Spectral optical constants of ethanol and isopropanol from ultraviolet to far infrared

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ABSTRACT

Ethanol and isopropanol are fluids of common use in different branches of materials science. In particular, in the ever growing field of nanoscience, they are dispersing media for nanoparticle suspensions. The knowledge of optical constants of these fluids is required for the characterization of optical properties of nanoparticles, besides providing insights into fundamental properties of fluids themselves. In this work, we calculated the real refractive index n of ethanol and isopropanol applying the Kramers-Kronig theory to the experimentally obtained k spectrum over an extremely wide spectral range, from 181 to ~ 54000 cm^{-1}.

1. Introduction

Spectral optical constants fully describe the behavior of materials when they interact with optical radiation. Thus they are important fundamental properties of matter. Moreover, several application fields of materials require the knowledge of optical constants. For the case of liquids, besides the impressively fast growing field of nanotechnology which will be discussed below in more detail, a recent application taking benefit of the knowledge of optical constants in the mid-infrared and extending sensing applications to this spectral range, is the measurement of pollutants in cloud aerosols [1]. As for nanotechnologies, so-called nanofluids (i.e. fluids with nanosized particles in suspension) are receiving an always increasing attention and are considered promising in a large variety of applications. Even if ions to control pH or surfactants can be added to improve stability, the two main ingredients of a nanofluid remain nanoparticles and base fluid. Nanofluids are expected, and in many cases proved, to show superior properties with respect to the pure fluid for many applications like for instance in thermal, optical or tribological fields [2–5]. Nanofluid properties can be controlled and tuned by the proper combination of nanoparticles and dispersing liquid. Nanoparticles can now be produced in a huge variety of materials, sizes and shapes, and new types are ever synthesized. The investigation of their optical properties is an important tool to understand their basic physics, as well as to assess their potential in all application fields requiring interaction with optical radiation. However, according to the Mie theory [6] optical properties of nanoparticles are influenced by those of the dispersing medium [7], so that their dependence as a function of the surrounding refractive index is an important characteristic widely investigated in the literature, of which Refs. [8–12] are only some examples among the many existing works.

Ethanol and isopropanol (2-propanol) are common dispersing media for nanoparticle suspensions and are used also by commercial suppliers of nanocolloids. Their refractive index and absorption coefficient are typically known in limited spectral ranges or even at the single wavelength of the sodium D-line [13–20]. However, new nanoparticles are recently raising the attention, with exotic absorption peaks spanning from visible to near-infrared wavelengths [21–23]. The knowledge of optical constants of the fluid surrounding these new kinds of nanomaterials is needed for different applications like for instance for modelling optical properties and radiative transfer. Moreover, emerging environmental applications [1] extend required spectral optical constants to mid

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infrared and, potentially, to even longer wavelengths. For this reason, in the present work we considerably increase the wavelength range of knowledge of (k,n) optical constants of ethanol and isopropanol.

This work is a part of a project aimed at obtaining optical constants of a significant number of fluids used in nanoparticle synthesis and characterization. Several methods for the experimental determination of the optical constants have been proposed and developed in the past. Each of those methods has advantages and drawbacks, which make it more preferable in some circumstances than in other ones, depending on the experimental apparatus at disposal. For a complete review about this topic see Ref. [24] and references therein. The measurement of specular reflectance at near-normal incidence and ellipsometry techniques are good methods for solids and in presence of a strong absorption, but they are insensitive to moderate to weak absorption. Moreover, liquids need to be deposed on a substrate, so that the system immediately gets more complicated and optical properties of substrates themselves have to be taken into account. In addition, ellipsometry requires the use of a dedicated, very expensive experimental apparatus, which is working in limited spectral ranges and cannot be available in all laboratories. Attenuated total reflection (ATR) is a powerful approach in presence of strong absorption bands. For this reason it is mainly used in Mid- and Far-IR, while in UV-Visible-Near-IR it is a niche technique, restricted to few particular cases of highly absorbing samples (e.g. inks). Moreover, it requires a dedicated setup where, on a side the internal reflection and other optical elements are optimized for a particular beam and spectral range, on the other hand the design itself of the setup is strictly related to the characteristics of the samples (in particular as for the number of reflections), so that eventually different ATR systems with different internal reflection crystals and/or architectures should be owned to cover without interruptions a wider region like that we are interested in. Fourier transform method is simple and reliable, but requires Fourier Transform spectrometers, which are rare and very expensive for UV-Visible-Near-IR wavelength range. In this work we use the transmission method. This approach is reliable and simple once reflection effects are properly taken into account. Moreover transmission method is particularly valuable for weak and moderately strong bands, and is limited only by the need for transmission cells with very short path lengths for the strongest IR bands. Introducing a substantial improvement, we are able to overcome this limitation, obtaining very short path length differences and a nonzero transmittance signal even at the most intense IR bands. Last but not least, our modified transmission method has the significative advantage of not requiring the knowledge of optical properties of cell windows for the correct treatment of reflection effects, as detailed in Section 3. The optical constant k is experimentally obtained from 0.185 μm to about 55 μm (~54000–181 cm^{-1}) from transmittance measurements. Then, the refractive index n is obtained from experimental k spectrum by means of the Kramers-Kronig transform. It is worthwhile to note that the extremely wide wavelength range we have explored makes negligible truncation errors over most of the spectral range. At the bounds of the interval, a special treatment is required, as discussed below.

