-3}) )</td>
<td>( 5.8058 \times 10^{2} \pm 0.5225 )</td>
<td>( 1.4619 \times 10^{3} \pm 0.1529 )</td>
<td>( 1.8294 \times 10^{4} \pm 0.1940 )</td>
</tr>
<tr>
<td>( C_S(10^{10} \text{ nm}^{-5}) )</td>
<td>( \rho^2 )</td>
<td>( \sigma(10^{-4}) )</td>
<td>( \sigma(10^{-4}) )</td>
</tr>
<tr>
<td>( \lambda ) (nm)</td>
<td>Calculated values ( n(\lambda)^{20} ) for CS₂:</td>
<td>Calculated values ( n(\lambda)^{20} ) for CS₂:</td>
<td>Calculated values ( n(\lambda)^{20} ) for CS₂:</td>
</tr>
<tr>
<td>514.5</td>
<td>( 1.643 \times 10^{8} )</td>
<td>( 1.643 \times 10^{8} )</td>
<td>( 1.643 \times 10^{8} )</td>
</tr>
<tr>
<td>532</td>
<td>( 1.639 \times 10^{8} )</td>
<td>( 1.639 \times 10^{8} )</td>
<td>( 1.639 \times 10^{8} )</td>
</tr>
<tr>
<td>589.3</td>
<td>( 1.627 \times 10^{8} )</td>
<td>( 1.627 \times 10^{8} )</td>
<td>( 1.627 \times 10^{8} )</td>
</tr>
<tr>
<td>632.8</td>
<td>( 1.621 \times 10^{8} )</td>
<td>( 1.621 \times 10^{8} )</td>
<td>( 1.621 \times 10^{8} )</td>
</tr>
<tr>
<td>800.0</td>
<td>( 1.605 \times 10^{8} )</td>
<td>( 1.605 \times 10^{8} )</td>
<td>( 1.605 \times 10^{8} )</td>
</tr>
<tr>
<td>1064</td>
<td>( 1.594 \times 10^{8} )</td>
<td>( 1.594 \times 10^{8} )</td>
<td>( 1.594 \times 10^{8} )</td>
</tr>
<tr>
<td>1550</td>
<td>( 1.587 \times 10^{8} )</td>
<td>( 1.587 \times 10^{8} )</td>
<td>( 1.587 \times 10^{8} )</td>
</tr>
</tbody>
</table>

aEquation (2).
bEquation (3).
cEquation (4).

Identical \( r^2 \) values were found using the equations based on three \( \lambda \)-dependent terms but the standard error for the constant \( A_0 \) was higher. The refractive indices, calculated from Eqs. (2) and (3) (see the lower part of Table VI) were slightly different if they were calculated with the formulas extrapolated to longer wavelengths. Figure 2 shows the experimental data of refractive indices, \( n^{20} \) of toluene, and the fit with Cauchy’s Eq. (3) using parameters of two \( \lambda \) terms from Table VI which are represented with curve 1. Curve 2 represents the fit, \( n = A + (B/\lambda^2) \), using the values \( A = 1.489 \times 10^{2} \) and \( B = 5.8058 \times 10^{2} \). It can be noticed that the experimental index values measured in Ref. 1 and these predicted with the calculated curve 2 have a weaker dispersion than that obtained from the fitting of the experimental data from many other references. The experimental \( n \) values from Ref. 1 were too different to be included in the derivation of the dispersion constants for toluene.

Refractive properties of liquid benzene were described with a large amount of refractive index data points (66). The dispersion coefficients, given in Table VII, were determined with the four \( \lambda \)-dependent terms of Eqs. (2) and (3), and using five \( \lambda \)-dependent terms in Eq. (4). The experimental data were more consistent than these for chloroform and toluene, the \( r^2 \) values being closer to 1. The presence of the fifth \( \lambda \)-dependent term in Eq. (4) increased the standard error for the constant \( C_0 \). Figure 3 shows the fit of the experimental refractive indices, \( n^{20} \), of liquid benzene with Cauchy’s Eq. (3) using parameters of four \( \lambda \) terms from Table VII in the wavelength range 240–2200 nm (curve 1). Curve 2 represents the fit, \( n = A + (B/\lambda^2) \), using the values \( A = 1.476 \times 10^{2} \) and \( B = 8654.7573 \) calculated in Ref. 1. The index data from Ref. 1 agreed well with other experimental data, curves 1 and 2 in Fig. 3 overlap well for benzene within the wavelength range 400–800 nm.
Among other standard liquids carbon disulfide has the biggest representation of the experimental values of refractive indices (88). The dispersion of $n^{20}$ was fitted with Eqs. (2)–(4) in the wavelength range 340.4–2430 nm. Table VIII shows the $r^2$ values close to 0.9994 indicating consistency in the experimental data. The standard deviation of the experimental $n$ value was about $3 \times 10^{-4}$, which was lower than in benzene proving better accuracy. Figure 4 shows the fit of the experimental refractive indices, $n^{20}$, of liquid CS$_2$ with Cauchy’s Eq. (3) using four $\lambda$ terms (the curve 1). The fitting parameters were taken from Table VIII. The dispersion of refractive index of CS$_2$ calculated in this work is different from the relation $n = A + (B/\lambda^2)$ represented by the curve 2 calculated using $A = 1.60049$ and $B = 9404.9747$ from Ref. 1. The dispersion of the linear refractive index obtained here (curve 1) is steeper than the dependence (curve 2) predicted in Ref. 1.

