

Contents lists available at ScienceDirect

Journal of Molecular Liquids



journal homepage: www.elsevier.com/locate/molliq

Theoretical and experimental comparative study of nonlinear properties of imidazolium cation based ionic liquids



Vinícius Castro Ferreira ^{a,*}, Letícia Zanchet ^b, Wesley Formentin Monteiro ^b, Letícia Guerreiro da Trindade ^c, Michèle Oberson de Souza ^b, Ricardo Rego Bordalo Correia ^{a,*}

^a OPTMA - Optics, Photonics and Materials Group, Institute of Physics, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

^b LRC - Laboratorio de Reatividade e Catalise, Institute of Chemistry, Universidade Federal do Rio Grande do Sul, Porto Alegre, Brazil

^c Department of Chemistry, Universidade Estadual Paulista, Bauru, São Paulo, Brazil

ARTICLE INFO

Article history: Received 10 August 2020 Received in revised form 21 December 2020 Accepted 12 January 2021 Available online 23 January 2021

Keywords: Ionic liquid Nonlinear refractive index Z-scan EZ-scan Thermo-optical properties

ABSTRACT

This work describes the experimental and theoretical investigation of the nonlinear optical properties of the imidazolium cation based ionic liquids and the corresponding thermo-optical parameters. The experimental results of nonlinear optical properties, such as nonlinear refractive index and thermo-optical properties are determined by *Z*-scan and EZ-scan techniques with a femtosecond laser source. Theoretical simulations of linear and nonlinear optical properties performed by density functional theory (DFT) are discussed in terms of polarizabilities and hyperpolarizabilities. A correlation between the theoretical and experimental results is presented, where the variation of the experimental signals of each ionic liquid can be compared with their calculated non-linear optical properties.

© 2021 Elsevier B.V. All rights reserved.

1. Introduction

lonic liquids (ILs), also named organic molten salts, are composed of ions, a large organic cation, and an anion having a delocalized charge. The cation's asymmetry and flexibility lead to weak ion interactions which result in compounds with a low tendency to crystallize [1,2]. Since their rediscovery, the ILs have been applied in several branches of chemistry due to a unique combination of physicochemical properties, highlighting a wide electrochemical window, negligible vapor pressure, high electrical conductivity, high ionic mobility, high thermal stability, low flammability and low toxicity [2]. This set of properties, coupled with the possibility of designing ILs by choosing the ions, enables the use of ILs in pharmaceutical and environmental applications [3,4].

The impact of ILs has become important due to their tunable physicochemical properties and electronic characteristics [5]. In recent years, ionic liquids have had their main characteristics explored, generating promising science and technologies for academic and industrial applications in areas such as catalysis [6–8], materials science [9,10], physical chemistry [11], electrochemistry [12], polymer science [13,14], biology [15], among others, which gives them a multidisciplinary character [16]. ILs can be part of new technologies that enable to solve current problems faced by society, emerging as effective alternatives.

Among the numerous ionic liquids properties that can be studied, optical characterizations are undoubtedly valuable because of the structural and electronic information provided. In the linear optical domain, the optical properties of materials are independent of the light intensity. In contrast, the light field can modify several optical properties in the nonlinear optical regime. The understandings of nonlinear optical (NLO) phenomena are essential to the development of new materials and technology applications, ranging from conversion of wavelength frequencies and optical switches [17] up to ultra-fast laser sources [18] and health sciences [19].

The optical properties of ILs have been widely studied since early 2000. A substance with NLO activity must be polarizable and/or have an asymmetric charge distribution and contain a π -conjugated electron moiety, so ILs were recognized as good candidates to be studied in NLO [20]. The ILs present a strong dependence on the properties and nature of the cation and anion. Thus the anionic and cationic moieties' choice may generate materials with optimized properties [21]. Several non-linear characteristics were studied in these materials, such as fast molecular dynamic processes [22–24]. The study of NLO properties in ILs is crucial since this response is fundamental in applications in supercapacitors, optoelectronics on a large scale, and laser ablation processes [25,26]. Few studies report data about ILs nonlinear index of refraction, property covered in this work. The variation in refractive index

^{*} Corresponding author.

E-mail addresses: castroferreiravinicius@gmail.com (V.C. Ferreira), rego@if.ufrgs.br (R.R.B. Correia).

generated by thermal effects was evaluated by self-induced thermal effects for different aromatic and alicyclic ILs [27,28]. Most of these values agree with standard interferometric measurements of ILs, as observed for eleven 1-alkyl-3-methylimidazolium-based ionic liquids, registering negative values of the thermo-optical coefficient, dn/dT, in the order of $10^{-4}-10^{-3}$ K⁻¹. Nonlinear indexes of refraction in the order of 10^{-16} cm² W⁻¹ were measured in femtosecond laser systems for colloidal solution of silver nanoparticles dispersed in BMI.BF₄ IL [29] and mixtures of azobenzene containing IL crystalline polymer [20], the latter displaying subpicosecond responses. However, to our knowledge, the literature does not describe thermal and electronic effects related to the nonlinear index of refraction of pure ILs exposed to a femtosecond laser source and discusses experimental data associating them to theoretical studies.

In order to study these effects, this paper aimed to evaluate the nonlinear optical behavior of four specific ILs, combining theoretical and experimental approach to prospect the prediction of its optical properties. The four ILs characterized and discussed here are the methylimidazole hydrogen sulfate (MImH.HSO₄), butylimidazole hydrogen sulfate (BImH.HSO₄), 1-butyl-3-methylimidazolium hydrogen sulfate (BMI. HSO₄), and 1-butyl-3-methylimidazolium trifluoromethane sulfonate (BMI.CF₃SO₃). The length and nature of the cation's alkyl chain, as well as the nature of the anion, were modified to verify their influence on the optical properties. Fast and slow response, related to the electronic and thermal effects, respectively, were characterized by Z-scan and EZ-scan techniques for these ILs. Theoretical simulation of the Fouriertransform infrared spectroscopy (FTIR) analysis of the ILs was also performed and corroborated with the experimental results.

2. Experimental

2.1. Materials

The ionic liquids were synthesized using 1-methyl imidazole 99%, (Sigma-Aldrich), 1-chlorobutane 99% (Sigma-Aldrich), ethyl acetate (Sigma-Aldrich) 99.8%, sulfuric acid 98% (Merck), trifluoromethanesulfonic acid 99% (Sigma-Aldrich), and 1- butylimidazole 98% (Sigma-Aldrich).

2.2. Synthesis and characterization of the ionic liquids

The 1-butyl-3-methylimidazolium hydrogen sulfate (BMI.HSO₄) and 1-butyl-3-methylimidazolium trifluoromethane sulfonate (BMI. CF₃SO₃) ionic liquids were synthesized by ion exchange reaction from the 1-butyl-3-methylimidazolium chloride (BMI.Cl) IL according to the procedures reported in the literature [30–32]. H₂SO₄ was added to a solution of BMI.Cl dissolved in deionized water. The resulting solution was maintained under reflux for 4 h at 100 °C and then dried under vacuum at 90 °C. The final compound is a colorless viscous liquid.

BMI.CF₃SO₃ was synthesized, adding dropwise the trifluoromethanesulfonic acid (CF₃SO₃H) to an aqueous solution of BMI.Cl placed in an ice bath. After the complete addition of the acid, the solution was kept under stirring for 24 h. Dichloromethane was then used (5 times 50 mL) to extract the IL from the aqueous phase. The organic phase was then washed with deionized water (10 times 100 mL) to remove any chloride salt and acid. Then the IL was dried under vacuum at 120 °C until the complete removal of the residual water and dichloromethane, resulting in yellowish IL.

