JOURNAL OF CHEMICAL & ENGINEERING DATA

ARTICLE

pubs.acs.org/jced

Refractive Index of Liquid D_2O for Visible Wavelengths

Hosanna Odhner[†] and D. T. Jacobs*

Department of Physics, The College of Wooster, Wooster, Ohio 44691, United States

ABSTRACT: The index of refraction for D_2O at common wavelengths was measured for several temperatures at atmospheric pressure. While heavy water's refractive index was precisely measured decades ago using the transition lines of elements, those wavelengths are seldom used now that inexpensive lasers provide a range of available wavelengths. We review those measurements, note some inconsistencies between research groups, and fit the best of the literature data to a simple equation that allows an easy calculation for the refractive index of D_2O with an accuracy of ± 0.0002 at any visible wavelength and between (278 and 359) K. To verify the equation, we then compare the calculated refractive index to our measured values for three He−Ne laser wavelengths (543.5, 594.1, and 632.8) nm over a temperature range from (288 to 338) K and find good agreement.

INTRODUCTION

H_2O and D_2O are often taken to be interchangeable as solvents. However, the hydrogen bonding strengths in H_2O and D_2O differ,[1] resulting in distinct differences[2] in physical properties such as density, viscosity, and heat capacity. Because deuterium atoms are heavier than hydrogen atoms, the amplitudes of the atomic vibrations are smaller, and a deuterium bond in D_2O is stronger than a hydrogen bond in H_2O. The refractive index also differs significantly: at 293 K and at 589.3 nm, the refractive index of water is 1.333 00, while heavy water is 1.328 30.[3] Historically, the refractive index was used to determine the purity of a material but now is needed in light scattering,[4] ultrasonic velocity,[5] and composition determinations.[6,7] The refractive index literature values[3,8,9] for D_2O are given as tables using wavelengths emitted by excited gases (mercury, sodium, etc.), and it is tedious to interpolate in both temperature and wavelength to arrive at a value needed at laser emissions in the visible. We determined an equation that is accurate yet greatly simplifies the determination of the refractive index for liquid D_2O in the visible part of the spectrum at atmospheric pressure over a broad range of temperatures.

Early measurements[8] were done on relatively impure D_2O, a common difficulty because its hydroscopic nature requires special handling. While recent reports of the refractive index n appear sporadically and sometimes with inaccurate values, the two most comprehensive measurements were done by Mehu et al.[9] and by Frontas'ev et al.,[3] both of whom used “99.7 % pure D_2O”. Mehu measured over a wider range of wavelengths but at far fewer temperatures than Fronas'ev who used fewer wavelengths. The two sets of measurements are consistent with each other to ± 0.0002, though each stated a precision of ± 0.000 01. Somewhat more recently, the small pressure dependence of D_2O's refractive index ($dn/dP = 1.6 \cdot 10^{-5}$/atm at atmospheric pressure) was measured at two wavelengths and one temperature.[10] The variation of n as H_2O is added to D_2O was measured to be $dn/dx = 4.87 \cdot 10^{-3}$, where x is the mole fraction of D_2O.[9,11] Thus, a 0.01 mole fraction water impurity would raise the refractive index of a D_2O sample by about $5 \cdot 10^{-5}$. Others[5] have used ultrasonic velocity data to calculate D_2O's refractive index at 298 K and 589 nm to be 1.3700, much larger than the literature value of 1.3279. More recently, “98 % pure D_2O” at 297 K and 632.8 nm had a measured[12] n = 1.3281 that was also significantly larger than an interpolated literature value of 1.3269 and our measured value of 1.3267. While such discrepancies may not be significant to the reported investigation, they do indicate a need for an easy way to obtain n for D_2O at different temperatures and wavelengths. More accurate and precise values for n are essential when using refractive index as a way of determining the composition of a D_2O mixture.[6,7]

To obtain a relation that allows such a calculation, we took advantage of Cauchy's formula[13] $n = A + B/\lambda^2$ which applies in wavelength regions sufficiently far from absorption bands. The refractive index of D_2O in the visible region has a contribution from absorption in the infrared using the Kramers−Kronig relation, but this has been determined at only one temperature.[14] We are using a more direct and useful approach that allows the refractive index to be accurately determined at any visible wavelength λ over the full temperature range of liquid D_2O. The refractive index data from Mehu and Frontas'ev are well-described by Cauchy's formula as is shown in Figure 1 where their data of n vs λ^{-2} are plotted and give straight lines for each temperature. There are deviations of their data from the line barely visible on this plot (about ± 0.0001 for each investigator and ± 0.0002 between investigators). Because Mehu et al.[9] did not measure n over the full temperature range of liquid D_2O and because at each temperature their n values deviated noticeably and randomly at different wavelengths from Cauchy's formula, we did not include their data in determining the parameter values in an equation that determines n for liquid D_2O. Rather, we used a cubic function for the temperature dependence, Cauchy's formula, and a cross term, to fit the function

$$n = A + B/\lambda^2 + C \cdot T + D \cdot T/\lambda^2 + E \cdot T^2 + F \cdot T^3 \tag{1}$$

to the refractive index data for D_2O reported by Frontas'ev et al.[3] over their full range of temperatures, (278 to 367) K, and wavelengths, (546.1, 589.3, and 656.3) nm. The parameter values

