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Solvatochromic absorbance probe behavior within 1-butyl-3-methylimidazolium hexafluorophosphate + propylene carbonate: Preferential solvation or solvent–solvent interaction?

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ABSTRACT

Physicochemical properties of ionic liquids (ILs) can be favorably modified by addition of appropriate cosolvents. Solvatochromic absorbance probes are used to assess physicochemical properties of the mixture of a common IL 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and propylene carbonate. Parameter E_T^N obtained from electronic absorbance of Reichardt's betaine dye within the mixture is observed to be higher than that predicted from ideal additive behavior. Absorbance from *N*,*N*-diethyl-4-nitroaniline and 4-nitroaniline in concert with absorbance from Reichardt's dye is used to obtain dipolarity/polarizability (π^*), hydrogen-bond donating (HBD) acidity (α), and hydrogen-bond accepting (HBA) basicity (β) of the mixture. While π^* and α of the mixture are observed to be higher than those expected from ideal additive behavior, β is observed to be lower. Solvatochromic absorbance probe behavior suggests solute-specific preferential solvation; FTIR absorbance of the mixture implies negligible specific solvent–solvent interaction(s) within the mixture. Combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) equation is demonstrated to predict the solvatochromic parameters satisfactorily.

1. Introduction

During the last decade or so room temperature ionic liquids (ILs) as potential environmentally friendly solvents have gathered widespread interest and curiosity from the scientific and engineering community alike. The number of research publications on investigations of ILs for properties, analysis, and applications has increased many-fold [1]. Almost every named synthesis and many more organic/inorganic/organometallic reactions have been reported in ILs [2,3]. Novel analytical applications of ILs are emerging everyday. Consequently, exploring the potential of ILs as solvent or one of the solution components for applications in chemical engineering is becoming a topic of increasing interest. In this regard, effective and in some cases unique utilization of ILs as solvents has been demonstrated in a variety of techniques in electroanalysis, separation, spectrometry, and sensing [1,4–10].

Though not reported explicitly, certain drawbacks have also emerged from the aforementioned detailed investigations of ILs. Perhaps, the most striking and crucial is the *limited* solubility of a fairly large number of common solutes in many popular ILs [11]. Further, important physicochemical properties of many ILs are either not favorable or may not be desirably modulated by changing external conditions such as temperature and pressure. Among the approaches to enhance solute solubility within ILs and to modify physicochemical properties of ILs in desirable fashion, addition of cosolvent(s) or mixing two or more ILs appears both simple and effective [12–18]. Towards this end, we have previously reported our investigations on the effects of added water [12,13], ethanol [14], aqueous-ethanol [15], poly(ethylene glycol)s [19], and other ILs [16] on a common and popular IL 1-butyl-3-methylimidazolioum hexafluorophosphate ([bmim][PF_6]).

Limited miscibility of many solvents or solvent systems in IL [bmim][PF_6] restricts the possibility of property modulation of this IL by addition of cosolvents. We have found that a cosolvent of significant importance in chemical engineering, propylene carbonate, is completely miscible with [bmim][PF_6]. In addition to its excellent solvation properties, propylene carbonate has valuable physical properties such as low viscosity (2.5 mPa s at 25 °C) [20], comparatively higher static dielectric constant (~65.0), lower solubility in water [21], stability at ordinary storage conditions, higher boiling point (~242 °C), very low freezing point (~−49 °C), and moderate density (~1.2 g/mL at 25 °C) [22], among others. It is essentially odorless, anhydrous, non-corrosive, non-toxic, and biodegradable. Propylene carbonate is used as a polar, aprotic solvent in many chemical engineering applications; it is frequently used as a high-permittivity component of electrolytes in lithium batteries, usually

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together with a low-viscosity solvent (e.g., dimethoxyethane). It may also be found in various adhesives, paint strippers, and in some cosmetics besides being used as plasticizer. It is widely used as a solvent for treating de-carbonation as well as for solubilizing polymers in the macromolecule industry.

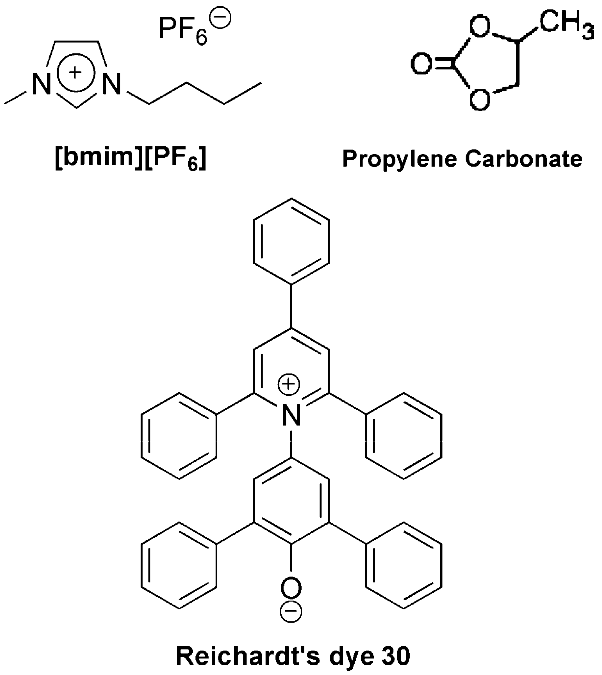
Due to its properties and applications, it is logical to use propylene carbonate as cosolvent with IL [bmim][PF$_6$] that may form a solvent system with superior properties. Interestingly, neat propylene carbonate shows negligible hydrogen-bond donating (HBD) acidity, hydrogen-bond accepting (HBA) basicity and dipolarity/polarizability of neat propylene carbonate are significant [23–27]. However, it is recently shown [28], by using temperature-dependent ^{19}F chemical shifts, that propylene carbonate can act both as Lewis acid (interacting with PF$_6^-$ anion) and Lewis base (interacting with bmim$^+$ cation) with IL [bmim][PF$_6$]. It is also demonstrated that a 20:80-mol% mixture of [bmim][PF$_6$]:propylene carbonate shows an almost six times increased ionic conductivity (1.50 and 9.37 mS cm^{-1} for neat [bmim][PF$_6$] and the mixture, respectively), providing a much favorable milieu for different reactions to occur [29]. Another aspect at the same mixture composition worth mentioning is that activation energy of neat [bmim][PF$_6$] is two times that of the mixture (37.9 and 18 kJ mol^{-1}, respectively) [29].

