



REICHARDT'S DYE AS SENSOR MATERIAL DETECTED OXYMETHYL GROUP IN THE CATION PART OF IMIDAZOLIUM IONIC LIQUID STRUCTURE

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ABSTRACT

A sensor that can detect methoxy group in cation part of imidazolium ionic liquid was developed based on Reichardt's solvatochromic dye. The Reichardt's dye incorporated into three ionic liquids: 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate, 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide, and 1-methyl-3-octylimidazolium tetrafluoroborate (without oxymethyl group in the structure), has been study by absorption and steady state fluorescence spectra. The striking solvatochromic effect was observed in ionic liquid includes oxymethyl group in the structure.

Keywords: reichardt's dye, oxymethyl group sensor, ionic liquids.

INTRODUCTION

The monitoring of oxygen molecules trapped in different new materials like ionic liquids is of great interest in the area of environmental protection and generally in so called 'green chemistry'. While the field of the fastest developing needs simple sensors quickly giving an answer the question - is oxymethyl group present in the cation part of imidazolium ionic liquid molecule?

Well known (Dickert, Geiger, Lieberzeit and Reutner, 2000) Reichardt's dye shows a strong solvatochromism. The electronic transition in Reichardt's dye, when changing the solvent from tetrahydrofuran to methanol, is associated with a hypsochromic solvatochromism of approximately 350 nm. Also the effects of dye absorption spectra in different environments have been study (Hubert, Fichou, Valat, Garnier and Villeret, 1995). Recently, a sensor that can detect polar gases was developed (Han, Inoue, Kurauchi and Ohga, 2007) based on Reichardt's dye solvatochromic effect.

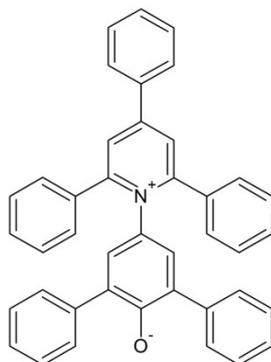


Figure-1. Reichardt's dye (R-dye) structure.

MATERIALS AND METHODS

Apparatus and reagents

Absorption and fluorescence spectra were measured using UV-VIS Lambda 20 Perkin-Elmer Spectrophotometer and LS-55 Perkin-Elmer fluorometer, respectively.

Reichardt's dye, 1-methyl-3-octylimidazolium tetrafluoroborate was purchased from the Sigma - Aldrich but 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate, 1-methyl-3-hexyloxymethylimidazolium bis(trifluoro-methylsulfonyl) imide were synthesized according to Pernak, Czepukowicz and Pozniak, 2001.

Preparation of 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide:

An anhydrous solution of 0.1 mol 1-methylimidazole in acetonitrile was added to appropriate 0.1 mol of chloromethylhexyl- ether. The reaction was carried out for 1 h and the solvent was evaporated in vacuum. Products were purified by extraction with hexane at 60 °C. The final products were hygroscopic compounds 1-methyl-3-hexyloxymethylimidazolium chloride with yield 89.3 %. To 0.09 mol of 1-methyl-3-hexyloxymethylimidazolium chloride dissolved in 50 cm³ of methanol, 0.1 mole of lithium bis(trifluoromethylsulfonyl)imide was added. The reaction was completed by heating at 80 °C and stirring for 24 h. The product was washed 5 times by 30 cm³ of distilled water. The product was a colorless liquid with the yield of 95%.

Preparation of 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate:

Preparation of 1-methyl-3-octyloxymethylimidazolium chloride was the same like preparation of 1-methyl-3-hexyloxymethyl chloride except adding chloromethyloctyl- ether instead of chloromethylhexyl- ether. To 0.09 mol of 1-methyl-3-octyloxymethylimidazolium chloride dissolved in 50 cm³



of methanol 0.1 mole of sodium tetrafluoroborate was added. The reaction was completed by heating at 50 °C and stirring for 24 h. After removing the solvent the product was dissolved in anhydrous acetone in order to remove the NaCl and excess of sodium tetrafluoroborate. The product was a colorless liquid with the yield of 91 %.

RESULTS AND DISCUSSIONS

In recent years has been a great deal of interest in the development of sensors selectively responding to particular molecules. We applied Reichardt's dye as a detector of oxymethyl group in cation part of imidazolium ionic liquid structure (see Figure-2).

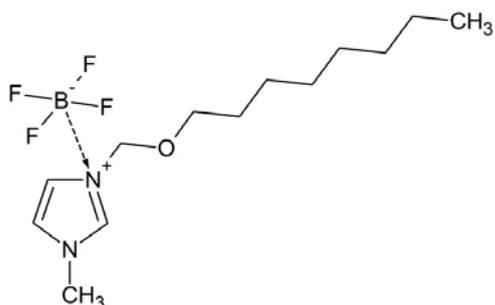


Figure-2a. 1-Methyl-3-octyloxymethylimidazolium tetrafluoroborate structure.