Received: September 5, 2011
Accepted: November 15, 2011
Published: November 29, 2011

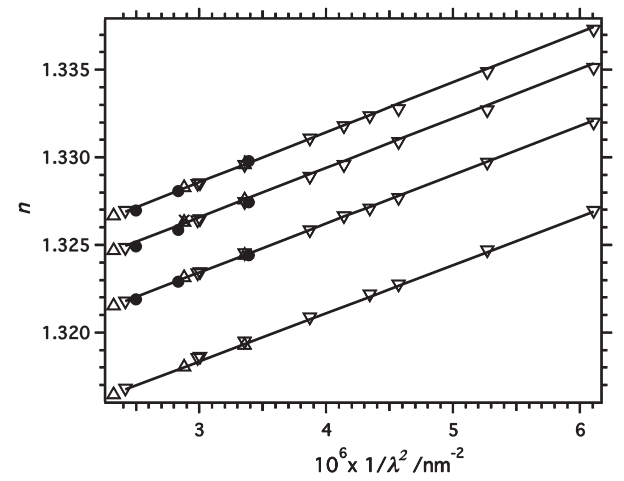

Figure 1. Refractive index n of D_2O at pressure p = 0.1 MPa as a function of $1/\lambda^2$ where λ is the wavelength in nanometers for four representative temperatures: (293, 313, 323, and 358) K for the data and lines from top to bottom, respectively. The data are ●, this work; △, ref 3; +, ref 10; ×, ref 11; and ▽, ref 9; the lines are calculated from eq 1.

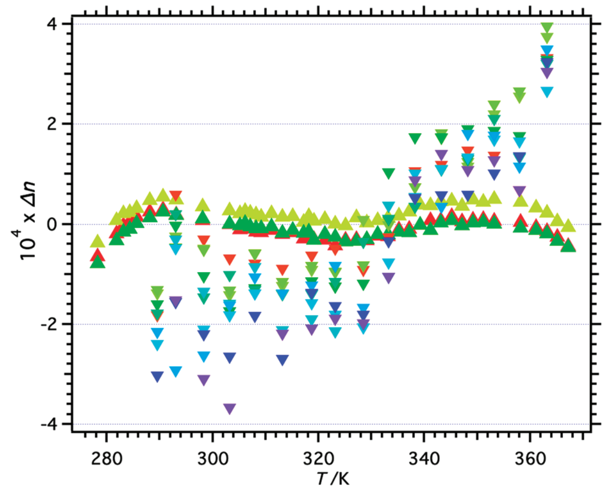

Figure 2. Deviation Δn = n(expt) − n(calc) of the experimental refractive indices n of D_2O at pressure p = 0.1 MPa as a function of temperature T where the calculated values use eq 1, which is the fit to the data △, ref 3; also plotted are deviations for data ▽, ref 9. The deviations for the several wavelengths at each temperature (indicated by the spread of symbols) show a systematic temperature deviation but random wavelength deviation for ref 9. The color roughly shows the wavelength.

were $A = 1.0244$, $B = 3329.2$, $C = 2.6048 \cdot 10^{-3}$, $D = -1.630$, $E = -7.248 \cdot 10^{-6}$, and $F = 6.15 \cdot 10^{-9}$ where T is the temperature in Kelvin and λ has units of nm. Similar to water, D_2O has a maximum in its density just above the freezing point which leads to a curvature for n as a function of temperature.

As expected, the calculated values compare well to the measured values of Frontas'ev, but they are also consistent at the 0.0002 level with Mehu's data as shown in the deviation plot of Figure 2. The consistency and inconsistency between these two sources is apparent in the figure. Of the two sets of data, 92 % are within ± 0.0002 from (278 to 359) K. However, the variation in the temperature dependence of Mehu's data indicates a systematic error between investigators. The spread in the deviation at each temperature of Mehu's data are due to a wavelength dependence that is more random than systematic; for example, red and violet overlap at 353 K but are far apart at 303 K, while the other wavelengths deviate about equally for all temperatures. This deviation plot indicates that eq 1 describes either set of refractive index data with an accuracy of ± 0.0002 from (278 to 359) K over the visible part of the spectrum. We tested the validity of eq 1 by measuring the refractive index of ultrapure D_2O at three laser wavelengths and a range of temperatures.

