AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **94**, 6167 (2003); doi: 10.1063/1.1615294
View online: http://dx.doi.org/10.1063/1.1615294
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/94/9?ver=pdfcov
Published by the AIP Publishing

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

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(Received 25 February 2003; accepted 10 August 2003)

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 (n^{20}) of four important liquids: chloroform ($CHCl_3$), toluene ($C_6H_5CH_3$), benzene (C_6H_6), and carbon disulfide (CS_2) 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, n_2, the third-order susceptibility, $\chi^{(3)}$) of solvents and solutes in solutions of organic materials.[14–22] The NLO measurements can be performed on films of neat solid substances 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 $\chi^{(3)}$ 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 paper[1] 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 $\lambda = 514.5$ and $\lambda = 632.8$ 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 ($dn/d\lambda$) at 600 nm, optical permittivity ($\varepsilon = n^2$), the dielectric dispersion ($d\varepsilon/d\lambda$), 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,[2] 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-

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

λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}
Data from Ref. 1		Data from Ref. 6		Data from Ref. 7[b]		Data from Ref. 7[b]	
514.5	1.456 661	434.0	1.4582	265.5	1.5051	589.3	1.4455
632.8	1.441 415	434.0	1.4570	289.4	1.4911	589.3	1.4454
Data from Ref. 5[a]		486.1	1.4529	313.1	1.4806	656.28	1.4430
396.8	1.463	486.1	1.4523	365.0	1.4661	Data from Ref. 11	
434.1	1.458	589.3	1.4467	435.8	1.4546	2130	1.4329
486.1	1.4530	589.3	1.4461	589.3	1.4467	2480	1.4317
589.3	1.4467	656.3	1.4440	589.3	1.4459		
656.3	1.4443	656.3	1.4435	589.3	1.4456		

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

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 other literature data except for those for liquid benzene.

II. EXPERIMENTAL DATA AND NUMERICAL DISPERSION RESULTS

This examination of the dependence of the refractive index n^{20} on wavelength in four neat liquids was based on the experimental values published in the reference sources[5–10] 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 $y=m_1x_1+m_2x_2+m_3x_3+\cdots+b$. The dependent y value was taken as a function of a range of multiple independent x_i variables ($x_i=\lambda^{\pm 2i}$, where λ 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 σ for the dependent y.

The refractive index spectrum can be described with various dispersion equations,[6,24] among them the Sellmeier, and the Cauchy equations are the most useful. Equation (1) represents the Sellmeier's formula:

$$n^2=1+\sum_j \frac{s_j\lambda^2}{\lambda^2-\lambda_{0j}^2}, \tag{1}$$

where λ_{0j} is the wavelength of a corresponding characteris-

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

λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}
Data from Ref. 1		Data from Ref. 7[b]		Data from Ref. 7[b]		Data from Ref. 9[c]	
514.5	1.498 921	404.66	1.526 120	632.8	1.493 680	435.6	1.518 00
632.8	1.495 612	435.84	1.517 830	643.85	1.493 005	486.1	1.508 47
Data from Ref. 5[a]		479.99	1.509 285	656.28	1.492 43	501.6	1.506 20
434.1	1.5170	486.13	1.508 315	656.28	1.492 285	546.1	1.500 86
486.1	1.5070	486.13	1.508 47	706.52	1.489 795	589.3	1.496 93
589.3	1.4955	546.07	1.500 715	Data from Ref. 12		656.3	1.492 43
656.3	1.4911	587.56	1.496 920	476.5	1.510 08	667.8	1.491 80
Data from Ref. 6		589.00	1.496 800	488.0	1.508 26	Data from Ref. 13	
434.0	1.5174	589.3	1.496 93	496.5	1.507 01	830	1.4855
486.1	1.5082	589.3	1.4969	514.5	1.504 56		
589.3	1.4970	589.3	1.496 91	632.8	1.493 90		
656.3	1.4912	589.59	1.496 755				

[a]The data for toluene in the source (Ref. 5) were obtained from Ref. 28.
[b]The source (Ref. 7) contains results from Refs. 33–37.
[c]The source (Ref. 9) contains results from Ref. 38.

TABLE III. Experimental values of linear refractive index of liquid benzene at 20 °C.

λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}
Data from Ref. 1		Data from Ref. 7[b]		Data from Ref. 7[b]		Data from Ref. 9[c]	
514.5	1.508 948	308.1	1.587	589.3	1.501 65	435.6	1.523 02
632.8	1.497 866	313.3	1.582	589.3	1.501 44	486.1	1.513 13
Data from Ref. 5[a]		326.1	1.570	589.3	1.501 42	501.6	1.510 77
434.1	1.5236	340.4	1.560	589.3	1.501 40	546.1	1.505 21
486.1	1.5132	346.6	1.556	589.3	1.501 12	589.3	1.501 12
589.3	1.5012	361.0	1.548	589.3	1.5011	656.3	1.496 43
656.3	1.4965	404.66	1.5318	589.3	1.501 00	667.8	1.495 78
Data from Ref. 6		434.05	1.523 61	643.85	1.497 40	Data from Ref. 12	
434.0	1.5236	434.05	1.523 60	656.28	1.496 63	476.5	1.514 73
486.1	1.5133	435.83	1.523 19	656.28	1.496 60	488.0	1.512 84
589.3	1.5014	467.82	1.516	656.28	1.496 43	496.5	1.511 52
589.3	1.5007	479.99	1.514 20	656.28	1.496 35	514.5	1.508 98
589.3	1.5014	479.99	1.514	768.20	1.4911	632.8	1.497 92
656.3	1.4966	486.13	1.513 27	800	1.489	Data from Ref. 10	
Data from Ref. 7[b]		486.13	1.513 20	1000	1.485	2010	1.479
276.3	1.625	486.13	1.513 13	1500	1.480	2090	1.480
283.7	1.619	486.13	1.513 05	1850	1.478	2120	1.479
288.1	1.612	508.6	1.509			2170	1.477
298.1	1.598	546.07	1.505 50			2190	1.477

[a]The data for benzene in the source (Ref. 5) were obtained from Ref. 28.
[b]The data in the source (Ref. 7) were derived from Refs. 30–34, 36, 39–41.
[c]The source (Ref. 9) contains results from Ref. 38.

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.[6]

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 λ yields Cauchy's equations[6,24] that can be represented by the formulas (2) and (3) (up to the fifth term of expansion):

TABLE IV. Experimental values of linear refractive index of liquid CS_2 at 20 °C.

λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}	λ (nm)	n^{20}
Data from Ref. 1		Data from Ref. 7[b]		Data from Ref. 8[c]		Data from Ref. 8[c]	
514.5	1.636 019	560.8	1.6333	546.1	1.636 08	435.9	1.673 77
632.8	1.623 977	578	1.6298	587.6	1.628 04	447.2	1.668 05
Data from Ref. 5[a]		587.56	1.628 04	589.3	1.627 74	471.3	1.657 71
434.1	1.6748	589.3	1.6278	643.85	1.619 66	486.1	1.652 30
486.1	1.6523	589.3	1.627 74	656.3	1.618 20	501.6	1.647 42
589.3	1.6276	589.3	1.6277	768.2	1.608 00	546.1	1.636 10
656.3	1.6182	589.3	1.6276	361.2	1.738 06	579.1	1.629 61
Data from Ref. 6		589.3	1.627	394.4	1.701 80	587.6	1.628 01
434.0	1.6752	610.4	1.6243	441.6	1.671 35	589.0	1.627 76
486.1	1.6527	643.85	1.619 66	467.8	1.659 23	656.3	1.618 16
656.3	1.6185	656.28	1.6182	480.0	1.654 66	667.8	1.616 86
Data from Ref. 7[b]		670.8	1.6168	508.6	1.645 41	397.0	1.699 40
404.66	1.6934	768.20	1.6080	533.9	1.638 77	434.0	1.674 80
434.05	1.6750	Data from Refs. 7 and 11		589.3	1.627 61	486.0	1.652 30
435.83	1.6742	2030	1.585	340.4	1.775 80	589.0	1.627 60
460.2	1.6618	2200	1.584	344.4	1.768 50	656.0	1.618 20
479.99	1.6544	2430	1.583	346.7	1.764 40	589.0	1.627 50
486.13	1.652 34	Data from Ref. 8[c]		361.2	1.739 50	777.0	1.607 20
486.13	1.652 25	589.0	1.628 00	366.4	1.732 50	873.0	1.601 70
497.2	1.6488	404.6	1.693 40	388.9	1.706 09	999.0	1.596 80
508.6	1.6455	434.0	1.675 00	396.5	1.699 60	1164	1.592 80
527	1.6405	435.8	1.674 20	402.6	1.694 78	1396	1.589 10
546.07	1.636 08	480.0	1.654 40	407.8	1.691 05	1745	1.585 60
546.07	1.6360	486.1	1.652 25	412.1	1.687 99	1998	1.584 00

[a]The data for CS_2 in the source (Ref. 5) were obtained from Ref. 28.
[b]The source (Ref. 7) contains results from Refs. 29, 33, 34, 39, 42–44.
[c]The source (Ref. 8) contains data from Refs. 45–50.

