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Studies of optical nonlinear properties of asymmetric ionic liquids

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ABSTRACT

Nonlinear refraction and absorption properties to twelve ionic liquids were measured by the Z-scan technique. *k/dn/dT* value reference was determinate by using only one measure. An Influence of anion and cation to nonlinear optical properties was analysed. Cations with mayor length chain and aromatic systems presented better nonlinear optical properties that the alicyclic cations. [NO_3] anion presented the best contribution to these properties independently of cation used.

1. Introduction

As it is well known, the *Z*-scan technique is used to determine the nonlinear optical properties such as nonlinear refraction index and nonlinear absorption index, due to its simplicity and accuracy [1]. It has been used to characterize hybrid materials [2,3], liquid crystals [4], organic dyes such as Hibiscus sabdariffa [5,6], gold and silver nanoparticles [7,8], among others. With this technique, it is possible to obtain the sign and magnitude of the nonlinear refractive index (n_2) at far field and with closed aperture. Furthermore, the nonlinear absorption (β) is measured at near field with open aperture. The technique consists in displacing the sample along the optical axis (z direction) of a focused laser beam, usually with Gaussian distribution, and detecting the transmitted power at far field or at near field. Different mathematical models have been proposed to adjust the experimental *Z*-scan data where both, nonlinear refraction and nonlinear absorption, are presented simultaneously. The mathematical model for the characterization proposed by I. Severiano et al. [9] considered the nonlinear thick media as a photoinduced thin lens, where the focal length is represented by a constant (a_m) multiplied by high power beam radius ($\omega(z)^m$), where m represents the type of nonlinearity of the material. This modification allows us to have a better understanding of the nonlinear physical phenomena present in a thick material or liquids where the thermal effects are predominant. Furthermore, it is possible to obtain the nonlinear absorption and the nonlinear refraction with only one measurement at far field. In this work, we present the study of twelve ionic liquids using the *Z*-scan technique by Severiano's Model.

Ionic liquids (ILs) are organic salts in liquid state at environment temperature. The IL's has been described as molecules with organic and inorganic moieties, which their physicochemical characteristics can be determined as viscosity, melting point, density, acid and basic behaviour among others. Due to this versatility, its use and application has been increased in different areas of science. For example, the catalysis process [10,11], chemistry industry [12,13], carbon dioxide capture [14], among others. There are several papers about their physical properties [15,16] or chemical properties [17,18], and one of the most interesting applications in optoelectronics is their nonlinear optical properties (NLO). However, there are few papers [19–26] about these NLO properties where the reported values of nonlinear refractive index to some ILs are 10^{-9} cm^2/W order and 10^{-3} cm/W to nonlinear absorption coefficient. Santos [20,24] reports that using different derivatives of imidazolium ([$C_n$mim], n = 4,6,7,10) as cation, the [BF_4] anion presents a better thermal nonlinear response comparing to [Tf_2N] and [PF_6] in the infrared region, and he refers that the best is [C_4mim][BF_4]. In the ultraviolet region, the [Tf_2N] anion is analysed with the same cations and changes are reported in thermal contribution to NLO. Novoa-Lopez [21] study methyl-imidazolium, pyridinium cations families with [BF_4] and [Tf_2N] anions, they confirm that the cations have a slight influence in the thermal NLO compared to the influence of the anion.

In this work, the synthesis of twelve IL's and the influence of the cations and anions to the nonlinear optical properties are analysed. Only one measure was used to obtain the principal nonlinear optical parameters such as: β, n_2, $k/dn/dT$, and σ. Then, the most of nonlinear

