



Optical constants of ethylene glycol over an extremely wide spectral range



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ABSTRACT

Besides providing insights into the fundamental properties of materials, the knowledge of optical constants is required for a large variety of applications. In this work, for the first time to the best of our knowledge, an extremely wide spectral range from 181 to $\sim 54,000$ cm^{-1} has been explored for ethylene glycol in the liquid phase, and optical constants in the whole range have been given. The approach we propose can also be applied to different fluids.

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1. Introduction

The knowledge of the complex refractive index of materials is required in many fields and both for fundamental and applied research. The present work reports on the determination of optical constants (i.e. the real n and the imaginary part k of the complex refractive index) of ethylene glycol in the liquid phase. Ethylene glycol is a fluid widely used in many industrial processes such as heating or cooling, chemical processes and thermal solar energy systems [1]. It is the main non-aqueous base fluid used for the preparation of so-called nanofluids [1–12], as well as in mixed aqueous–nonaqueous systems [13–15] for different thermal applications. Recently, it has been proposed as base fluid for novel direct solar absorbers [16,17]. However, for a realistic assessment of the system performances when a direct interaction with light is required, both fundamental optical constants, including n , have to be characterized. The transmission spectrum and the k optical constant of liquid ethylene glycol have been reported in the literature for the spectral range 0.2–1.5 μm [18]. Some discrete infrared absorption peaks for glycol molecules isolated in Ar or Xe matrices have been listed in [19] and for the liquid phase in [20]. Infrared transmittance spectra in limited spectral ranges have been reported in [21] (300–1500 cm^{-1}) and in [22] (~ 450 –3794 cm^{-1}) but without giving any optical constant. n has been measured by

several authors at the single wavelength of the sodium D line (0.5893 μm) [23–30] or at few discrete wavelengths in the range 0.22–0.58 μm [31]. In this work, the optical constant k is obtained in an extremely wide wavelength range, from 0.185 μm to about 55 μm ($\sim 54,000$ –181 cm^{-1}) from transmittance measurements. The experimental k spectrum is then used to calculate n in the whole investigated range by means of a Kramers–Kronig transform.

2. Experimental setup

The optical transmittance spectra of ethylene glycol (Aldrich $\geq 99\%$) have been measured over the considered spectral range by means of three different experimental setups: a “Lambda 900” Perkin–Elmer dispersive spectrophotometer for the range $\sim 54,054$ to 3333 cm^{-1} (0.185–3 μm), a Fourier transform “Excalibur” Bio-Rad spectrometer with KBr optics for the wavenumber range 5500–400 cm^{-1} (~ 1.8 to 25 μm) and finally a Fourier transform “Scimitar” Bio-Rad spectrometer with polyethylene windows and mylar beam splitter for the range 420–181 cm^{-1} (~ 24 to 55 μm). Except when differently specified, the transmittance has been measured at different sample thicknesses using a demountable variable-path cell composed by two optical windows and by a series of calibrated spacers. When the sample transmittance was too low to have a detectable signal at the output, we assembled the cell without spacer as described in the following. We choose the cell window materials on the basis of their spectral

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transparency: CaF₂ for the 0.185–3 μm range, KBr for ~1.8–25 μm (available spacers from 50 to 350 μm) and polyethylene for ~24–55 μm (available spacers from 15 to 350 μm). Moreover, for the visible range, where the ethylene glycol transmittance was very high, we used also quartz cuvettes with 5 and 10 mm path length to reduce the relative uncertainty on k , as discussed in the following.

3. Transmittance

The spectral transmittance of the liquid $\tau(\nu)$, with ν wavenumber, can be expressed as a simple function of the spectral absorption coefficient $\alpha(\nu)$ as

$$\tau(\nu) = \exp(-\alpha(\nu) \cdot x) \quad (1)$$

where x is the liquid thickness. However, the transmittance T we measure is the total transmittance of the layered system window-liquid-window, immersed in air. At each interface (air-window, window-liquid) the light is partially reflected and partially transmitted. Let's we consider, for simplicity, that the window has no absorption in the considered spectral range. Under the hypotheses of absence of scattering and negligible coherent effects [32], the total transmittance T can be expressed as a function of τ and of reflectances R_1 and R_2 at the interfaces as follows [33]:

$$T = (1 - R_1)^2 (1 - R_2)^2 \tau \left[1 + \frac{2R_1 R_2}{1 - R_1 R_2} + (R_1 + R_2)^2 \tau^2 + S(\tau^4) \right] \quad (2)$$

in this expression, $S(\tau^4)$ is the sum of contributions with powers of τ higher than four. The terms with powers of τ are generated by multiple passes through the liquid due to multiple reflections. If they are negligible compared to other terms, the total transmittance T is proportional to the transmittance τ of the liquid sample. The reflectances R_1 (at the air-window interface) and R_2 (at the window-liquid interface) are given by [34]:

$$R_1 = \frac{(n_w - 1)^2}{(n_w + 1)^2} \quad (3)$$

$$R_2 = \frac{(n_w - n)^2 + k^2}{(n_w + n)^2 + k^2} \quad (4)$$

with n_w real part of the refractive index of the window and n , k optical constants of the liquid. The optical constant $k(\nu)$ is connected to α by [32]:

$$k = \frac{\alpha(\nu)}{4\pi\nu} \quad (5)$$

Eqs. (3) and (4) assume, for the medium surrounding the cell, optical constants $n_m = 1$ and $k_m = 0$.