The two protic ILs, the methylimidazole hydrogen sulfate (MImH. HSO_4) and butylimidazole hydrogen sulfate (BImH. HSO_4), were produced by reacting a 0.2 mol of sulfuric acid with 1-methylimidazole and 1-butylimidazole respectively at room temperature placed under stirring in an ice bath for 24 h. The resulting solution was heated below 90 °C for removing the solvent leading to the production of a white viscous liquid (MImH. HSO_4 , 98% yield) and a brown viscous liquid (BImH. HSO_4 , 93% yield) respectively.

The synthesized ILs were characterized by Fourier-transform infrared spectroscopy (FTIR) using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) with a Bruker Alpha-P in the spectral range 4000–500 cm⁻¹, and ultraviolet-visible spectrophotometry performed in a Cary 5000 UV–Vis-NIR equipment from Agilent using a 2.0 mm quartz cuvette.

2.3. Theoretical calculations

Density functional theory (DFT) study was performed to understand the molecular behavior and structural conformation of the ionic liquids. DFT calculations were achieved using the Becke's three-parameter exchange functional in combination with the Lee, Yang and Parr correlation functional (B3LYP) [33,34] with a 6–311++G(d,p) basis set as implemented in the GAUSSIAN 16 package. Structures were fully optimized, under no symmetry constraints, and vibrational frequency calculations were performed. Final structures have no imaginary frequencies associated with them. The frontier orbital energies were calculated in a single point run in the same theory level. Molecular electrostatic potential maps (MEPs) of total electronic densities using the partial charges were analyzed with Gabedit software [35]. For each ILs, a DFT study was performed for determining the polarizability (α), the first-order hyperpolarizability (β), and the second-order hyperpolarizability (γ), varying the frequencies relations.

2.4. Nonlinear optical and thermo-optical properties measurements

The optical and thermo-optical properties of the ILs were evaluated by Z-scan and EZ-scan techniques for the determination of the thermooptical coefficient, nonlinear absorption and nonlinear refractive index (also called intensity-dependent refractive index). Z-scan is a widely used technique that characterizes the nonlinear refractive index, nonlinear absorption/saturation, and thermo-optical properties by the variation of wavefront curvature [36]. The eclipse configuration, EZ-scan, can measure the same properties of the Z-scan technique but with better sensitivity and signal-noise ratio [37]. The difference between them is the spatial filter used to select the portion of the beam to be detected: Z-scan uses an aperture while EZ-scan uses a disc. In both cases, a laser source with a high repetition rate produces cumulative effects, which must be distinguished between fast (electronic) and slow (thermal) effects [38,39]. A third experimental setup variant without a spatial filter was also used. In this case, any change transmittance variation will be due to the nonlinear absorption/saturation in the sample [36]. These configurations were used to characterize the nonlinear optical properties of the ILs. The experimental setup was the same, only the change of the spatial filter (disc or aperture) or no filter according to their intended measurement. The light source was a chopped laser beam of a mode-locked Ti: Sapphire laser oscillator (76 MHz, 150 fs, 780 nm) focused at a beam waist radius of 35 µm, where the sample is scanned in the z-direction over a range of few Rayleigh lengths (z_0) . The detection was performed by a fast Si photodiode detector positioned in front of the spatial filter. A second chopper generates a beam modulation at 9 Hz (duty cycle of 2.4% and beam time exposure of 2.66 ms), providing the relaxing time needed for the thermal management procedure [40]. At each sample position, the time evolution of the transmitted signal was recorded with a digital oscilloscope, which allows time-resolved analyses. The normalized transmittance to the fast response is acquired at the beginning of the time exposure window, t = 0.

The EZ-scan configuration was used to characterize the fast response properties, as in the case of a nonlinear refractive index. A measurement without spatial filter, open aperture Z-scan, was performed to measure the nonlinear absorption/saturation of the liquids. The Z-scan configuration was used to evaluate the thermal response, since this method allows the fitting of the Z-scan curve by an analytical model based on the thermo-optical properties [39].

3. Results and discussion

3.1. Ionic liquids characterizations

Fig. 1a shows the experimental Fourier-transform infrared spectroscopy (FTIR) of BMI.CF₃SO₃, BMI.HSO₄, MImH.HSO₄ and BImH.HSO₄, and the corresponding theoretical spectra performed for this study (Fig. 2b). The results show that experimental and theoretical data converge. The BMI.CF₃SO₃ IL spectrum (Fig. 1a) shows the following vibration bands: C–H aromatic at 3173 and 3107 cm⁻¹; aliphatic C–H at 2968 and 2882 cm⁻¹; C–N at 1573 cm⁻¹; C=C at 1468 cm⁻¹; C–F at 1249 cm⁻¹; O=S=O at 1031 cm⁻¹ and S–O at 1157 cm⁻¹. The band at 853 cm⁻¹ is due to the C–H in-plane bending vibration of the imidazolium ring, and the band at 750 cm⁻¹ can be assigned to the C– H out-of-plane bending vibration of the imidazolium ring [41,42].

The spectrum of BMI.HSO₄ presents vibrations of imidazolium ring at 3149 and 3105 cm⁻¹ corresponding to the C–H bonds, and the bands at 1467 and 1571 cm⁻¹ correspond to the C=C and C=N bonds. The band at 837 cm⁻¹ is due to C–H in-plane bending vibration of the imidazolium ring, and the band at 753 cm⁻¹ can be assigned to the C–H out-of-plane bending vibration of the imidazolium ring. The aliphatic C–H asymmetric and symmetric stretching vibrations of the alkyl chain are represented by the bands at 2962 and 2875 cm⁻¹, while the peaks at 1024 and 1229 cm⁻¹ are assigned to the S–O and S –OH stretching vibrations of HSO₄. The band at 1161 cm⁻¹ indicates the stretching vibration of C–N [43,44].

About the MImH.HSO₄ and BImH.HSO₄ ILs, the bands at 3150 and 3075 cm⁻¹ are attributed to the stretching vibrations of the imidazole ring C-H bonds. The aliphatic asymmetric and symmetric (C-H) stretching vibrations of the lateral chain of the imidazole ring appears at 2960 cm^{-1} for MImH.HSO₄ and at 2965 and 2930 cm^{-1} for BImH. HSO₄. The bands at 1578 and 1454 cm^{-1} in both ionic liquids correspond to C=C and C=N stretching vibrations of the imidazole ring, respectively. The bands at 1222 and 1023 cm⁻¹ are assigned to the S-O and S–OH stretching vibrations of HSO_4 [43]. The bands at 1162, 840, and 752 cm^{-1} can be attributed to the stretching vibration of C–N, the C-H in-plane bending vibration and the C-H out-of-plane bending vibration of the imidazole ring [45,46]. The simulated spectra (Fig. 1b) of the four ILs structures reported in Fig. 1a, besides being like the experimental spectra do not present imaginary frequencies, i.e., no negative wavenumber. These results confirm that the molecular model obtained theoretically is satisfactory.

Fig. 2 presents the absorbance spectra to the ILs studied. This analysis allows us to choose $\lambda = 780$ nm for the laser wavelength value to be



Fig. 2. Absorption spectra of the ILs studied. The arrow pointing at $\lambda = 780$ nm indicates the absorption coefficient values of the experimental laser wavelength used in the experimental optical study.

used in the study of optical and thermo-optical properties of the ILs since low UV absorption interference occurs in this region. The determined absorption coefficient values (*a*) related to the laser wavelength used experimentally ($\lambda = 780$ nm) for MImH.HSO₄ was 0.1 \pm 0.04 cm⁻¹, for BImH.HSO₄ was 0.05 \pm 0.01 cm⁻¹, for BMI.HSO₄ was 0.02 \pm 0.01 cm⁻¹ and for BMI.CF₃SO₃ was 0.04 \pm 0.01 cm⁻¹.