TABLE V. Constants of Cauchy's equations and calculated refractive indices of liquid chloroform at 20 °C.

Parameter[a]	$y=n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6})$[a]	Parameter[b]	$y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6})$[b]
A_0	2.048 766±0.001 728	B_0	1.431 364±0.000 595
$A_1(10^3$ nm$^2)$	16.1937±1.0373	$B_1(10^3$ nm$^2)$	5.632 41±0.357 09
$A_2(10^8$ nm$^4)$	−5.9111±1.8380	$B_2(10^8$ nm$^4)$	−2.0805±0.6327
$A_3(10^{13}$ nm$^6)$	3.7358±0.8978	$B_3(10^{13}$ nm$^6)$	1.2613±0.3091
r^2	0.997 85	r^2	0.997 81
$\sigma(10^{-4})$	24.00	$\sigma(10^{-4})$	8.26
Calculated values n^{20} for $CHCl_3$:			
λ (nm)	$n_{calc.}$ from $y=n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6})$[a]	λ (nm)	$n_{calc.}$ from $y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6})$[b]
514.5	1.450 35	514.5	1.450 35
532	1.449 22	532	1.449 22
589.3	1.446 16	589.3	1.446 16
632.8	1.444 33	632.8	1.444 33
800.0	1.439 71	800.0	1.439 70
1064	1.436 19	1064	1.436 19
1550	1.433 67	1550	1.433 67

[a]Equation (2).
[b]Equation (3).

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

and

$$n=B_0+\frac{B_1}{\lambda^2}+\frac{B_2}{\lambda^4}+\frac{B_3}{\lambda^6}+\frac{B_4}{\lambda^8}. \tag{3}$$

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_∞ for infinite wavelength $(\lambda\to\infty)$, respectively.

An improvement in fitting of the refractive indices of liquids in the UV-visible-near-IR range is expected[24,25] if the additional term in Eq. (4), due to the infrared vibrational absorption,[25] $C_5\lambda^2$, is added to the terms in λ^{-2i}, which arise from the contribution of the ultraviolet electronic absorption:

$$n=C_0+\frac{C_1}{\lambda^2}+\frac{C_2}{\lambda^4}+\frac{C_3}{\lambda^6}+\frac{C_4}{\lambda^8}+C_5\lambda^2. \tag{4}$$

In order to obtain a satisfactory dispersion formula, it was necessary to consider all possible representations given by formulas (1)–(3) as well as those mentioned in Ref. 6. The regression statistics were used as a tool to choose the equations for the best fitting of refractive index experimental data. Initially the analysis was performed using a one term Sellmeier equation (1). The wavelength λ_0 was derived for each liquid, for example, 108 nm was obtained for chloroform, 138 nm for toluene, 146 nm for benzene, and 183 nm for CS_2. A careful inspection of the graphs made of the one-term Sellmeier Eq. (1), represented in the linear form $(n^2-1)^{-1}=(s_1)^{-1}-(\lambda_{01}/\lambda)^2$, showed that the experimental points formed a curvature, and the value of the regression coefficient was not satisfactory (r^2 was 0.995 77 for chloroform, 0.997 53 for toluene, 0.997 92 for benzene, 0.995 22 for CS_2) indicating that more than one UV resonance should be taken into account in these considerations. A similar conclusion was drawn from the inspection of a modified Sellmeier equation, Eq. (20-10) in Ref. 23. There the relation $n^2=1+s[(1-(\lambda_0/\lambda)^2]^{-1}=1+s+s(\lambda_0/\lambda)^2+s(\lambda_0/\lambda)^4+\cdots$, has the form similar to Cauchy's equation, Eq. (2). The formula was derived[23] for the case of a single absorption band and when a distance to the short wavelength side of the region, for which 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 λ_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).