If we acquire two transmittance spectra T_1 and T_2 at two different thicknesses x_1 and x_2 of the liquid, α can be directly obtained from the expression:

$$\alpha(\nu) = -\frac{1}{x_2 - x_1} \ln \frac{T_2(\nu)}{T_1(\nu)} = -\frac{1}{\Delta x} \ln \frac{T_2(\nu)}{T_1(\nu)} \quad (6)$$

without requirement of a prior knowledge of optical properties of the window and with no need of a fitting procedure for n , k , as it would be required using a single transmittance measurement and Eqs. (1)–(5).

The possibility to obtain α from two independent transmittance measurements relies on the experimental error on a single transmittance and how much the considered transmittance values differ each other. The smaller is α , the more T_1 and T_2 must be different, i.e. the larger the difference of thicknesses $|x_2 - x_1| = |\Delta x|$ should be. A simple analysis of the error propagation shows that, in the hypothesis here fulfilled that the error on

the thicknesses is negligible respect to $|\Delta x|$, the obtained value of α is at least twice as large as its error, if α itself is larger than $2\sqrt{2}\epsilon/|\Delta x|$, where ϵ is the relative uncertainty of transmittance. This condition is fulfilled simply when

$$\frac{|T_1 - T_2|}{T_2} > 2\sqrt{2}\epsilon \quad (7)$$

In the determination of α we checked this condition and, in the spectral regions where it was not satisfied, we took as upper limit for α its standard error.

In the range 0.185–3.00 μm we acquired the transmittance spectra at several cell thicknesses from 50 to 350 μm, and we kept as α to be used in further calculations the value obtained by averaging the result of Eq. (6) for several (x_1, x_2) couples. Moreover, as in the spectral range from about 0.3 μm to 1.1 μm wavelength the transmittance was very high and near to 100% also with the largest available spacer, to reduce as much as possible the spectral interval of uncertainty of α discussed above, additional transmittance measurements were carried out, with a different cell model allowing much longer path lengths of 5 and 10 mm. The spectral resolution is 5×10^{-3} μm in the range 0.185–0.860 μm and varies from 7×10^{-3} to 2×10^{-2} μm at longer wavelengths. The relative uncertainty ϵ of transmittance values is 0.5%.

For the Mid-Infrared range (5500–400 cm⁻¹ wavenumbers, ~1.8 to 25 μm wavelength), the transmittance fell to zero in a large part of the spectrum even with the thinnest spacer available for KBr windows (50 μm). Thus, we used the demountable cell without spacer. This allowed to measure the transmittance for a very thin layer of liquid. Similarly to the method described in [33], we took several measurements at different tightening levels of the cell nuts (i.e. at different sample thicknesses). The spectral resolution is 4 cm⁻¹. The relative uncertainty on transmittance is between 0.05% and 0.3% depending on the spectral region. For the determination of α , Eq. (6) requires only the knowledge of the thickness difference Δx among two measurements, which was inferred as follows: for each considered couple of Mid-IR measurements, Δx was chosen to match, in the regions of spectral superposition of the Mid-IR and UV–vis–NIR instruments, the value of α determined by the UV–vis–NIR measurements.

In the Far Infrared (FIR) (420–181 cm⁻¹, ~24 to 55 μm) we used a slightly different cell model, able to mount polyethylene windows and equipped with thinner spacers than the previous one. Transmittance measurements were taken at different thicknesses, analogously to the UV–vis–NIR case, and α was analogously calculated. The minimum available thickness was 15 μm.

In the infrared, the spectra we acquired (Fig. 1) are in good agreement with published transmittance data ([22], available from ~450 to 3794 cm⁻¹ and [21] from 400 to 1500 cm⁻¹). In the region 300–400 cm⁻¹ our results show a better agreement with [20], which lists a weak transmittance minimum at 360 cm⁻¹, rather than [21], observing instead two weak minima at 430 and 330 cm⁻¹.

Once $\alpha(\nu)$ was obtained as described for the whole investigated range, we calculated the optical constant $k(\nu)$ from Eq. (5). The experimental values of k versus the wavenumbers, for the whole investigated range, are plotted in red color in Fig. 2. The obtained k values in the range ~6670 to 45,000 cm⁻¹ (1.40–0.22 μm) well agree with the data in [18], while some discrepancies can be found around 50,000 cm⁻¹. Table 1 lists at the third column the values of k at some discrete wavelengths.

4. Refractive index

On the basis of the experimental value of $k(\nu)$ we calculated the corresponding values of the refractive index $n(\nu)$. Being $n(\nu)$ and

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