Table 1. Refractive Index n of D_2O Relative to Air for Different Temperatures T and Wavelengths (in nm) at Pressure p = 0.1 MPa

T/K	n (632.8)	n (594.1)	n (543.5)
288.351	1.3272	1.3283	1.3300
293.293	1.3270	1.3281	1.3298
298.122	1.3267	1.3278	1.3293
303.147	1.3260	1.3271	1.3285
308.093	1.3254	1.3266	1.3280
313.114	1.3249	1.3259	1.3275
318.129	1.3243	1.3254	1.3269
323.138	1.3237	1.3248	1.3263
328.119	1.3225	1.3236	1.3251
333.064	1.3219	1.3229	1.3244
337.982	1.3211	1.3221	1.3237

[a] Standard uncertainty in n = 0.0002 from a quadrature combination of the propagated uncertainties in the prism and deviated angles.

■ EXPERIMENTAL SECTION

The D_2O was purchased from Aldrich (mole fraction 0.9998) in sealed glass vials. The cell holding the sample was heated overnight in a vacuum oven along with the transfer syringe and then cooled in a drybox. Fluid transfer took place in the drybox (where the cell was also sealed) using a dry nitrogen atmosphere to avoid water contamination.

The refractive index was measured using a minimum deviation technique with a prism-shaped cell.[15] The volume of sample was about 6 cm^3 with an air bubble of 0.5 cm^3 to maintain a pressure of 1 atm. The cell was surrounded by two concentric temperature-controlled cylindrical shells with air between them. The cell temperature was monitored with a thermistor to a precision better than 0.0001 K and an accuracy of 0.02 K as determined by a calibrated platinum resistance thermometer.

The refractive index was determined using three He−Ne laser lines (λ_o = 543.5, 594.1, and 632.8) nm passing through the sample and measuring the minimum deviated angle using a Gaertner spectrometer with a precision of $1 \cdot 10^{-4}$ rad. The cell's prism angle was measured to be 1.0440 rad. The resulting refractive indices (relative to air) had a resolution of ± 0.0002. Several hours were allowed for temperature equilibrium as measurements were taken about every five degrees from (288 to 338) K. The data are shown in Table 1.

■ RESULTS AND DISCUSSION

We can compare our measured refractive indices with those calculated using eq 1. The agreement is quite good as shown in Figure 3. Our slightly smaller values of n are still within the expected accuracy of eq 1 and could be due to the higher purity of

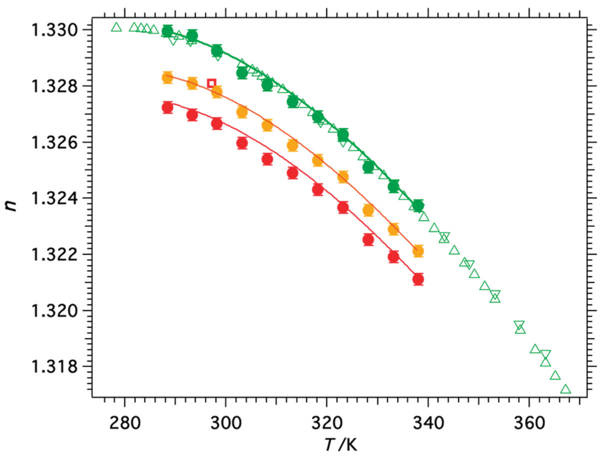

Figure 3. Our refractive index n of D_2O at pressure p = 0.1 MPa as a function of temperature T from Table 1 compared to the calculated solid lines from eq 1 for our wavelengths which are (from top to bottom) (543.5, 594.1, and 632.8) nm. Data are ●, this work; and literature values whose wavelengths are sufficiently close for comparison: △, 546.1 nm, ref 3; +, 546.1 nm, ref 10; □, 632.8 nm, ref 12; and ▽, 546.1 nm, ref 9. Color approximately indicates the wavelength.

our D_2O and prevention of water contamination. While a number of factors contribute to the measured refractive index for D_2O, the most significant is the purity of D_2O, either as purchased or after handling, which can cause a larger refractive index (by 0.0001) if exposed to water (0.02 mole fraction); this was certainly a problem with early measurements.[8] Wavelength differences, as when comparing our data at 594.1 nm to Frontas'ev 589.3 nm, can be significant if the difference in wavelength is large enough (a 5 nm difference approximately corresponds to 0.0001 in n). However, temperature control is not too important since even for temperatures larger than 298 K, a temperature difference of 0.6 K only corresponds to a change in n of 0.0001. Nor are pressure variations, room humidity, or oxygen isotope abundance significant at the resolution of our data and equation.