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 σ for the dependent y fitting the experimental index data with $y=n^2$ and $y=n$ for each liquid. The choice of a number of terms in $\lambda^{\pm 2i}$ was dependent on the r^2 value (being closer to 1), and the values of the standard errors. The data from Refs. 1–4 were not included in these calculations. The lower parts of Tables V–VIII contain the values of refractive index calculated at several wavelengths 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 $(\varepsilon=n^2)$ of studied liquids is represented with constants of Eq. (2). It can be noticed that the fitting coefficients of the Cauchy's Eq. (2) or Eq. (3) give identical values of calculated refractive indices.

Refractive properties of liquid chloroform were represented with 25 experimental values of n^{20}. The wavelength dependence was characterized with three λ-dependent terms as it is shown in Table V. Adding the term in $1/\lambda^8$ slightly improved the r^2 value from 0.997 85 to 0.997 91 when $y=n^2$, or from 0.997 81 to 0.997 88 when $y=n$, 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 VI. Constants of Cauchy's equations and calculated refractive indices of liquid toluene at 20 °C.

Parameter[a]	$y=n^2(\lambda^{-2},\lambda^{-2},\lambda^{-4})$[a]	Parameter[b]	$y=n(\lambda^{-2},\lambda^{-4})$[b]
A_0	2.175 132± 0.002 395	B_0	1.474 775± 0.000 797
$A_1(10^3$ nm$^2)$	20.4682± 1.3647	$B_1(10^3$ nm$^2)$	6.990 31± 0.453 79
$A_2(10^8$ nm$^4)$	7.3100± 1.8139	$B_2(10^8$ nm$^4)$	2.1776± 0.6032
r^2	0.997 64	r^2	0.997 64
$\sigma(10^{-4})$	14.51	$\sigma(10^{-4})$	4.82
Calculated values n^{20} for $C_6H_5CH_3$:			
λ (nm)	$n_{calc.}$ from $y=n^2(\lambda^{-2},\lambda^{-4})$[a]	λ (nm)	$n_{calc.}$ from $y=n(\lambda^{-2},\lambda^{-4})$[b]
514.5	1.504 29	514.5	1.504 29
532	1.502 19	532	1.502 19
589.3	1.496 71	589.3	1.496 71
632.8	1.493 59	632.8	1.493 59
800.0	1.486 24	800.0	1.486 23
1064	1.481 14	1064	1.481 12

[a]Equation (2).
[b]Equation (3).

A graphic representation of the experimental refractive indices of chloroform and these calculated from the fit with the three λ-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 λ-dependent term of the Cauchy equation of the type $n=A+(B/\lambda^2)$, taking values of the constants $A=1.411\,67$, and $B=11\,909.0909$.[1] 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 μm. 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.[25] 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[25] 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 λ-dependent terms. Almost

TABLE VII. Constants of Cauchy's equations and calculated refractive indices of liquid benzene at 20 °C.

Parameter[a,b,c]	$y=n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[a]	$y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[b]	$y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8},\lambda^{2})$[c]
A_0,B_0,C_0	2.178 271± 0.000 989	1.475 922± 0.000 315	1.473 644± 0.001 304
$A_1,B_1,C_1(10^3$ nm$^2)$	28.7420± 1.1374	9.671 57± 0.361 81	11.269 20± 0.956 79
$A_2,B_2,C_2(10^8$ nm$^4)$	−15.5591± 4.0503	−5.2538± 1.2884	−9.2034± 2.5347
$A_3,B_3,C_3(10^{13}$ nm$^6)$	26.1346± 5.0427	8.5442± 1.6041	12.430± 2.674
$A_4,B_4,C_4(10^{18}$ nm$^8)$	−7.6948± 2.0083	−2.6163± 0.6388	−3.9224± 0.9598
$C_5(10^{-10}$ nm$^{-2})$			4.8623± 2.7035
r^2	0.999 603	0.999 616	0.999 635
$\sigma(10^{-4})$	21.40	6.81	6.69
Calculated values n^{20} for C_6H_6:			
λ (nm)	n_{calc} from $y=n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[a]	n_{calc} from $y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[b]	n_{calc} from $y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8},\lambda^{2})$[c]
514.5	1.509 03	1.509 03	1.509 11
532.0	1.506 89	1.506 90	1.506 98
589.3	1.501 28	1.501 28	1.501 33
632.8	1.498 04	1.498 03	1.498 02
800.0	1.490 08	1.490 06	1.489 77
1064	1.484 12	1.484 11	1.483 51
1550	1.479 86	1.479 86	1.479 35

[a]Equation (2).
[b]Equation (3).
[c]Equation (4).