3.2. Theoretical calculations

Fig. 3 presents the DFT results corresponding to the molecular electrostatic potential (MEP) maps obtained for the four ionic liquids (MImH.HSO₄, BImH.HSO₄ BMI.HSO₄ and, BMI.CF₃SO₃). According to the color scale, the red color present on all the anions' surface indicates nucleophilic domains, while the blue color on the surface of the cation represents their electrophilic character [47].

In the case of the protic ILs (MImH.HSO₄ and BImH.HSO₄), this study enables to identify the acidic hydrogen of the cation that is interacting highly, probably through an H-bonds with the oxygen atoms of the anion. Both of these ILs present favored anion-cation charge transfer due to this interaction. The observed distance in the interaction



Fig. 1. FTIR spectrum of ILs: a) experimental and b) simulated with DFT/B3LYP/6-311++G(d,p).

Journal of Molecular Liquids 328 (2021) 115391



Fig. 3. Molecular electrostatic potential maps for ionic liquids. Red color: negative potential; blue color: positive potential.

between the cation's hydrogen atom and the anion's oxygen atom involved in this charge transfer was 1.45, 1.46, 1.95, and 2.09 Å (for the ILs MIMH.HSO₄, BIMH.HSO₄, BMI.HSO₄, and BMI.CF₃SO₃, respectively). About the BMI.CF₃SO₃ and BMI.HSO₄ ILs, the HSO₄ anion is located at a more centralized place, comparing the structure of MIMH.HSO₄ and BIMH.HSO₄. This localization of the anion regarding to the imidazolium ring is probably due to the presence of a methyl group on it.

Fig. 4 shows the results of the frontier molecular orbital (FMO) analysis of the studied ILs. The Highest Occupied Molecular Orbital (HOMO) is nucleophilic and it is considered as an electron donor, while the Lowest Unoccupied Molecular Orbital (LUMO) is usually electrophilic and it is then an acceptor of electron given by a nucleophilic species [48]. The larger orbital volumes represented in Fig. 4 evidence that for all the ILs, the HOMOs are localized in the anion, while the LUMOs are localized in the imidazole ring where the positive charge density is located. The energy difference between the HOMO and LUMO energy (energy gap) is associated with the charge transfer interaction within the frontier orbitals. Comparing the gap energy obtained for all the ILs, the lowest one is observed for the BMI.HSO₄ IL. This result can be attributed to the presence of the methyl group in the imidazolium ring that generates an increase in the HOMO and a decrease in the LUMO values. This reduced gap energy allows the transfer of electrons from the anion to the cation.

Fig. 4 also shows that the HOMO orbitals have the lowest electron distribution in the atoms that have the shortest distances of interaction. This correlation is the most significant in the case of MImH. HSO_4 and BImH. HSO_4 that are protic ionic liquids. This result can be associated with an important degree of intramolecular charge transfer from the anion to the cation [49]. The interaction energies of ion-pairs are defined as follows:

$$E_{(kj mol^{-1})} = 2625.5 \left[E_{is} - (E^+ + E^-) \right]$$
(1)

where E_{is} is the energy of the ionic system, and E^+ and E^- are the energy of the cation and anion, respectively. The interaction energies values obtained for MImH.HSO₄, BImH.HSO₄, BMI.HSO₄ and BMI. CF₃SO₃ were -412.20 kJ.mol⁻¹, -401.70 kJ.mol⁻¹, -360.20 and -339.21 kJ.mol⁻¹. The comparison of the values obtained for the two



Fig. 4. Atomic orbital HOMO - LUMO composition of the frontier molecular orbital of ILs.

protic ILs (BImH.HSO₄ and MImH.HSO₄) shows that the increase in the alkyl chain of the imidazole ring leads to an increase in the interaction energy, indicating a favorable charge transfer between the ions [49].

The interaction energy obtained values for BMI.HSO₄ and BMI. CF₃SO₃, in comparison with the results obtained for BImH.HSO₄ and MImH.HSO₄, indicates that the presence of a methyl group in the imidazolium ring increases the values of interaction energy between the cation and the anion. This result can be corroborated with the results obtained through the MEPs study (Fig. 3), which showed that the anion HSO₄ was located nearest to the imidazolium ring center in comparison with the protic ILs. A correlation between the interaction energies and the HOMO-LUMO energy gap can then be made.

The dipole moment (μ) in a molecule infers the molecular charge distribution, and its determination enables the study of intermolecular interactions [49]. The polarizability (α) and the first hyperpolarizability (β) of a compound, that are associated with the intramolecular charge transfer, result from the electron cloud movement, for example, from an electron donor group to an acceptor group through the π -conjugated framework. Results obtained with DFT are directly related to the linear and nonlinear optical properties. The polarizability is proportional to the static or the frequency-dependence polarizability, while $\Delta \alpha$ represents the anisotropy of polarizability, i.e., the variation between the polarizability value obtained on the axis of the polarizability and a perpendicular axis to the polarizability axis. The first-order hyperpolarizability, (β) , is proportional to the second-order susceptibility effects, as second a harmonic generation, optical rectification, electro-optical Pockels effect and three-wave mixing. The secondorder hyperpolarizability (γ) is proportional to the effects of the thirdorder susceptibility, as four-wave mixing and the responses measured by the Z-scan and EZ-scan techniques.

We evaluated the linear and nonlinear optical properties of the ILs to several optical responses using the wavelength $\lambda = 780$ nm. Table 1 presents the theoretical values of μ , α and β , as well the anisotropy of polarizability $\Delta \alpha$ calculated for the studded ILs. The comparison of the μ values obtained for the protic ILs (MImH.HSO₄ and BImH.HSO₄) reported in Table 1 shows that the increase in the alkyl chain of the IL (BImH.HSO₄) causes an increase in the dipole moment. The presence of the methyl group in the imidazole ring rather than a proton decreases the dipole moment.

The highest first hyperpolarizability values (α) are observed for the BMI.HSO₄ and BMI.CF₃SO₃. As this property is dependent on the dipole moment, this result can be associated with the presence of the methyl group in the imidazole ring that promotes a change in the symmetry of the molecule, increasing then the α values [50].

Table 2 presents the polarizability, α , and the first-order hyperpolarizability, β , for different frequencies relations: $\alpha(-\omega; \omega)$ is the frequency-dependent polarizability, $\beta(-\omega; \omega, 0)$ and $\beta(-2\omega; \omega, \omega)$ are related to the electro-optic Pockels effect and the second harmonic generation respectively, both effects from the second-order susceptibility. Related to the terms of the second-order hyperpolarizability (Table 2), $\gamma(-\omega; \omega, 0, 0)$ presents electro-optic Kerr effect, $\gamma(-2\omega; \omega, \omega, 0)$ presents a DC-induced second harmonic generation or electric field-induced second harmonic. Another response of the second-order hyperpolarizability, dependent refractive index or degenerate four-wave mixing, but the

Table 1

Theoretical values of dipole moment, μ , polarizability, α , the anisotropy of polarizability, $\Delta \alpha$, and first hyperpolarizability, β , for the ionic liquids.

