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Imidazolium based ionic liquids as novel benign media for liquid-dye laser systems

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ABSTRACT

Room temperature ionic liquids (RTILs) have emerged as nature-friendly media suitable for various applications. In this work, Optical absorption, fluorescence behavior and fluorescence lifetime of three rigorously purified imidazolium ionic liquids, 1-butyl-3-methylimidazolium chloride (**BMIM Cl**), 1-Butyl-3-methylimidazolium tetrachloroaluminate (**BMIM $AlCl_4$**), 1-Butyl-3-methylimidazolium tetrafluoro-borate (**BMIM BF_4**) are studied in the neat condition and with two types of laser dyes (PM-597, Fluorescein). The absorption spectra for this dyes in all the ionic liquid solvents investigated looked very similar while the PL emission spectra differed markedly depending on the type of ionic liquid. In pure imidazolium ionic liquids, non-negligible absorption in the UV region with a long tail extending into the visible region is the main feature of the absorption. The emission behavior of neat ionic liquids is found to be strongly dependent on the excitation wavelength. That ion association gives rise to the long absorption tail and shifting fluorescence maximum. While the emission behavior of dye dissolved in ionic liquids independent on the excitation wavelength. Finally, we discuss the suitability of the imidazolium ionic liquids in optical studies taking into consideration their absorption and fluorescence behavior.

1. Introduction

Throughout the recent decades, RTILs as novel media have garnered widespread attention and curiosity from the academic and industrial research communities because of their unusual and favorable properties. Ionic liquids (ILs) consist of large, asymmetric organic cation and usually an inorganic anion. Due to the large size of their molecules and the nature of the chemical groups of the anions, the charges on the ions of these salts are usually diffuse [1]. RTILs based on imidazolium cation have attracted considerable attention in recent years because of the possibility that these substances can serve as environmentally benign media, in place of volatile organic compounds [2,3,4].The discovery of air and water stable ionic liquids based on substituted imidazolium cation in 1992 has given a boost to the research activities on the ionic liquids [5]. The sudden spurt in this activity can be understood when taking into consideration that these salts are low melting, thermally stable, highly conducting, less reactive, less sensitive towards moisture, possess a wide liquid range, and are able to dissolve a wide variety of inorganic and organic substances. However, the property of the imidazolium ionic liquids that is considered most attractive from the viewpoint of the environment is their negligible vapor pressure. The nonvolatility, nonflammability and nontoxic nature of the imidazolium ionic liquids has made them environmentally benign 'green' media for carrying out various chemical reactions [6,7,8].

RTILs are viscous media consisting entirely of ions. Viscosity of ILs is also controlled by number of hydrogen bonding between cation and anion, as well as Vander Waal interactions present in it. The higher number of hydrogen bonding present in Piperidinium based ILs than imidazolium based ILs [9]. Because of the complex nature of various interactions in these media, the solvent properties of the RTILs are very little understood. Different combinations of cations and anions give rise to different RTILs of the required properties. Due to different sizes of cations and anions of RTILs, mobility of cation is different from anion so we have observed biphasic dynamics compare to monophasic dynamics observed in some polar solvent.

In this paper, some photo-physical properties of laser dyes (PM 597, Fluorescein) dissolved in different ILs are presented. In addition some photo-physical properties of neat ILs. These include the absorption and emission spectra with different excitation wavelengths, fluorescence quantum yield, and fluorescence lifetime. In addition to transmission spectra of neat ILs.

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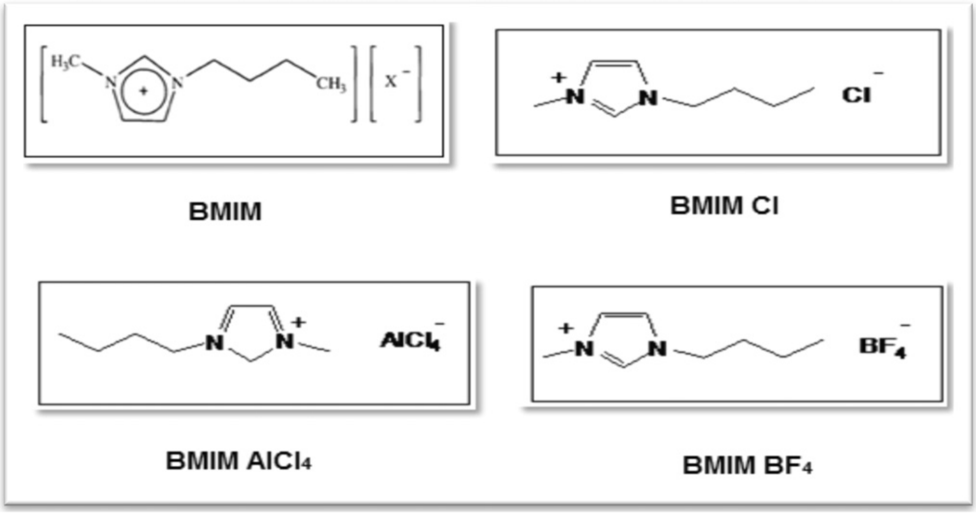

Fig. 1. molecular structure of ionic liquids.