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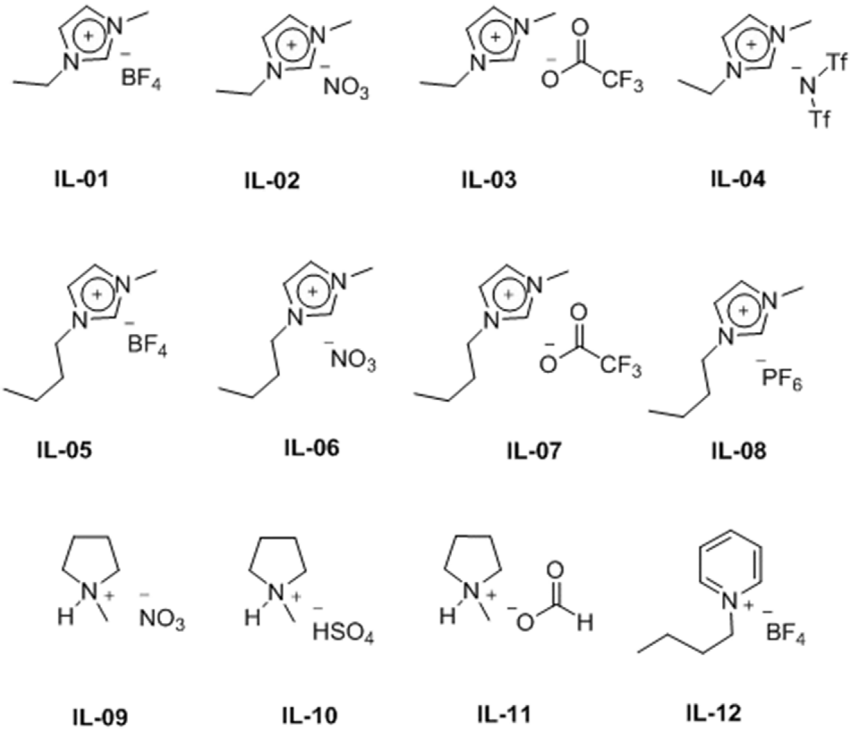

Scheme 1. Structure of twelve different ionic liquids.

absorption coefficients and nonlinear optical properties of IL with $[NO_3]^-$ anion have not been reported to our knowledge. We found that the best NLO are due to influence of $[NO_3]$ anion despite the cation used. Aromatic cation presents better nonlinear response that alicyclic cation, and it is confirmed that the length of chain in aromatic cation have influence on NLO.

2. Experimental

2.1. Synthesis of ionic liquids

The synthesis of ionic liquids was based on previous reports. $[EMIM]^+$ $[BF_4]^-$, and $[BMIM]^+$ $[BF_4]^-$ [27], $[BuPy]^+$ $[CF_3COO]^-$, and $[BuPy]^+$ $[BF_4]^-$ [28], $[EMIM]^+[NO_3]^-$, and $[BMIM]^+[NO_3]^-$ [29], $[EMIM]^+[Tf_2N]^-$, $[BuPy]^+[TF_2N]^-$, $[EMIM]^+[CF_3COO]^-$, and $[BMIM]^+[CF_3COO]^-$ [30], $[MePyrr]^+[HCOO]^-$$[MePyrr]^+[NO_3]^-$, and $[MePyrr]^+[HSO_4]^-$ [31] (Scheme 1)-The spectroscopy of this ILs was reported in Ref. [32].