Sample	μ (Debye)	α (x 10 $^{-24}\text{esu})$	$\Delta\alpha~(x~10~^{-24}~esu)$	$\beta(x \ 10^{-31} \ esu)$
MImH.HSO ₄	12.47	14.08	6.66	18.37
BImH.HSO ₄	12.96	19.64	7.96	16.42
BMI.HSO ₄	12.55	21.29	6.95	28.51
BMI.CF ₃ SO ₃	13.78	22.92	7.00	31.87

Table 2

DFT results for the polarizability α , and the first-order hyperpolarizability, β , and for the second-order hyperpolarizability, γ , for different frequencies relations.

Properties	MImH.HSO ₄	BImH.HSO ₄	BMI.HSO ₄	BMI.CF ₃ SO ₃
$\alpha(-\omega;\omega)$ (10 ⁻²⁴ esu)	14.31	19.95	21.63	23.28
$\beta(-\omega; \omega, 0) \ (10^{-31} \text{ esu})$	19.98	17.76	31.43	35.10
$\beta(-2\omega; \omega, \omega) (10^{-31} \text{ esu})$	24.40	21.48	40.05	44.11
$\gamma(-\omega; \omega, 0, 0) (10^{-36} \text{ esu})$	10.84	16.17	19.44	20.22
$\gamma(-2\omega;\omega,\omega,0)$ (10^{-36} esu)	13.94	20.30	25.76	26.30

DFT software has no library to evaluate this. These three presented terms are all related to the third-order susceptibility. The theoretical results presented are the response of parallel polarization in relation to the applied field.

The values of polarizability, the first-order hyperpolarizability and the second-order hyperpolarizability are higher for BMI.CF₃SO₃, followed by BMI.HSO₄, indicating that a large chain in the cation, following by the presence of the methyl group in the imidazolium ring presented a stronger influence in these properties. The IL MIMH.HSO₄, which has the smallest chain in the cation, showed the lowest values of the first-order hyperpolarizability and the second-order hyperpolarizability. The unique difference observed is for $\beta(-\omega; \omega, 0)$ (10⁻³¹ esu) obtained for BImH.HSO₄ IL, that is the lowest value comparing all ILs. The imidazolium ring of this IL presented an acid hydrogen that favored charge transfer (see results of Figs. 3 and 4) associated to the cation chain can be related to these values, however, more detailed studies need to be carried out to better explain this phenomenon.

To compare the obtained results, we evaluated by DFT analyses, under the same conditions, properties of urea and carbon disulfide since they are standard comparative molecules in NLO studies [40,49,51]. The results obtained for urea to terms of first-order hyperpolarizability was $\beta(-\omega; \omega, 0) = 0.91 \times 10^{-34}$ esu and $\beta(-2\omega; \omega, \omega) = 1.02 \times 10^{-34}$ esu. These values are typically 10^4 times smaller than the obtained values to ILs presented in this work. The second-order hyperpolarizability of carbon disulfide was $\gamma(-\omega; \omega, 0, 0) = 4.17 \times 10^{-36}$ esu and $\gamma(-2\omega; \omega, \omega, 0) = 5.61 \times 10^{-36}$ esu. Both values vary from 2 to 5 times smaller than the obtained to studied ILs.

3.3. Local and nonlocal nonlinear optical characterization

The fast responses of molecules measured by the refractive index change techniques are usually generated by effects related to the highorders of the susceptibility. These effects are spatially restricted to the presence of the light fields, corresponding to a local response. Examples of these effects are nonlinear refractive index and nonlinear absorption. Otherwise, thermal effects, which are slower and promote heat diffusion, are not spatially restricted to the beam region and are, therefore, a nonlocal effect.

The measurements for rapid response analysis were performed in the EZ-scan configuration. The nonlinear refractive index was evaluated using a model based on literature [37]:

$$n_2 = \frac{\Delta T_{p-\nu}}{0.68 (1-S)^{-0.44} L_{eff} k I_0},$$
(2)

where ΔT_{p-v} is the peak-valley amplitude of the normalized transmittance variation in the EZ-scan technique, S is the factor of disc blockage of the total beam power, *k* is the wave vector, I₀ is the peak intensity and $L_{eff} = (1 - \exp(-aL))/a$ is the sample effective length.

A previously presented procedure of systematic errors reduction was employed by our group in these measurements [52]. The scans corresponding to the fast responses obtained with the ILs are presented in the left graphs of Fig. 5. In these results, the light leak through the disc was S = 3.3%; the beam waist radius was $w_0 = 32 \mu m$; the Rayleigh length was $z_R = 4.0 mm$, and liquid sample cell thickness was L =



Fig. 5. Variation of transmittance registered for the four ILs exposed to a laser beam ($\lambda = 780$ nm). The left side graphs were registered in the time equals zero (condition for minimizing the thermal effects [39]), while the right-side graphs were recorded after 2.3 ms of beam exposure to identify predominantly the thermal effects. The respectively IL is presented in the figure and as well as the intensity and power used in the measurements. Open aperture *Z*-scan are inset, all them performed with beam peak intensity equals to 1.7 GW/cm⁻².

2.0 mm. The right side of Fig. 5 presents the results of measurement in the EZ-scan setup 2.3 ms after the chopper aperture corresponding to exposure time to the beam. Under these conditions, the thermal effects influenced by the average power predominate, which is why this is shown instead of the peak intensity. In order to optimize the fast response signal at the beginning of the temporal exposure window, the used power of the laser beam was reduced accordingly for each sample. An open aperture Z-scan was also performed to analyze nonlinear absorption/saturation, but no sample evidenced that type of response. These results are present inset of Fig. 5. All open aperture measurements were performed with beam peak intensity of 1.7 GW/cm². The nonlinear refractive indices of those ILs were determined according to

Eq. (2) and are summarized in Table 3. The system was calibrated using a carbon disulfide sample as the reference. To this sample, the nonlinear refractive index of carbon disulfide was determined as $n_2 = 2.6 \pm 0.3 \times 10^{-15} \text{ cm}^2 \text{ W}^{-1}$, which is consistent with the literature [38,40].

The real part of the third-order susceptibility, $\chi^{(3)}$, is directly related to the degenerate nonlinear refractive index. This term can be evaluated by the equation [53],

$$\chi^{(3)}(-\omega;\omega,\omega,-\omega) = \frac{n_0^2}{283}n_2(\omega) \tag{3}$$

Table 3

Experimental nonlinear optical properties values of the ILs obtained: values of the nonlinear refractive index (n_2), third-order susceptibility, $\chi^{(3)}$, the molecular number density (N), and the second-order susceptibility, $\chi(-\omega; \omega; -\omega)$.