CONCLUSIONS

We determined a simple equation that accurately calculates the refractive index n of liquid D_2O to ± 0.0002 for visible wavelengths at atmospheric pressure. We compared that equation to two sets of literature measurements[3,9] as well as to data we measured for the refractive index for pure D_2O at atmospheric pressure and over a range of temperatures and three common laser wavelengths. These data are consistent with n values calculated from our equation and demonstrate an accuracy for the equation of ± 0.0002 from (278 to 359) K. The equation allows an easy yet accurate way to calculate the refractive index of liquid D_2O over the visible portion of the spectrum.

AUTHOR INFORMATION

Corresponding Author

*E-mail: djacobs@wooster.edu. Fax: (330)263-2516.

Present Addresses

†Bryn Mawr College, Department of Physics, Bryn Mawr, PA 19010. E-mail: hodhner@brynmawr.edu.

Funding Sources

We acknowledge support by NSF REU Grant No. DMR-0649112, Research Corporation, and The College of Wooster.

REFERENCES

(1) Engdahl, A.; Nelander, B. On the relative stabilities of H- and D-bonded water dimers. *J. Chem. Phys.* **1987**, *86*, 1819–1823.

(2) Luan, C. H.; Urry, D. W. Solvent deuteration enhancement of hydrophobicity: DSC study of the inverse temperature transition of elastin-based polypeptides. *J. Phys. Chem.* **1991**, *95*, 7896–7900.

(3) Frontas'ev, V. P.; Shraiber, L. S. Study of the variation in the electron polarizability of molecules of ordinary and heavy water under the influence of temperature. *Zh. Strukt. Khim.* **1965**, *6*, 512–521.

(4) Benmouna, M.; Reed, W. F. Theoretical developments in static light scattering from polymers. In *Light scattering: principles and development*; Brown, W., Ed.; Clarendon Press: Oxford, 1996; pp 1−29.

(5) Bhatti, S. S.; Singh, D. P. Studies of ultrasonic velocity in heavy water. *Acoust. Lett.* **1983**, *7*, 17–20.

(6) Souza, G. P.; Oliveira, D. A.; Luders, D. D.; Kimura, N. M.; Simoes, M.; Palangana, A. J. An analogy between biaxial crystal and biaxial nematic lyotropic phase. *J. Mol. Liq.* **2010**, *156*, 184–186.

(7) Huff, A.; Patton, K.; Odhner, H.; Jacobs, D. T.; Clover, B. C.; Greer, S. C. Micellization and phase separation for triblock copolymer 17R4 in H_2O and D_2O. *Langmuir* **2011**, *27*, 1707–1712.

(8) Luten, D. B. The refractive index of H^2H^2O; the refractive index and density of solutions of H^2H^2O and H^1H^1O. *Phys. Rev.* **1934**, *45*, 161–165.

(9) Mehu, A.; Abjean, R.; Johannin-Gilles, A. Comparative measurement of the refractive indices of light and heavy water at different temperatures. *J. Chim. Phys. (France)* **1966**, *63*, 1569–1574.

(10) Chen, C. C.; Vedam, K. Piezo- and eleasto-optic properties of deuterium oxide under high pressure. *J. Chem. Phys.* **1980**, *72*, 1410–1411.

(11) Azuaga, N. S.; Djega-Mariadassou, G.; Marques, A. R. Refractive index calculation for analysis of aqueous solutions of heavy water. *Analusis* **1978**, *6*, 34–37.

(12) Shukla, R. P.; Udupa, D. V. Zygo interferometer for measuring refractive index of liquids and its application for heavy water analysis. *Opt. Laser Technol.* **2000**, *32*, 355–360.

(13) Born, M.; Wolf, E. *Principles of Optics*, 7th ed.; Cambridge University Press: New York, 1999; p 100.

(14) Bertie, J. E.; Lan, Z. The refractive index of colorless liquids in the visible and infrared: contributions from the absorption of infrared and ultraviolet radiation and the electronic molar polarizability below 20 500 cm^{-1}. *J. Chem. Phys.* **1995**, *103*, 10152–10161.

(15) Jacobs, D. T.; Anthony, D. J.; Mockler, R. C.; O'Sullivan, W. J. Coexistence curve of a binary mixture. *Chem. Phys.* **1977**, *20*, 219–226.