In order to obtain information on structural and physicochemical properties of [bmim][PF$_6$] + propylene carbonate, we have monitored the behavior of judiciously selected solvatochromic absorbance probes within this mixture [30]. The most important among the several fold motivation to investigate this system is to explore the presence of solute–solvent and/or solvent–solvent interactions within this 'hybrid' system. Depending on the solute–solvent interaction(s), solubilizing media may exert a profound effect on the electronic transition. Many of such interactions, e.g., dipolarity/polarizability, HBD acidity and HBA basicity, are readily manifested through molecular absorbance spectra of a variety of solvatochromic probes [31]. Further, specific solute–solvent interaction(s) may result in preferential solvation of the solute by one of the components in the solution [32]. Alternatively, solvent–solvent interactions may manifest themselves via the absorbance probe response. In this paper, we present behavior of a variety of molecular absorbance probes dissolved in [bmim][PF$_6$] + propylene carbonate mixture. On the basis of these probe responses, using empirical relationships established in the literature, dipolarity/polarizability (π^*), HBD acidity (α), and HBA basicity (β) of [bmim][PF$_6$] + propylene carbonate are calculated. A proposition to whether the preferential solvation (i.e., specific solute–solvent interaction) or the solvent–solvent interaction is the reason for the deviation from ideal additive behavior of the probes is also put forth.

2. Materials and methods

2.1. Materials

2,6-Diphenyl-4-(2,4,6-triphenylpyridinium-1-yl)phenolate (Reichardt's dye 30, Scheme 1) was purchased from Fluka (≥99% by HPLC) and were recrystallized several times before use. 4-Nitroaniline (≥90%) and *N*,*N*-diethyl-4-nitroaniline were purchased from Spectrochem Co. Ltd. and Frinton Laboratories, respectively, and recrystallized multiple times before use. IL [bmim][PF$_6$] (Scheme 1) was purchased from Merck (ultra-pure, halide content <10 ppm, water content <10 ppm) and stored under argon. Water contents of [bmim][PF$_6$] were checked using a Karl–Fisher titrator prior to every experiment and the IL was only used if the water content was <10 ppm. Otherwise [bmim][PF$_6$] were dried under vacuum at ~70 °C until the concentration of the water reached <10 ppm. Propylene carbonate (purity >99.7%) (Scheme 1) was purchased from Sigma–Aldrich and was used as received.



Scheme 1.

2.2. Method

All probe stock solutions were prepared in ethanol and stored in ambered glass vials at 4 ± 1 °C. Required amount of probes were weighed using Mettler Toledo AB104-S balance with a precision of ±0.1 mg. Appropriate amount of the probe solution from the stock was transferred to the quartz cuvette and ethanol was evaporated using a gentle stream of high-purity nitrogen gas. [bmim][PF$_6$] + propylene carbonate solutions of different compositions were prepared by mass and added to the cuvette to achieve desired probe concentration. This system was allowed to equilibrate to ambient conditions before any data acquisition. A Perkin-Elmer Lambdabio 20 double-beam spectrophotometer with variable band width was used for acquisition of the UV–vis molecular absorbance data. All the data were acquired using 1-cm^2 path length quartz cuvettes. FTIR data were acquired on a Nicolet Protège 460 E.S.P. double-beam spectrophotometer using CaF$_2$ windows. Spectral response from appropriate blank was subtracted before any data analysis for all spectroscopic measurements. All the measurements were performed three separate times starting from sample preparation and taken in triplicate every time before averaging.

3. Results and discussion

3.1. Behavior of Reichardt's dye and E_T^N values

2,6-Diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (Reichardt's dye 30) exhibits an unusually high-solvatochromic absorbance band shift [33–35]. The lowest energy intramolecular charge-transfer absorption band of the Reichardt's dye is hypsochromically shifted by *ca.* 357 nm on going from relatively non-polar diphenyl ether ($\lambda_{\max}$ ~ 810 nm) to water ($\lambda_{\max}$ ~ 453 nm). There is a considerable charge transfer from the phenolate to the pyridinium part of the zwitterionic molecule (see structure in Scheme 1). Because of its zwitterionic nature,