Sample	$n_2 (10^{-16} \text{ cm}^2 \text{ W}^{-1})$	$\chi^{(3)}$ (10 ⁻²² m ² /V ²)	$\chi^{(3)}$ (10 ⁻¹⁴ esu)	N (10 ²¹ cm ⁻³)	$\gamma(-\omega; \omega, \omega, -\omega),$ (10 ⁻³⁶ esu)
MImH.HSO4 BImH.HSO4 BMI.HSO4 BMI.CF3SO3	$\begin{array}{l} 2.7 \ \pm \ 0.7 \\ 4.2 \ \pm \ 0.6 \\ 4.5 \ \pm \ 0.5 \\ 2.7 \ \pm \ 0.4 \end{array}$	$\begin{array}{l} 2.0 \ \pm \ 0.6 \\ 3.1 \ \pm \ 0.5 \\ 3.3 \ \pm \ 0.4 \\ 2.3 \ \pm \ 0.4 \end{array}$	$\begin{array}{l} 1.4 \pm 0.5 \\ 2.2 \pm 0.3 \\ 2.4 \pm 0.4 \\ 1.6 \pm 0.3 \end{array}$	$\begin{array}{l} 4.7 \pm 0.1 \\ 3.8 \pm 0.1 \\ 3.6 \pm 0.1 \\ 3.1 \pm 0.1 \end{array}$	$\begin{array}{l} 0.9\pm0.2\\ 1.6\pm0.3\\ 1.9\pm0.2\\ 1.3\pm0.2 \end{array}$

Table 4

Experimental optical properties values of the ILs obtained: values of the absorption (α), characteristic thermal lens time (t_{c0}), thermal lens strength to the laser power of 300 mW (θ), thermal conductivity (κ), thermo-optical coefficient (dn/dT) and the thermal diffusivity (D). The laser beam wavelength was $\lambda = 780$ nm.

Sample	a (cm ⁻¹)	t _{c0} (ms)	θ	κ (W m ⁻¹ K ⁻¹)	dn/dT (10 ⁻⁶ K ⁻¹)	D $(10^{-3} \text{ cm}^2 \text{ s}^{-1})$
MImH.HSO4 BImH.HSO4 BMI.HSO4 BMI.CF3SO3	$\begin{array}{c} 0.13 \pm 0.04 \\ 0.05 \pm 0.01 \\ 0.02 \pm 0.01 \\ 0.04 \pm 0.01 \end{array}$	$\begin{array}{l} 2.3 \pm 0.2 \\ 2.6 \pm 0.4 \\ 3.0 \pm 0.3 \\ 4.5 \pm 0.5 \end{array}$	$\begin{array}{l} 0.31 \pm 0.03 \\ 1.04 \pm 0.02 \\ 0.58 \pm 0.05 \\ 0.36 \pm 0.03 \end{array}$	$\begin{array}{c} 0.17 \pm 0.02 \\ 0.15 \pm 0.02 \\ 0.14 \pm 0.02 \\ 0.13 \pm 0.02 \end{array}$	$\begin{array}{l} 5.2 \pm 0.8 \\ 4.6 \pm 0.6 \\ 5.4 \pm 0.7 \\ 1.5 \pm 0.6 \end{array}$	$\begin{array}{c} 1.1 \ \pm \ 0.1 \\ 0.9 \ \pm \ 0.2 \\ 0.8 \ \pm \ 0.2 \\ 0.6 \ \pm \ 0.2 \end{array}$



Fig. 6. Temporal evolution for the four ILs exposed to a laser beam ($\lambda = 780$ nm) with the power equals of 300 mW. The fits were performed using the Eq. (5). The respectively IL is presented in the figure.

where n_0 is the linear refractive index at the same frequency. Considering that the main contribution would correspond to the electronic portion of the second-order hyperpolarizability, $\gamma(-\omega; \omega, \omega, -\omega)$, can be estimated from the correspondent susceptibility and thus from the nonlinear refractive index by the relation considering the local field factor [54]:

$$\gamma = \frac{\chi^{(3)}}{\left[\frac{1}{3}\left(n_0^2 + 2\right)\right]^4 N} \tag{4}$$

where N is the molecular number density, presented in Table 3. In this analysis, the linear refractive index used for estimation for all liquids ranges from $n_0 = 1.42$ to 1.45 [55,56], and this deviation is smaller than the error associated of the measured nonlinear refractive index.

Table 3 shows these estimated hyperpolarizabilities values for each IL. In comparison, these are an order of magnitude smaller than theoretical results obtained with the DFT theory. This discrepancy may be associated with a refractive different response, e.g., with the one corresponding to the signal modified by the ILs local structure and the interaction with their vicinities. Another behavior that can result in this difference is the induced birefringence. Based on the value evaluated for the polarization anisotropy, $\Delta \alpha$, one should also consider the optical Kerr effect, which arises from the molecular alignment produced by the optical torque on the induced dipoles [57]. This effect could be evidenced by a technique that discriminated against these effects, as the polarization-resolved Z-scan technique [58], or performing analyses via OKE spectroscopy [59]. Although the demonstrated discrepancy between theoretical and experimental values of the second-order hyperpolarizability, the results obtained by the EZ-scan technique for the first three ILs shown in Table 3 presented the same growth rate verified by DFT to the terms $\gamma(-\omega; \omega; 0, 0)$ and $\gamma(-2\omega; \omega, \omega, 0)$, which can assist in predicting the nonlinear properties prior to sample synthesis.

Even if a short femtosecond pulse with nanojoules of energy is sufficient not to heat the sample during a single propagation, high repetition rates of these pulses produce cumulative effects that alter the wavefront curvature of the propagating beam. The time evolution of transmittance variation in a high-repetition system was modeled by Falconieri [60]. In the case of linear absorption, i.e. in our situation, the variation of transmittance can be written as [61,62]:

$$T = \left\{ 1 + \frac{\theta}{2} \tan^{-1} \left(\frac{2\tilde{z}}{\left(9 + \tilde{z}^2\right) \left(1 + \tilde{z}^2\right) t_{c0}/2t + 3 + \tilde{z}^2} \right) \right\}^2$$
(5)

where t_{c0} is the characteristic thermal lens time associated with the beam waist radius and $\tilde{z} = z/z_0$ is the normalized scanning parameter. The thermal diffusivity is related to the t_{c0} by $D = w_0 / 4 t_{c0}$. The thermal lens strength, θ , represents the intensity of the lens induced by the sample heating, which curves the beam wavefront and generates the variation of transmittance in this regime. Eq. (5) considers the quadratic terms of thermal lens strength since it is not negligible in our situation. The thermo-optical coefficient, the variation of refractive index (*n*) with the temperature, can be determined by:

$$\frac{dn}{dT} = -\frac{\lambda\kappa}{P \, a \, L_{eff}} \,\theta \tag{6}$$

where *P* is the laser power in the sample and κ is the thermal conductivity, which can be evaluated for ILs applying the model based on equation proposed by Fröba et al. [63]:

$$k = \frac{AM + B}{M\rho} \tag{7}$$

where A = 0.1130 g cm⁻³ W m⁻¹ K⁻¹, and B = 22.65 g² cm⁻³ W m⁻¹ K⁻¹ mol⁻¹ are constants defined in the temperature of 293.15 K, ρ is the density, and M is the molar mass of the liquid. The thermal conductivity values and uncertainties calculated from the respective densities of each IL studied here are displayed in Table 4.

These properties were estimated to perform a *Z*-scan analysis with the ILs. The absorption coefficient (*a*), the thermal characteristic time (t_c), the thermal lens strength for a laser power of 300 mW (θ), the thermal conductivity (κ) calculated from Eq. (7) and the thermo-optical coefficient (dn/dT), are given in Table 4 for the four ILs. The thermo-optical values obtained on these samples are consistent with the typical values reported for ionic liquids [64,65]. The characteristic thermal lens time also agrees with previous results of similar samples referenced in the literature [66,67]. Fig. 6 presents the time evolution for each ILs, in the maximum and minimum (peak and valley) of the Z-scan curve, all of them acquired with the laser power of 300 mW. The adjustments were performed with the Eq. (5). Except for the absorption coefficient, all results presented in Table 4 were obtained by this fit in the temporal evolution of the Z-scan measurements or from derivations of these values.