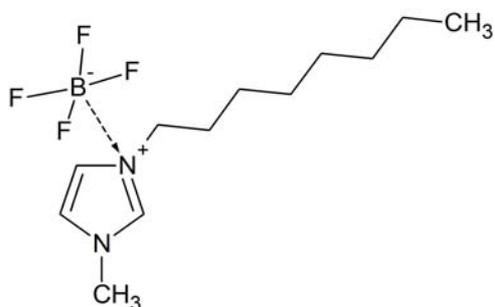


Figure-2b. 1-Methyl-3-octylimidazolium tetrafluoroborate structure.

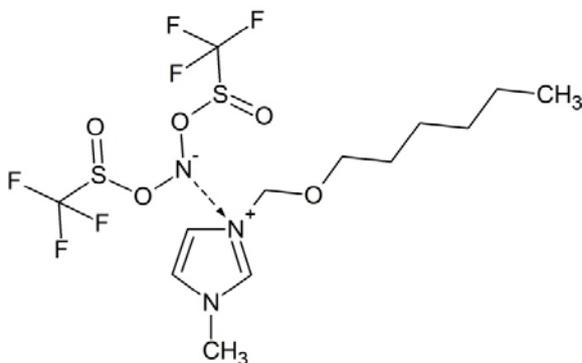


Figure-2c. 1-Methyl-3-hexyloxymethylimidazolium structure.

In the present study, the solvatochromic and/or environment-sensitive Reichardt's dye incorporated into

ionic liquids: 1-Methyl-3-octyloxymethyl-imidazolium tetrafluoroborate, 1-Methyl-3-hexyloxymethyl-imidazolium bis(trifluoro-methylsulfonyl) imide with and without 1-Methyl-3-octyl-imidazolium tetrafluoroborate oxygen molecules has been investigated showing response for oxygen in investigated structures.

In Figure-3 one can see absorption spectra of three ionic liquids: 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate, 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl) imide and 1-methyl-3-octyl-imidazolium tetrafluoroborate. Two of them: 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate and 1-methyl-3-octylimidazolium tetrafluoroborate are the same except that in the first structure an oxymethyl group is present.

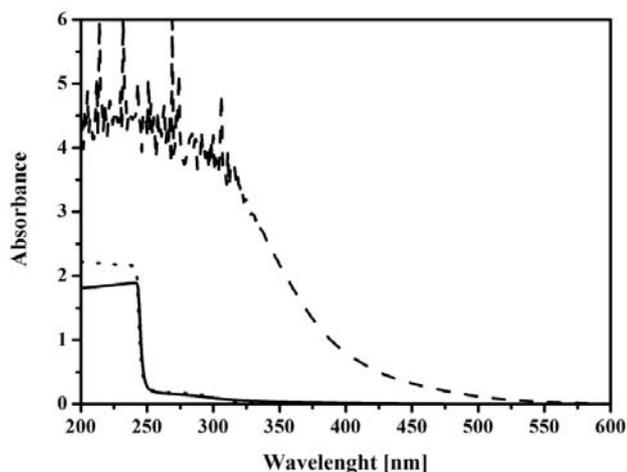


Figure-3. Absorption spectra of ionic liquids: 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate (—), 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide (•••) and 1-methyl-3-octylimidazolium tetrafluoroborate (---).

The results of fluorescence measurements of ionic liquids: 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate, 1-methyl-3-hexyloxymethylimidazolium bis(trifluoro-methylsulfonyl)imide and 1-methyl-3-octylimidazolium tetrafluoroborate are shown in Figure-4.

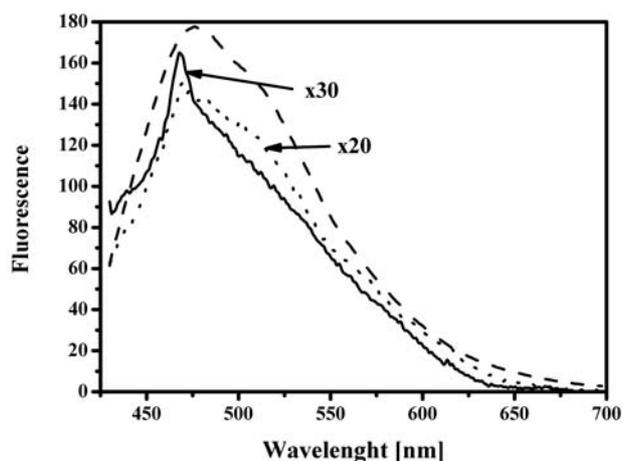


Figure-4. Fluorescence spectra of ionic liquids: 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate (—), 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide (•••) and 1-methyl-3-octylimidazolium tetrafluoroborate (— —) measured in quartz Suprasil micro cell; excitation at 413 nm.