2. Experimental setup

The optical transmittance spectra of ethanol (J.T. Baker, purity ≥99.9%) and isopropanol (Merck, purity ≥99.8%) have been measured by means of three different experimental setups: a "Lambda 900" Perkin-Elmer dispersive spectrophotometer for the range ~ 54054–~ 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–~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–~55 μm). The combination of these three instruments allows to span a spectral interval as wide as from ~54000 (0.185 μm) to 181 cm^{-1} (~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 with 50–1130 μm thickness. When the sample transmittance was too low to have a detectable signal at the output (like in mid- and far-infrared), we assembled the cell without spacer as described in the following. On the contrary, when the transmittance of fluids was very high (e.g. in the visible range), arising in very low k values with high relative uncertainty, we used a specially designed demountable cell with 5, 8, 10 and 12.5 mm path length, as recommended by Ref. [24]. The materials we have chosen for cell windows in the different spectral regions have been CaF$_2$ for the 0.185–3.00 μm range, with exception of the interval 0.25–1.40 μm, where fused silica was used (long path cell for reducing the relative uncertainty on k, as explained above); KBr for ~1.8–25 μm and polyethylene for ~24–55 μm.

3. Transmittance measurements

We obtained the spectral optical constant k from transmittance measurements using the technique described in Ref. [25] and here recalled for clarity.

Under the hypotheses, which we have verified, of absence of scattering, negligible coherent effects [6] and negligible multiple transmissions through the sample, the measured transmittance T as a function of the wavenumber ν can be expressed as a simple function of the spectral absorption coefficient α(ν) as

$$T(\nu) = C \exp(-\alpha(\nu) \cdot x) \tag{1}$$

where x indicates the sample thickness and the constant C includes contributions from window transmittance and reflections at interfaces [25]. Therefore, if we acquire two transmittance spectra T_1 and T_2 at two different thicknesses x_1 and x_2, α can be obtained from the equation:

$$\alpha(\nu) = -\frac{1}{x_2 - x_1} \ln \frac{T_2(\nu)}{T_1(\nu)} = -\frac{1}{\Delta x} \ln \frac{T_2(\nu)}{T_1(\nu)} \tag{2}$$

This simple method allows to directly obtain α for the liquid sample without requirement of a prior knowledge of optical properties (complex refractive index) of window materials and without the need of using complex equations like those arising from the three-layer system approach. The spectral optical constant k(ν), i.e. the imaginary part of the complex refractive index, is connected to α(ν) by the relationship [6]:

$$k = \frac{\alpha(\nu)}{4\pi\nu} \tag{3}$$

In the range 0.185–3.00 μm (UV–Vis–NIR) we acquired the transmittance spectra at several cell thicknesses from 50 to 1130 μm, and we kept as α to be used in further calculations the value obtained by averaging the result of Eq. (2) for several couples of thicknesses (x_1, x_2). Moreover, as explained above, in the spectral range from about 0.25 μm to 1.40 μm wavelength, additional transmittance measurements were carried out to reduce the uncertainty on k using a special cell allowing much longer millimetric path lengths, from 5 to 12.5 mm. The spectral resolution is 1×10^{-3} μm in the range 0.185–0.860 μm and varies from 3×10^{-3} to 2×10^{-2}