All these data were determined for the first time for the MImH.HSO₄, BImH.HSO₄, BMI.HSO₄, and BMI.CF₃SO₃ ILs. As previously pointed, the literature of thermo-optical properties and nonlinear refractive index involving ILs with a femtosecond laser source is not extensive. Beyond that, no further studies for ILs were found that relate the electronic effects on experimental results with theoretical simulations.

4. Conclusion

The nonlinear optical properties of four ILs, MIMH.HSO₄, BIMH.HSO₄, BMI.HSO₄ and BMI.CF₃SO₃ were determined theoretically and experimentally. All four ILs exhibited nonlinear refractive indices under our experimental conditions, and their thermo-optical coefficients were also evaluated. The DFT analysis was able to estimate the polarizability as well as first- and second-order hyperpolarizabilities.

Based on this comparison we observe that in accordance to the increase of the alkyl chain of the imidazole ring on the sulfate ILs, the growth of nonlinear values in the DFT analyses of the second-order hyperpolarizabilities, γ , is coherent with the measured growing nonlinear susceptibilities. This result shows that the DFT method can help in a qualitative prediction of ILs before they are synthesized and characterized. However, this correlation was not observed for BMI.CF₃SO₃, for which the difference between DTF and the nonlinear susceptibility was the largest when compared to the result set, which could be due to a contrasting charge transfer. Moreover, an exact agreement was not expected because DFT analysis simulates only a single molecule and does not consider the entire vicinity or the orientational molecular dynamics responsible for the optical Kerr effect. The technique of polarization-resolved Z-scan measurements will now be introduced to discriminate between electronic and orientational nonlinear effects in these systems. Exceptionally, various thermo-optical coefficients to the ILs were determined in the same procedure, which extends the characterization of these materials. The thermodynamic properties of thermal characteristic time, thermal lens strength, thermal conductivity an diffusivity were here evaluated and presented.

Authorship statement

All persons who meet authorship criteria are listed as authors, and all authors certify that they have participated sufficiently in the work to take public responsibility for the content, including participation in the concept, design, analysis, writing, or revision of the manuscript. Furthermore, each author certifies that this material or similar material has not been and will not be submitted to or published in any other publication before its appearance in the *Journal of Molecular Liquids*.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

Vinícius Castro Ferreira and Letícia Zanchet thank the finance in part by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Letícia Guerreiro da Trindade thanks the finance in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001. Wesley Formentin Monteiro thanks the CNPq (PDJ process number 157931/2018-8). The authors would like to thank the Theoretical Chemistry Group (TCG/UFRGS) for providing computational resources and the Universidade Federal do Rio Grande do Sul (UFRGS).

References

- L. Liang, Q. Gan, P. Nancarrow, Composite ionic liquid and polymer membranes for gas separation at elevated temperatures, J. Membr. Sci. 450 (2014) 407–417, https:// doi.org/10.1016/j.memsci.2013.09.033.
- [2] A.G. Wallace, M.D. Symes, Water-splitting electrocatalysts synthesized using ionic liquids, Trends Chem. 1 (2019) 247–258, https://doi.org/10.1016/j.trechm.2019.03. 003.
- [3] Z. Lei, B. Chen, Y.M. Koo, D.R. Macfarlane, Introduction: Ionic Liquids, Chem. Rev. 117 (2017) 6633–6635, https://doi.org/10.1021/acs.chemrev.7b00246.
- [4] T.L. Greaves, C.J. Drummond, Protic ionic liquids: properties and applications, Chem. Rev. 108 (2008) 206–237, https://doi.org/10.1021/cr068040u.
- [5] F.I. López, J.M. Domínguez, A.D. Miranda, M. Trejo-Durán, E. Alvarado-Méndez, M.A. Vázquez, Synthesis of symmetric ionic liquids and their evaluation of nonlinear optical properties, Opt. Mater. (Amst). 96 (2019) 109276, https://doi.org/10.1016/j. optmat.2019.109276.
- [6] A.S. Aquino, M.O. Vieira, A.S.D. Ferreira, E.J. Cabrita, S. Einloft, M.O. de Souza, Hybrid ionic liquid-silica xerogels applied in CO₂ capture, Appl. Sci. 9 (2019)https://doi.org/ 10.3390/app9132614.
- [7] W.F. Monteiro, M.O. Vieira, E.F. Laschuk, P.R. Livotto, S.M.O. Einloft, M.O. De Souza, R.A. Ligabue, Experimental-theoretical study of the epoxide structures effect on the CO₂ conversion to cyclic carbonates catalyzed by hybrid titanate nanostructures, J. CO₂ Util. 37 (2020) 20–28, https://doi.org/10.1016/j.jcou.2019.11.024.
- [8] H.P. Steinrück, P. Wasserscheid, Ionic liquids in catalysis, Catal. Lett. 145 (2015) 380–397, https://doi.org/10.1007/s10562-014-1435-x.
- [9] L.G. da Trindade, L. Zanchet, A.B. Trench, J.C. Souza, M.H. Carvalho, A.J.A. de Oliveira, E.C. Pereira, T.M. Mazzo, E. Longo, Flower-like ZnO/ionic liquid composites: structure, morphology, and photocatalytic activity, Ionics (Kiel). 25 (2019) 3197–3210, https://doi.org/10.1007/s11581-018-2822-x.
- [10] M. Watanabe, M.L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K. Dokko, Application of ionic liquids to energy storage and conversion materials and devices, Chem. Rev. 117 (2017) 7190–7239, https://doi.org/10.1021/acs.chemrev.6b00504.
- [11] H. Hirayama, N. Tachikawa, K. Yoshii, M. Watanabe, Y. Katayama, lonic conductivity and viscosity of solvate ionic liquids composed of glymes and excess lithium bis (trifluoromethylsulfonyl)amide, Electrochemistry. 83 (2015) 824–827, https://doi. org/10.5796/electrochemistry.83.824.
- [12] R.C. da Silva, M. Heinen, G.A. Lorenzi, D.W. Lima, J.H. Lingner Moura, J.M. de Freitas, E.M.A. Martini, C.L. Petzhold, Carbon steel corrosion controlled by vegetable polyol phosphate, in medium containing chloride and glyoxal: influence of phosphate content and CO₂, Heliyon. 5 (2019), e01720, https://doi.org/10.1016/j.heliyon.2019. e01720.
- [13] V. Demétrio da Silva, Í.R. de Barros, D.K.S. da Conceição, K.N. de Almeida, H.S. Schrekker, S.C. Amico, M.M. Jacobi, Aramid pulp reinforced hydrogenated nitrile butadiene rubber composites with ionic liquid compatibilizers, J. Appl. Polym. Sci. 137 (2020) 1–7, https://doi.org/10.1002/app.48702.
- [14] B.G. Soares, Ionic liquid: a smart approach for developing conducting polymer composites: a review, J. Mol. Liq. 262 (2018) 8–18, https://doi.org/10.1016/j.molliq. 2018.04.049.
- [15] C.M.L. Schrekker, Y.C.A. Sokolovicz, M.G. Raucci, B.S. Selukar, J.S. Klitzke, W. Lopes, C.A.M. Leal, I.O.P. De Souza, G.B. Galland, J.H.Z. Dos Santos, R.S. Mauler, M. Kol, S. Dagorne, L. Ambrosio, M.L. Teixeira, J. Morais, R. Landers, A.M. Fuentefria, H.S. Schrekker, Multitask imidazolium salt additives for innovative poly(l-lactide) biomaterials: morphology control, Candida spp. biofilm inhibition, human mesenchymal stem cell biocompatibility, and skin tolerance, ACS Appl. Mater. Interfaces 8 (2016) 21163–21176, https://doi.org/10.1021/acsami.6b06005.
- [16] S.K. Singh, A.W. Savoy, Ionic liquids synthesis and applications: an overview, J. Mol. Liq. 297 (2020) 112038, https://doi.org/10.1016/j.molliq.2019.112038.