Recently (Bialek-Bylka, Jazurek, Pawlak, Skrzypczak and Koyama, 2007; Bialek-Bylka, Kakitani, Li, Koyama, Kuki, Yamano and Nagae, 2008) found unique fluorescence properties of β -carotene in ionic liquids and mixture of ionic liquids with DMF. Since, Reichardt's dye is almost not fluorescing, the fluorescence measurement of this dye in ionic liquids was impossible, especially that in order to get ionic liquid fluorescence spectra without inner fluorescence filter effect one has to use special quartz Suprasil micro cell.

Up to date in the field of ionic liquids most of the Reichardt's dye research concentrates on polarity determination. It is well known that the Reichardt's dye is a solvatochromic molecule which absorbed wavelength caused displacement when the polarity of the environment is changed. Our data (see Figure-5) indicating normal

behavior of Reichardt's dye in classical solvents like: DMF (dimethylformamide) and methanol and ionic liquid without oxygen in the structure. But ionic liquids: 1-methyl-3-octyloxymethylimidazolium tetrafluoroborate and 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide with oxymethyl group in their structure did not show any solvatochromic effect. It means that Reichardt's dye is sensitive to the oxymethyl group in the structure of cationic part of imidazolium ionic liquids and can be used as sensor indicating this group.

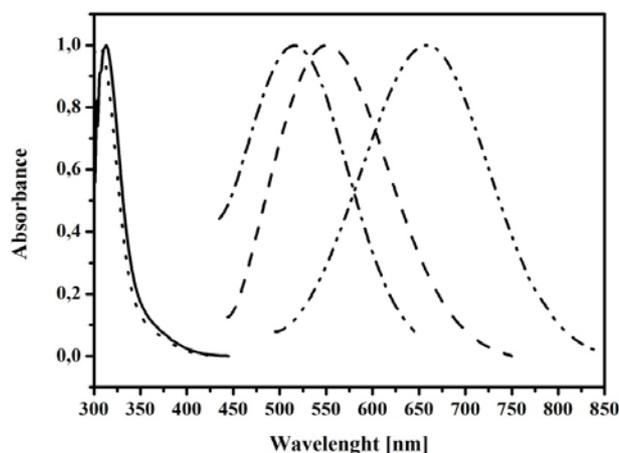


Figure-5. Normalized (at absorption maxima) absorption spectra of Reichardt's dye in the solvents of different polarity: methanol (—•—) and DMF (—••—) and ionic liquids with oxygen in their structure: 1-methyl-3-octyloxymethyl-imidazolium tetrafluoroborate (—), 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide (•••) and in ionic liquid without oxygen: 1-methyl-3-octylimidazolium tetrafluoroborate (— —).

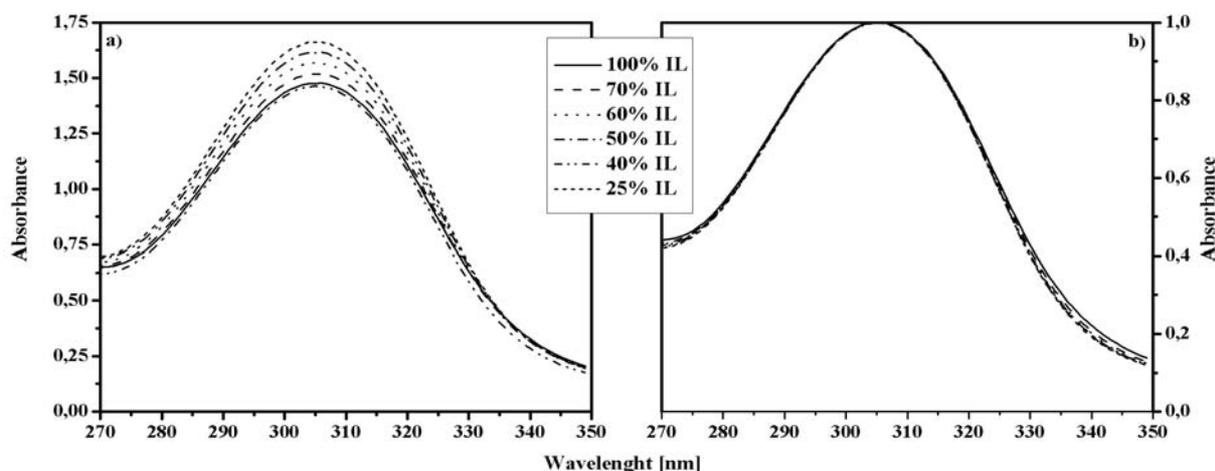


Figure-6. a) Reichardt's dye absorption spectra in the mixture of methanol and different percentage of ionic liquid: 1-methyl-3-hexyloxymethylimidazolium bis(trifluoromethylsulfonyl)imide (dye concentration $5 \cdot 10^{-4}$ M);
b) normalized at absorption maxima.



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Reichardt's dye oxygen sensor in ionic liquid is stable and effect is not reversible after adding classical solvents like methanol in the concentration range between 70 and 25 %.

ACKNOWLEDGEMENT

Authors thank project: BW-62-199/09

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