To comment on the alternate way of obtaining dispersion of the refractive index by semiempirical quantum chemical calculations, the values of refractive index and dispersion were also estimated using the Molecular Orbital Package, version 93 (MOPAC-93) program. The geometry of molecules was initially set with the CSC CHEM3D PLUS program, then optimized with MOPAC-93. The Austin Model 1 (AM1) method was used in the MOPAC to perform computations of electronic properties of molecules in the ground state, the polarizability $\alpha$, first hyperpolarizability $\beta_{(SHO)}$, and second hyperpolarizability $\gamma_{(TH)}$, as a function of frequency, by the time-dependent coupled perturbed Hartree–Fock method. The theoretical $\alpha$ values were used to calculate refractive indices using the Lorentz–Lorenz equation. It appeared that the theoretical $n$ values do not agree with the experimental data. The dispersion curve was parallel to the experimental one at longer wavelengths (above 1.5 $\mu$m), however, the slope was different at shorter wavelength when the electronic resonance was approached.

From the experimental point of view it is useful to learn about the temperature derivative of refractive index $dn/dT$ for these standard liquids. The data listed in Ref. 1 are quite different from these collected in Ref. 7. For example, the gradient $dn/dT$ at 632.8 nm is equal to $-6.328 \times 10^{-4}$ K$^{-1}$ in chloroform, while it is equal to $-5.98 \times 10^{-4}$ K$^{-1}$ in the citation. A similar discrepancy was found in toluene, where $dn/dT = -5.273 \times 10^{-4}$ K$^{-1}$ at 632.8 nm. $dn/dT$ was calculated using $dn/dT = -5.94 \times 10^{-4}$ K$^{-1}$ at 632.8 nm in Refs. 1 and 3 and $-6.40 \times 10^{-4}$ K$^{-1}$ in Ref. 7. However, the data for CS$_2$ were found to be similar, $dn/dT = -7.91 \times 10^{-4}$ K$^{-1}$ at 632.8 nm in Refs. 1 and 2 and $-7.96 \times 10^{-4}$ K$^{-1}$ in Ref. 7. The origin of the scatter of the values is not known. A similar divergence in the temperature gradient data was found at 514.5 nm in these solvents in comparison to other literature data. One needs to conclude that the physical parameters derived from the results obtained in Refs. 1–4, i.e., optical permittivity, molar refraction, polarizability, and molecular radius for these liquids, except for benzene, may need to be reconsidered.

### III. CONCLUDING REMARKS

A critical examination and least-squares fitting of the available experimental refractive indices for four important solvents gave accurate values of coefficients of dispersion equations. The constants listed in the Tables V–VIII gave consistent $n$ values from Cauchy’s equations, Eqs. (2) and (3).

The survey of the experimental results showed some scatter of the data. Nevertheless, due to a large number of data, the values of the standard deviation indicate relatively good quality of the fitted. The error in the $n$ values was about $8.3 \times 10^{-4}$ in chloroform, $4.8 \times 10^{-4}$ in toluene, $6.8 \times 10^{-4}$ in benzene, and $3.2 \times 10^{-4}$ in CS$_2$.

A substantial improvement in the precision of the derived dispersion parameters could be achieved with measurements using interferometry. The interferometric technique was used in Refs. 1–4. For unknown reasons the values of refractive index and dispersion given there do not coincide with other published data, except those for benzene.
The dispersion curves of Cauchy’s formulas were obtained in a broad wavelength range, about 0.3–2.5 μm for these liquids, but toluene was investigated up to 830 nm only. More experimental studies in the near-infrared range are required for toluene and chloroform. Although these organic liquids are among the most commonly used solvents, their refractive properties in the near-infrared region are not sufficiently well known.

The theoretical values of refractive index and dispersion curves calculated with the MOPAC-93 do not overlap the experimental data. The slopes depart in a region of strong dispersion.

ACKNOWLEDGMENT

Australian Photonics CRC is acknowledged for support.

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