TABLE VIII. Constants of Cauchy's equations and calculated refractive indices of liquid CS_2 at 20 °C.

Parameter[a,b,c]	$y=n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[a]	$y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[b]	$y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8},\lambda^{2})$[c]
A_0,B_0,C_0	2.499 210± 0.000 608	1.580 826± 0.000 178	1.582 445± 0.000 585
$A_1,B_1,C_1(10^3$ nm$^2)$	47.4871± 1.0077	15.2389± 0.2949	13.7372± 0.5910
$A_2,B_2,C_2(10^8$ nm$^4)$	22.644± 4.987	4.8578± 1.4596	10.0243± 2.2686
$A_3,B_3,C_3(10^{13}$ nm$^6)$	− 38.030± 8.947	− 8.2863± 2.6186	− 15.6572± 3.5766
$A_4,B_4,C_4(10^{19}$ nm$^8)$	5.8058± 0.5225	1.4619± 0.1529	1.8294± 0.1940
$C_5(10^{-10}$ nm$^{-2})$			− 3.2117± 1.1099
r^2	0.999 939	0.999 942	0.999 947
$\sigma(10^{-4})$	10.99	3.22	3.08
Calculated values n^{20} for CS_2:			
λ (nm)	n_{calc} from $y=n^2(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[a]	n_{calc} from $y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8})$[b]	n_{calc} from $y=n(\lambda^{-2},\lambda^{-4},\lambda^{-6},\lambda^{-8},\lambda^{2})$[c]
514.5	1.643 85	1.643 84	1.643 85
532	1.639 37	1.639 36	1.639 35
589.3	1.627 77	1.627 76	1.627 72
632.8	1.621 19	1.621 19	1.621 15
800.0	1.605 56	1.605 59	1.605 66
1064	1.594 58	1.594 62	1.594 90
1550	1.587 24	1.587 25	1.587 55

[a]Equation (2).
[b]Equation (3).
[c]Equation (4).

identical r^2 values were found using the equations based on three λ-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 λ terms from Table VI which are represented with curve 1. Curve 2 represents the fit, $n=A+(B/\lambda^2)$, using the values $A=1.489\,16$ and $B=2584.4419$.[1] 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 λ-dependent terms of Eqs. (2) and (3), and using five λ-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 λ-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 λ 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 $A=1.476\,25$ 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.

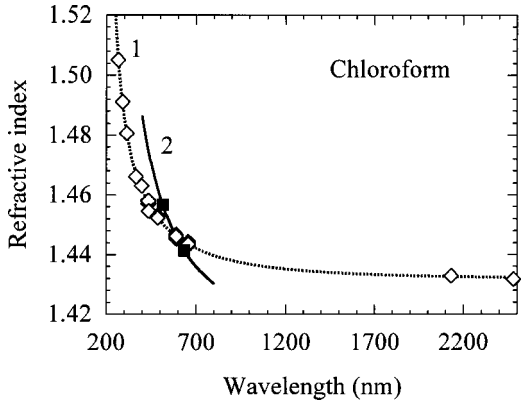

FIG. 1. Dispersion of refractive index of liquid chloroform at 20 °C. Diamonds are the experimental data from Table I; closed squares are the data measured in Ref. 1. Curve 1 (dotted line) was calculated using $n=1.431\,364+5632.41/\lambda^2-2.0805\times10^8/\lambda^4+1.2613\times10^{13}/\lambda^6$; curve 2 (solid line) is the dispersion curve from Ref. 1.

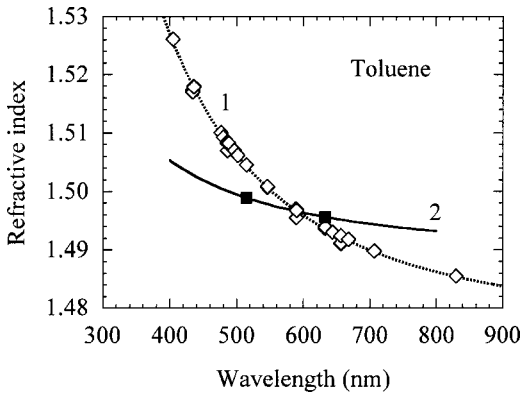

FIG. 2. Dispersion of refractive index of liquid toluene at 20 °C. Diamonds are the experimental refractive index data from Table II; closed squares are the data measured in Ref. 1. Curve 1 (dotted line) was calculated using $n=1.474\,775+6990.31/\lambda^2+2.1776\times10^8/\lambda^4$; curve 2 (solid line) is the dispersion curve shown in Ref. 1.