- [17] B.E.A. Saleh, M.C. Teich, Fundamentals of Photonics, https://www.crcpress.com/Fundamentals-of-Picoscience/Sattler/p/book/9781466505094#googlePreviewContainer 2019.
- [18] C. Rullière, Femtosecond Laser Pulses: Principles and Experiments, 2003https://doi. org/10.1007/b137908.
- [19] H. Lubatschowski, A. Heisterkamp, F. Will, J. Serbin, T. Bauer, C. Fallnich, H. Welling, W. Mueller, B. Schwab, A.I. Singh, W. Ertmer, Ultrafast laser pulses for medical applications, Commer. Biomed. Appl. Ultrafast Free. Lasers. 4633 (2002) 38, https://doi. org/10.1117/12.461386.
- [20] F. Zhao, C. Wang, J. Zhang, Y. Zeng, Femtosecond third-order optical nonlinearity of an azobenzene-containing ionic liquid crystalline polymer, Opt. Express 20 (2012) 26845, https://doi.org/10.1364/oe.20.026845.
- [21] C.E.A. Santos, M.A.R.C. Alencar, P. Migowski, J. Dupont, J.M. Hickmann, Anionic and cationic influence on the nonlocal nonlinear optical response of ionic liquids, Chem. Phys. 403 (2012) 33–36, https://doi.org/10.1016/j.chemphys.2012.05.001.
- [22] H. Shirota, A.M. Funston, J.F. Wishart, E.W. Castner, Ultrafast dynamics of pyrrolidinium cation ionic liquids, J. Chem. Phys. 122 (2005)https://doi.org/10. 1063/1.1893797.
- [23] G. Giraud, C.M. Gordon, I.R. Dunkin, K. Wynne, The effects of anion and cation substitution on the ultrafast solvent dynamics of ionic liquids: a time-resolved optical Kerr-effect spectroscopic study, J. Chem. Phys. 119 (2003) 464–477, https://doi. org/10.1063/1.1578056.
- [24] B.R. Hyun, S.V. Dzyuba, R.A. Bartsch, E.L. Quitevis, Intermolecular dynamics of room-temperature ionic liquids: femtosecond optical Kerr effect measurements on 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imides, J. Phys. Chem. A 106 (2002) 7579–7585, https://doi.org/10.1021/jp0141575.
- [25] M.A. Gelesky, A.P. Umpierre, G. Machado, R.R.B. Correia, W.C. Magno, J. Morais, G. Ebeling, J. Dupont, Laser-induced fragmentation of transition metal nanoparticles in ionic liquids, J. Am. Chem. Soc. 127 (2005) 4588–4589, https://doi.org/10.1021/ja042711t.
- [26] M. Trejo-Durán, E. Alvarado-Méndez, K.A. Barrera-Rivera, V.M. Castaño, Nonlinear optical phenomena in bi-ionic liquids, Optik (Stuttg). 130 (2017) 895–899, https://doi.org/10.1016/j.ijleo.2016.11.008.
- [27] R.F. Souza, M.A.R.C. Alencar, M.R. Meneghetti, J. Dupont, J.M. Hickmann, Nonlocal optical nonlinearity of ionic liquids, J. Phys. Condens. Matter 20 (2008)https://doi. org/10.1088/0953-8984/20/15/155102.
- [28] I. Severiano-Carrillo, E. Alvarado-Méndez, K.A. Barrera-Rivera, M.A. Vázquez, M. Ortiz-Gutierrez, M. Trejo-Durán, Studies of optical nonlinear properties of asymmetric ionic liquids, Opt. Mater. (Amst). 84 (2018) 166–171, https://doi.org/10.1016/j. optmat.2018.06.063.
- [29] N.F. Corrêa, C.E.A. Santos, D.R.B. Valadão, L.F. de Oliveira, J. Dupont, M.A.R.C. Alencar, J.M. Hickmann, Third-order nonlinear optical responses of colloidal Ag nanoparticles dispersed in BMIBF₄ ionic liquid, Opt. Mater. Exp. 6 (2016) 244, https://doi.org/10. 1364/ome.6.000244.
- [30] J.S. Wilkes, J.A. Levisky, R.A. Wilson, C.L. Hussey, Dialkylimidazolium chloroaluminate melts: a new class of room-temperature ionic liquids for electrochemistry, spectroscopy, and synthesis, Inorg. Chem. 21 (1982) 1263–1264, https://doi.org/10.1021/ic00133a078.
- [31] E. Cortés, A. Dondero, H. Aros, C. Carlesi, Síntesis del líquido iónico bmin⁺HSO 4 mediante una sola etapa, para aplicaciones en hidrometalurgia, Inf. Tecnol. 21 (2010) 67–76, https://doi.org/10.1612/inf.tecnol.4272bit.09.
- [32] M. Shamsipur, A.A.M. Beigi, M. Teymouri, S.M. Pourmortazavi, M. Irandoust, Physical and electrochemical properties of ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium trifluoromethanesulfonate and 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, J. Mol. Liq. 157 (2010) 43–50, https://doi.org/10.1016/j.molliq.2010.08.005.
- [33] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785–789, https://doi.org/10.1103/PhysRevB.37.785.
- [34] A.D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648–5652, https://doi.org/10.1063/1.464913.
- [35] A.-R. Allouche, Gabedit—a graphical user interface for computational chemistry softwares, J. Comput. Chem. 32 (2010) 174–182, https://doi.org/10.1002/jcc.
- [36] M. Sheik-Bahae, A.A. Said, T.H. Wei, D.J. Hagan, E.W. Van Stryland, Sensitive measurement of optical nonlinearities using a single beam, IEEE J. Quantum Electron. 26 (1990) 760–769, https://doi.org/10.1109/3.53394.
- [37] T. Xia, D.J. Hagan, E.W. Van Stryland, Eclipsing Z-scan measurement of $\lambda/10^4$ wave-front distortion, Opt. Lett. 19 (1994) 317–319.
- [38] A.S.L. Gomes, E.L. Filho, C.B. de Araújo, D. Rativa, R.E. de Araujo, Thermally managed eclipse Z-scan, Opt. Express 15 (2007) 1712, https://doi.org/10.1364/oe.15.001712.
- [39] M. Falconieri, G. Salvetti, Simultaneous measurement of pure-optical and thermooptical nonlinearities induced by high-repetition-rate, femtosecond laser pulses: application to CS₂, Appl. Phys. B Lasers Opt. 69 (1999) 133–136, https://doi.org/10. 1007/s003400050785.
- [40] A. Gnoli, L. Razzari, M. Righini, Z-scan measurements using high repetition rate lasers: how to manage thermal effects, Opt. Express 13 (2005) 7976, https://doi. org/10.1364/opex.13.007976.
- [41] S.A. Dharaskar, M.N. Varma, D.Z. Shende, C.K. Yoo, K.L. Wasewar, Synthesis, characterization and application of 1-butyl-3 methylimidazolium chloride as green material for extractive desulfurization of liquid fuel, Sci. World J. 2013 (2013) 1–9, https://doi.org/10.1155/2013/395274.
- [42] N.A.S.N. Zulkepeli, T. Winie, R.H.Y. Subban, Characterisation of polymer electrolytes based on high molecular weight PVC and BMIMCF₃SO₃, Key Eng. Mater. 705 (2016) 150–154, https://doi.org/10.4028/www.scientific.net/KEM.705.150.