2.1.1. Synthesis of *IL01*, *IL05* and *IL08*

Synthesis of $[EMIM]^+[BF_4]^-$(**IL01**). Tetrafluoroboric acid (22.34 mL, 0.171 mol, 48% solution in water) was slowly added to a stirred slurry of silver (I) oxide (19.83 g, 0.0855 mol) in 50 mL distilled water over a period of 10 min. To avoid silver (I) oxide photodegradation, the reaction of the mixture was fully covered with aluminium foil. After silver (I) oxide was completely consumed, a solution of 1-ethyl-3-methylimidazolium chloride (25.0 g, 0.171 mol) in 150 mL distilled water was added to the reaction mixture and stirred at room temperature for 2 h. The white precipitate of silver (I) chloride was filtered off, and the solvent was removed at 65 °C under vacuum. The resulting salt is a pale-yellow liquid. For the synthesis of $[BMIM]^+$ $[BF_4]^-$ (**IL05**) the same procedure was followed by using a 1-butyl-3-methylimidazolium chloride (29.90 g, 0.171 mol) solution instead of 1-ethyl-3-methylimidazolium chloride solution (25.0 g, 0.171 mol). $[EMIM]^+$ $[BF_4]^-$ Yield: 95%. $[BMIM]^+$ $[BF_4]^-$ Yield: 95%. ^{1}H NMR (acetone-d_6): δ 1.52 (t, 3H), 4.00 (s, 3H), 4.33 (q, 2H), 7.67 (t, 1.85), 7.74 (t, 1.94), 9.05 (s, 1H); ^{13}C NMR: δ 15.2, 36.0, 45.1, 122.2, 123.8, 135.9. IR (cm^{-1}): 3162, 3120 (ν C-H) aromatic stretching; 2992, 2954, 2886 (ν C-H) aliphatic stretching; 1634, 1575, 1467 (ν ring) symmetrical stretching; 1340 MeC-H asymmetrical, 1170 ring stretching; 1060, 850 and 756. $[BMIM]^+$ $[PF_6]^-$ (**IL08**). A 1-L, one-necked, round-bottomed flask was charged with 65.6 g (0.37 mol, 1 equiv) of 1-butyl-3-methylimidazolium chloride, and 69.3 g (0.37 mol, 1 equiv) of potassium hexafluorophosphate in 70 mL of distilled water. The reaction mixture was stirred at room temperature for 2 h affording a two-phase system. The organic phase was washed with 3 × 50 mL of water and dried under reduced pressure (0.1 mbar, 0.001 mm). Then 100 mL of dichloromethane and 35 g of anhydrous magnesium sulfate were added. After 1 h, the suspension was filtered, and the volatile material was removed under reduced pressure (0.1 bar, 0.1 mm) at 30 °C for 2 h to afford 86.4 g (0.29 mol, 81%) of 1-butyl-3-methylimidazolium hexafluorophosphate as a light yellow viscous liquid. $[BMIM]^+$ $[PF_6]^-$ Yield: 95%. [^{1}H NMR (acetone-d_6) δ: 0.96 (t, 3H), 1.37 (m, 2H), 1.93 (m, 2H), 4.05 (s, 3H), 4.36 (t, 2H), 7.68 (s, 1H), 7.74 (s, 1H), 8.95 (s, 1H); ^{13}C NMR (acetone-d_6) δ: 13.0, 19.3, 32.1, 36.0, 49.6, 122.7, 124.1, 137.0; IR cm^{-1}: 3171, 3125, 2965, 2939, 2878, 1571, 1167, 836.

2.1.2. Synthesis of *IL02* and *IL06*

Synthesis of $[EMIM]^+[NO_3]^-$ (**IL02**). An aqueous solution (30 mL) of silver nitrate (8.48 g, 0.05 mol) was added dropwise to a stirred ice-cooled aqueous solution (50 mL) of 1-ethyl-3-methylimidazolium chloride (2.14 g, 0.046 mol). The solution was slowly brought to room temperature and the white precipitate was removed by filtration. The filtrate was concentrated in vacuo. For the synthesis of $[BMIM]^+[NO3]^-$ (**IL06**) the same procedure using an aqueous solution was carried out (50 mL) of 1-butyl-3-methylimidazolium bromide instead side 1-ethyl-3-methylimidazolium chloride. $[EMIM]^+[NO_3]^-$Yield: 93%. $[BMIM]^+[NO_3]^-$Yield: 93%. ^{1}H NMR (D_2O): δ 1.4 (t, 3H), 3.8 (s, 3H), 4.1 (q, 2H), 7.3 (d, 2H), 8.5 (s, 1H); ^{13}C NMR: δ 14.01, 35.13, 44.33, 121.4, 122.9, and 132.2. IR (cm^{-1}): 3156, 3110 ($\nu_{C\text{-}H}$) aromatic stretching; 2990, 2946 ($\upsilon_{C\text{-}H}$) aliphatic stretching; 1644, 1575 (ν_{ring}) symmetrical stretching; 1360 MeC-H asymmetrical; 1170 ring stretching, symmetrical; 832 and 758.