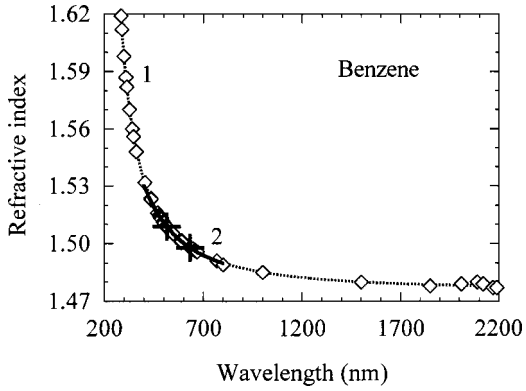

FIG. 3. Dispersion of refractive index of liquid benzene at 20 °C. Diamonds are the experimental index data from Table III; crosses are the data measured in Ref. 1. Curve 1 (dotted line) was calculated using $n=1.475\,922+9671.57/\lambda^2-5.2538\times10^8/\lambda^4+8.5442\times10^{13}/\lambda^6-2.6163\times10^{18}/\lambda^8$; curve 2 (solid line) is the dispersion curve from Ref. 1.

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 0.999 94 indicating consistency in the experimental data. The standard deviation of the experimental n value was about 3×10^{-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 λ 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 $A=1.600\,49$ 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.[26] The geometry of molecules was initially set with the CSC CHEM3D PLUS program,[27] 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 α, first hyperpolarizability $\beta_{(SHG)}$, and second hyperpolarizability $\gamma_{(THG)}$, as a function of frequency, by the time-dependent coupled perturbed Hartree–Fock method. The theoretical α values were used to calculate refractive indices using the Lorentz–Lorenz equation.[6] 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 μm), 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 -6.328×10^{-4} K^{-1} in chloroform,[1,3] while it is equal to -5.98×10^{-4} K^{-1} in the citation.[7] A similar discrepancy was found in toluene, where $dn/dT=-5.273\times10^{-4}$ K^{-1} at 632.8 nm,[1,2] -5.55×10^{-4} K^{-1} in Ref. 7. A bigger disagreement was found for benzene between the value of $dn/dT=-7.594\times10^{-4}$ K^{-1} at 632.8 nm in Refs. 1 and 3 and -6.40×10^{-4} K^{-1} in Ref. 7. However, the data for CS_2 were found to be similar, $dn/dT=-7.91\times10^{-4}$ K^{-1} at 632.8 nm in Refs. 1 and 2 and -7.96×10^{-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[1,4] 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.

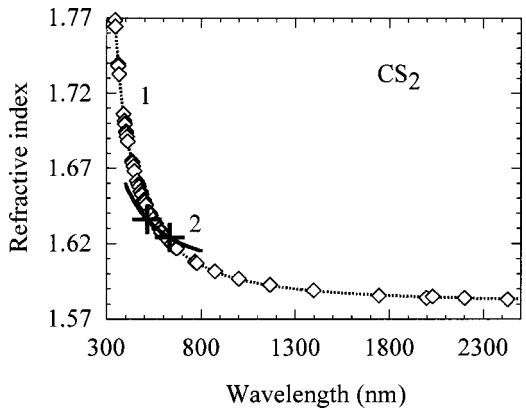

FIG. 4. Dispersion of refractive index of liquid CS_2 at 20 °C. Diamonds are the experimental data from Table IV; crosses are the data measured in Ref. 1. Curve 1 (dotted line) was calculated using $n=1.580\,826+15\,238.9/\lambda^2+4.8578\times10^8/\lambda^4-8.2863\times10^{13}/\lambda^6+1.4619\times10^{19}/\lambda^8$; curve 2 (solid line) is the dispersion curve from Ref. 1.

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 fits. The error in the n values was about 8.3×10^{-4} in chloroform, 4.8×10^{-4} in toluene, 6.8×10^{-4} in benzene, and 3.2×10^{-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.[13] 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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