- [43] Q. Zeng, J. Zhang, H. Cheng, L. Chen, Z. Qi, Corrosion properties of steel in 1-butyl-3methylimidazolium hydrogen sulfate ionic liquid systems for desulfurization application, RSC Adv. 7 (2017) 48526–48536, https://doi.org/10.1039/c7ra09137k.
- [44] J. Xu, Z. Feng, J. Zhang, Y. Wang, The study on fuel-cell performance by using alkylimidazole ionic liquid as electrolytes for fuel cell, IOP Conf. Ser. Earth Environ. Sci. 300 (2019), 052025, https://doi.org/10.1088/1755-1315/300/5/052025.
- [45] R. Ramasamy, Vibrational spectroscopic studies of imidazole, Armen. J. Phys. 8 (2015) 51–55.
- [46] L. Zanchet, L.G. da Trindade, D.W. Lima, W. Bariviera, F. Trombetta, M.O. de Souza, E.M.A. Martini, Cation influence of new imidazolium-based ionic liquids on hydrogen production from water electrolysis, Ionics (Kiel). 25 (2019) 1167–1176, https://doi.org/10.1007/s11581-018-2803-0.
- [47] M.C. Özdemir, B. Özgün, E. Aktan, 1-Aryl-3,5-dimethylpyrazolium based tunable protic ionic liquids (TPILs), J. Mol. Struct. 1180 (2019) 564–572, https://doi.org/10. 1016/j.molstruc.2018.12.027.
- [48] E. Barim, F. Akman, Synthesis, characterization and spectroscopic investigation of N-(2-acetylbenzofuran-3-yl)acrylamide monomer: molecular structure, HOMO-LUMO study, TD-DFT and MEP analysis, J. Mol. Struct. 1195 (2019) 506–513, https://doi.org/10.1016/j.molstruc.2019.06.015.
- [49] J.E. Castellanos-Águila, M.A. Olea-Amezcua, H. Hernández-Cocoletzi, M. Trejo-Durán, Tuning the nonlinear optical properties of the [alkyl-Py]⁺[NO₃]⁻ and [alkyl-MIM]⁺[NO₃]⁻ ionic liquids, J. Mol. Liq. 285 (2019) 803–810, https://doi.org/10. 1016/j.molliq.2019.04.075.
- [50] J.E. Castellanos Águila, M. Trejo-Durán, Theoretical study of the second-order nonlinear optical properties of ionic liquids, J. Mol. Liq. 269 (2018) 833–838, https:// doi.org/10.1016/j.molliq.2018.08.057.
- [51] A. Esme, S.G. Sagdinc, The vibrational studies and theoretical investigation of structure, electronic and non-linear optical properties of Sudan III [1-{[4-(phenylazo) phenyl]azo}-2-naphthalenol], J. Mol. Struct. 1048 (2013) 185–195, https://doi.org/ 10.1016/j.molstruc.2013.05.022.
- [52] G. Marin, J.A. Fernandes, J. Dupont, V.C. Ferreira, R.R.B. Correia, Nonlinear optical characterization of new ionic liquids by a noise reduced thermally managed EZ-Scan technique, SPIE Photonics Eur. 106841E (1–8) (2018)https://doi.org/10.1117/ 12.2305879.
- [53] R.W. Boyd, Nonlinear Optics, Third Edit368, 2007.
- [54] Q. Gong, Y. Sun, Z. Xia, Y.H. Zou, Z. Gu, X. Zhou, D. Qiang, Nonresonant third-order optical nonlinearity of all-carbon molecules C 60, J. Appl. Phys. 71 (1992) 3025–3026, https://doi.org/10.1063/1.351391.
- [55] S. Seki, S. Tsuzuki, K. Hayamizu, Y. Umebayashi, N. Serizawa, K. Takei, H. Miyashiro, Comprehensive refractive index property for room-temperature ionic liquids, J. Chem. Eng. Data 57 (2012) 2211–2216, https://doi.org/10.1021/je201289w.

- [56] Y. Arosa, C.D. Rodríguez Fernández, E. López Lago, A. Amigo, L.M. Varela, O. Cabeza, R. de la Fuente, Refractive index measurement of imidazolium based ionic liquids in the Vis-NIR, Opt. Mater. (Amst). 73 (2017) 647–657, https://doi.org/10.1016/j. optmat.2017.09.028.
- [57] H. Cang, J. Li, M.D. Fayer, Orientational dynamics of the ionic organic liquid 1-ethyl-3-methylimidazolium nitrate, J. Chem. Phys. 119 (2003) 13017–13023, https://doi. org/10.1063/1.1628668.
- [58] M.L. Miguez, E.C. Barbano, S.C. Zilio, L. Misoguti, Accurate measurement of nonlinear ellipse rotation using a phase-sensitive method, Opt. Express 22 (2014) 25530, https://doi.org/10.1364/oe.22.025530.
- [59] Q. Zhong, J.T. Fourkas, Optical kerr effect spectroscopy of simple liquids, J. Phys. Chem. B 112 (2008) 15529–15539, https://doi.org/10.1021/jp807730u.
- [60] M. Falconieri, Thermo-optical effects in Z-scan measurements using high-repetitionrate lasers, J. Opt. A Pure Appl. Opt. 1 (1999) 662–667, https://doi.org/10.1088/ 1464-4258/1/6/302.
- [61] S.M. Lima, J.A. Sampaio, T. Catunda, A.C. Bento, L.C.M. Miranda, M.L. Baesso, Modemismatched thermal lens spectrometry for thermo-optical properties measurement in optical glasses: a review, J. Non-Cryst. Solids 273 (2000) 215–227, https://doi.org/ 10.1016/S0022-3093(00)00169-1.
- [62] J. Shen, R.D. Lowe, R.D. Snook, A model for cw laser induced mode-mismatched dual-beam thermal lens spectrometry, Chem. Phys. 165 (1992) 385–396, https:// doi.org/10.1016/0301-0104(92)87053-C.
- [63] A.P. Fröba, M.H. Rausch, K. Krzeminski, D. Assenbaum, P. Wasserscheid, A. Leipertz, Thermal conductivity of ionic liquids: measurement and prediction, Int. J. Thermophys. 31 (2010) 2059–2077, https://doi.org/10.1007/s10765-010-0889-3.
- [64] J.A. Nóvoa-López, E. López Lago, M. Domínguez-Pérez, J. Troncoso, L.M. Varela, R. De La Fuente, O. Cabeza, H. Michinel, J.R. Rodríguez, Thermal refraction in ionic liquids induced by a train of femtosecond laser pulses, Opt. Laser Technol. 61 (2014) 1–7, https://doi.org/10.1016/j.optlastec.2014.01.017.
- [65] M. Trejo-Durán, E. Alvarado-Méndez, J.M. Estudillo-Ayala, et al., Nonlinear Opt. (2014) 179–201.
- [66] C. Frez, G.J. Diebold, C.D. Tran, S. Yu, Determination of thermal diffusivities, thermal conductivities, and sound speeds of room-temperature ionic liquids by the transient grating technique, J. Chem. Eng. Data 51 (2006) 1250–1255, https://doi.org/10. 1021/je0600092.
- [67] Y. Zhao, Y. Zhen, B.P. Jelle, T. Boström, Measurements of ionic liquids thermal conductivity and thermal diffusivity, J. Therm. Anal. Calorim. 128 (2017) 279–288, https://doi.org/10.1007/s10973-016-5881-0.