



Dielectric functions of *iso*-propanol and di-*iso*-propylether in the infrared



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ABSTRACT

High-frequency dielectric functions of neat liquid *iso*-propanol and di-*iso*-propylether have been investigated and discussed. This included determining the spectra of real and imaginary components of complex electric permittivity and complex polarizability in the NIR–MIR–FIR spectral regions (12,000–200 cm⁻¹) and also calculation and analysis of molar vibrational polarization for both liquids.

The molar vibrational polarization originating from internal vibrational modes has been determined for both molecules for the entire studied spectral region and for various spectral subranges as well. By the use of a recently developed method an attempt was made to ascribe molar vibrational polarization values to particular modes. The vibrational polarization values obtained for di-*iso*-propylether have been compared with the data determined earlier for di-*n*-propylether.

The obtained results also allowed for an estimation of vibrational polarization due to hydrogen-bond formation in neat liquid *iso*-propanol. It was found that the vibrational polarization of hydrogen-bonded OH group increases significantly when compared to non-bonded OH group.

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1. Introduction

Owing to valuable properties *iso*-propanol (IP) has been extensively investigated in many fields of research, including recent physico-chemical studies [1], interactions with drugs [2], applications in biofuels [3] and also in numerous other engineering applications [4,5]. Di-*iso*-propylether (DIPE) drew attention of researchers over the past years as well, with a numerous thermodynamic and physico-chemical data reported [6–8]. DIPE remains being investigated in its ubiquitous solvent role as well [9]. No attention though was paid to the dielectric properties of these liquids in the infrared region, as such investigation was never reported in the literature. The analysis of high-frequency dielectric functions can provide useful data on a number of properties of molecular liquids, including the hydrogen-bond related association. In a recent work [10] we studied the infrared dispersion of liquid di-*n*-propylether (DNPE). We made an attempt there to quantify the impact of hydrogen bonding on molar vibrational polarization of *n*-propanol (NP), by using the data derived for the adequate aliphatic ether – di-*n*-propylether (DNPE).

The aim of present work is twofold. Firstly, we aim to confront the outcome of the current study of *iso*-propanol and di-*iso*-propylether with the results obtained for the above mentioned similar pair of compounds (NP and DNPE respectively), with the hope to obtain a more general view of the impact of H-bond on the molar vibrational polarization of the OH group. Secondly, we would like to compare the

high-frequency dielectric properties of DIPE with the data derived previously for DNPE.

The main aspects of this research are similar to those described earlier [10]. The general aim was to determine high-frequency (internal vibrations related) dielectric properties of liquid IP and DIPE in the wavenumber range covering the visible and infrared (near, mid and far infrared) spectral ranges (25,000–200 cm⁻¹). For the determination of those properties an exact knowledge of the spectra of both components of complex refractive index in the whole relevant spectral region is required. The complex refractive index is given as

$$\hat{n}(\nu) = n(\nu) + ik(\nu). \quad (1)$$

Let's note that ν indicates wavenumbers [cm⁻¹] and $i = \sqrt{-1}$ throughout this work.

In our research we determine these spectra by following an approach based on transmission spectroscopy [11] with a number of refinements developed later [12]. The major difficulty in the experimental part of this study arises from particularly high absorption of molecular liquids in the Mid Infrared (MIR) range. Thus extremely thin layers, in the range of 1–8 μm thickness need to be used in the MIR region to obtain reliable quantitative data.

Basing on the complex refractive index (Eq. (1)) in the following step the spectrum of complex electric permittivity is obtained:

$$\hat{\epsilon}(\nu) = \epsilon'(\nu) + i\epsilon''(\nu) \quad (2)$$

in accordance with Maxwell relations. Eq. (2) in fact describes the high-frequency dielectric properties of studied liquids. From the spectra of

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Table 1

Refractive index and Cauchy coefficients determined for *iso*-propanol and di-*iso*-propylether (T = 298 K).

line	λ [nm]	ν [cm ⁻¹]	$n_{\text{exp}}(\nu)/n_{\text{calc}}(\nu)$	
			IP	DIPE
Hg	435.8	22,946.3	1.38365/1.38365	1.37286/1.37285
Hg	546.1	18,311.7	1.37726/1.37722	1.36696/1.36718
Na	589.6	16,960.7	1.37559/1.37565	1.36572/1.36536
Cd	643.8	15,532.8	1.37417/1.37414	1.36328/1.36343
Cauchy coefficients				
A		1.36651		1.35091
B		3.0878.10 ⁻¹¹ cm ²		6.0555.10 ⁻¹¹ cm ²
C		3.2022.10 ⁻¹¹ cm ⁴		-3.5891.10 ⁻¹¹ cm ⁴

$\epsilon'(\nu)$ and $\epsilon''(\nu)$ other dielectric data including the spectra of complex polarizability and the molar vibrational polarization will be subsequently derived.