2. Experiments

The structures of the used imidazolium salts are given in Fig. 1. RTILs were obtained from Aldrich. The chemical structures of the used dyes are also shown in Fig. 2. Fluorescein and pyrromethene dyes purchased from Aldrich chemical company (England) has been used without further purification.

Absorption and excitation-emission spectra were measured by Camspec M501 UV–Vis spectrophotometer and PF-6300 spectrofluorometer respectively. For the measurement of the absorption spectra of the samples were carried out in a quartz cuvette with a path length of 2 mm. The laser dyes (**PM-597, Fluorescein**) dissolved into three types of ILs (**BMIM Cl, BMIM** $\mathbf{AlCl_4}$**, BMIM** $\mathbf{BF_4}$). Liquid solutions of dyes were contained in 1 cm optical-path quartz cells that were transversely pumped by the second harmonic (532 nm) Nd:YAG laser (Continuum, PL7010) at a repetition rate of 10 Hz for PM-597 laser dye and blue diode laser (450 nm) for Fluorescein laser dye. The exciting pulses were directed towards the surface of the samples with a combination of concave lens ($f = -10$ cm) and a cylindrical quartz lens ($f = 10$ cm), the concave lens widened the spherical cross section of the pump beam to illuminate the complete 1 cm length of the dye sample. The radiation emitted from the sample perpendicular to the pumping beam was attenuated by neutral density filter and then focused on the spectrometer through optical fiber. The ASE spectrum was recorded using the Oplenic spectrophotometer which was connected to a computer unit for processing the spectrum. The pumping energy (input energy) was measured using a beam splitter (4%) and the Gentec power meter (Model QE50) detector head. In case of PM-597 the output energy was focused using a convex lens ($f = 15$ cm) onto the Gentec power meter head (model XLE4). The fluorescence lifetime (τ_f) were measured by using nitrogen laser (laser photonics LN1000) of pulse duration of 800 ps and wavelength 337.1 nm. The maximum energy per pulse was 2 mJ. Fluorescence signal registration with a fast phototube (Hamamatsu R1328U-03) through optical fiber. The fast phototube (+H.V) powered by power supply at 750 V and connected to the 300 MHz εZ-digital oscilloscope (DS-1530) attached to the computer processing unit for processing the spectrum.

3. Results and discussion

The absorption and transmission spectra of neat [BMIM Cl, BMIM $AlCl_4$, BMIM BF_4] are shown in Fig. 3. The transmission features of the two imidazolium ILs (BMIM Cl, BMIM BF_4) are very similar(81.7%, 86.8%) respectively. The transmittance of this solvents were very high compared to the other IL (BMIM $AlCl_4$) (9.5%) at 550 nm. The imidazolium ILs are usually regarded as transparent substances having no absorption in the UV (above 250 nm) and visible region [10,11,12, 13]. However, during the course of our studies we discovered that not all the imidazolium ionic liquids are optically transparent Fig. 3. The absorbance due to these ILs in a quartz cuvette of 2 mm path length varies

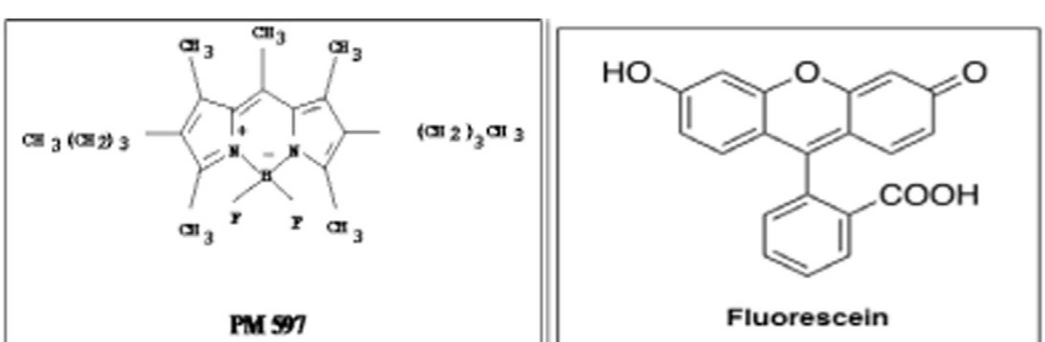

Fig. 2. Molecular structure of laser dyes.