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Polymeric chain dependent anomalous solvatochromism of ionic liquid + poly(ethylene glycol) mixtures

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ABSTRACT

To alter the physicochemical properties of ILs with green cosolvents, molecular level understanding of the resultant mixtures is hotbed of the current research. In the present study, changes in the physicochemical properties of the IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([bmim][Tf_2N]) on the addition of different polyethylene glycols (PEGs) (average MW 200, 400, 600, and 1500) by means of solvatochromic probes are investigated. The addition of the PEGs to IL [bmim][Tf_2N] changes the physicochemical properties of the solvent mixtures in unusual and favorable fashion. The response of the solvatochromic probes Reichardt dye 33 and Nile Red hints about the "hyperpolarity" of the IL + PEG mixtures which is rare in the literature. The Kamlet–Taft parameters, hydrogen bond donor ability (HBD) (α), hydrogen bond acceptor ability (HBA) (β), and dipolarity/polarizability (π^*) display nonideality, and show strong and unusual "hyperpolarity" behavior on the addition of PEGs to [bmim][Tf_2N]. A solvent–solvent along with solute–solvent interaction hypothesis is proposed to explain the "hyperpolarity" of the mixtures. Further, the solvation models are used to delineate the solute–solvent/solvent–solvent interactions present in the binary mixtures. Combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) equation was demonstrated to predict the solvatochromic parameters satisfactorily.

1. Introduction

Over the past few decades, ionic liquids (ILs) have become solvents of choice for several chemical and biochemical applications because of their potentially green nature and unique physicochemical properties [1–6]. Generally, ILs are made up of bulky organic cations and inorganic anions, remain in liquid state at room temperature, and offer several favorable physiochemical properties in contrast to molecular organic solvents [7]. IL_s are interesting because of the fact that they show variable physicochemical properties depending upon the nature of the cations and anions, and hence are called tunable solvents. ILs have been used as solvents as well as catalysts for various organic, inorganic and organometallic reactions [8–10]. They have also demonstrated their importance in several analytical fields, such as extraction, separation of metal ions, electroanalysis, as stationary phase in GC and HPLC, and in sensor technology, etc [11–13]. ILs have also shown their potential in changing the behavior of dyes and probes [14–20]. Moreover, the biochemical and biotechnological applications of ILs are emerging every day [21–25]

Tuning the physicochemical properties of ILs with green cosolvents is an important field of current research, because addition of a cosolvent may suitably alter the solvent features of an IL for a specified purpose, and it is also helpful to enhance the overall utility of ILs in many chemical and technological fields [26]. Towards this end, a number of researchers have begun to focus on hybrid systems, and it is well documented that several green polymeric solvents (e.g. PEG, PPG) tune the physicochemical properties of ILs in anomalous and interesting fashion [27,28]. IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][Tf_2N], used here, is hydrophobic in nature, has limited solubility in water (~2.0 wt%) and in several organic solvents (e.g. hexane, toluene, ethyl acetate, butyl acetate, and diethyl ether, etc.) [29]. To expand the utility of this IL it will be useful to tune the physicochemical properties of [bmim][Tf_2N] with cosolvents (preferably with the green solvents) in favorable manner. In the present study, we utilize polyethylene glycols (PEGs) to tune the physicochemical properties of IL [bmim][Tf_2N]. It is interesting to mention here that mixing of the two solvents will offer a new potentially green hybrid media, and the physicochemical properties of the mixture can be tuned by altering the polymeric chain of PEGs.

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