In our approach the experimental complex electric permittivity spectrum is then compared with a simulated one, which is obtained in a numerical procedure employing the Classical Damped Harmonic Oscillator band shape model (CDHO). The achieved results allow for a more detailed analysis of molar vibrational polarization (P^{vib}) of both liquids and in particular to evaluate more exactly the impact of hydrogen bond formation in alcohol on its molar vibrational polarization.

2. Experimental details

Since the experimental details were described in detail in our earlier study [10], only a short brief will be given here. The spectra in the MIR and NIR region were recorded on a Magna 860 FT IR/Raman Spectrometer equipped with a DTGS detector with the resolution of 0.5 cm⁻¹ and a relatively large scan number of 1024. In the MIR range custom build thin film cells with KBr and NaCl windows and thickness in the range of 1 to 10 μm were used. Recordings in the FIR range (700–200 cm⁻¹) were done on a Bruker IFS/66 Spectrometer, with a resolution of 2 cm⁻¹ using 50 μm cells made out of SPECAC high-density polyethylene windows. All measurements were carried out at controlled temperature 298 K \pm 0.1 K.

The investigated chemicals were obtained from leading chemical manufacturers at the highest purity available (IP – Fluka, ACS, >99.8%; DIPE – Fluka, puriss. p.a., >99%) and additionally distilled, dried and

Table 2

Molar refractions of *iso*-propanol and di-*iso*-propylether.

	IP	DIPE
n_D	1.37559	1.36572
R_D [cm ³ · mol ⁻¹]	17.65	31.85
n_0	1.36651	1.35091
R_0 [cm ³ · mol ⁻¹]	17.27	30.69
$\Delta R = R_D - R_0$ [cm ³ · mol ⁻¹]	0.38	1.16

stored over molecular sieves under nitrogen. The measured density of DIPE was 0.7182 g cm⁻³, and the refractive index at sodium D-line was 1.36572. For IP these values equaled 0.7807 g cm⁻³ and 1.37559 respectively. The measurements were carried out at 298 \pm 0.1 K.

3. Results and discussion

3.1. Dispersion of the refractive index in the visible range

The spectra of both components of the complex refractive index (Eq. (1)) were determined following an earlier developed procedure [12]. The method takes into account the dispersion of the refractive index in the visible region and the absorption spectrum in the remaining ranges (NIR, MIR and FIR). In the VIS range the spectrum of the refractive index $n_{\text{el}}(\nu)$ was described using the Cauchy equation, in a three parameter form:

$$n_{\text{el}}(\nu) = A + B\nu^2 + C\nu^4. \quad (3)$$

The A, B, C constants in Eq. (3) were determined by applying a least-squares regression to the values of the refractive index determined experimentally. The experimental values of refractive index were measured at several wavelengths in the visible range, at controlled temperature of 298 K and are presented in Table 1 along with the derived Cauchy equation coefficients. Fig. 1 presents the relevant Cauchy curves obtained for IP and DIPE.

Let's note that the studied liquids are non-absorbing in the visible region thus $k(\nu)$ is equal to zero in this range. In the discussed region the spectrum of the real part of the complex refractive index is not constant but decreases gradually. That part of "normal" dispersion is the decaying branch of the anomalous dispersion related to absorption in the UV

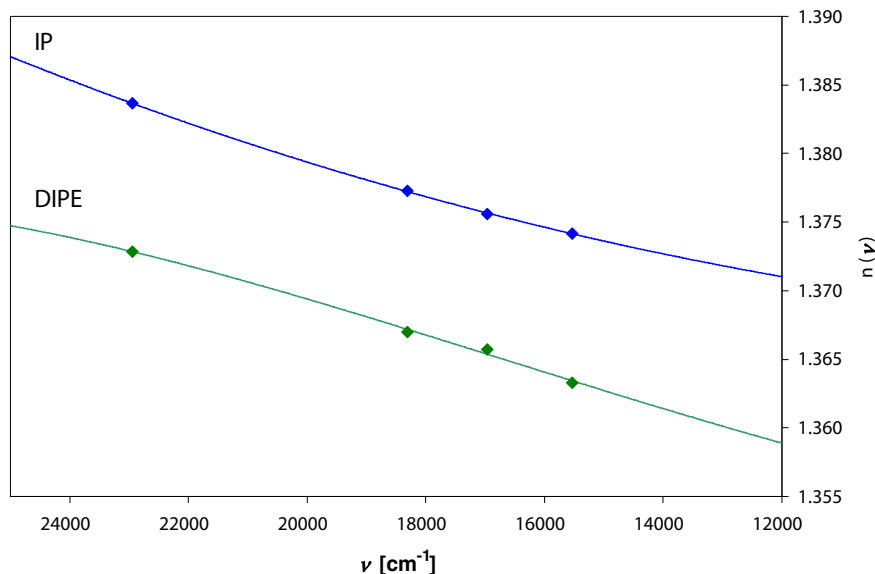


Fig. 1. The dispersion of the refractive index of examined liquids in the visible range; ◆ – experimental values, --- Cauchy curve; T = 298 K.

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