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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.

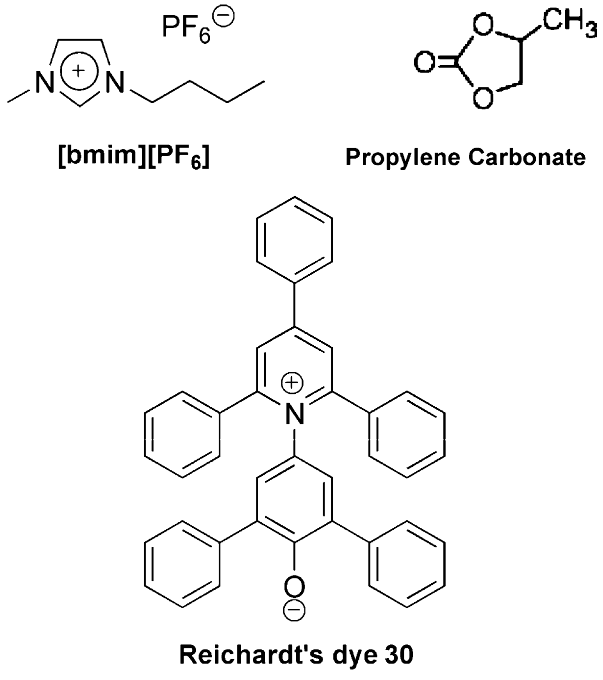
Due to its properties and applications, it is logical to use propylene carbonate as cosolvent with IL [bmim][PF_6] that may form a solvent system with superior properties. Interestingly, neat propylene carbonate shows negligible hydrogen-bond donating (HBD) acidity, hydrogen-bond accepting (HBA) basicity 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 (λ_{max} ~ 810 nm) to water (λ_{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,

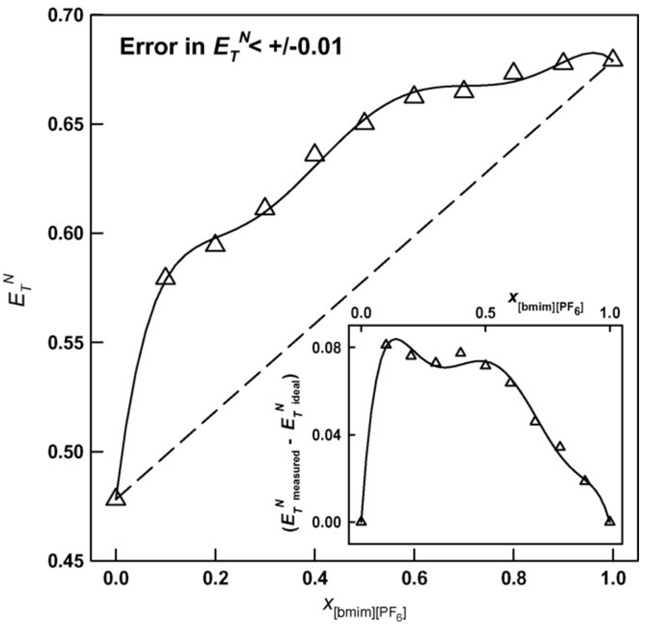


Fig. 1. Variation in E_T^N with $x_{[bmim][PF_6]}$ within [bmim][PF$_6$] + propylene carbonate at ambient conditions. Dashed line represents ideal additive E_T^N, while solid curve shows fit according to Redlich–Kister equation (Eq. (8)) with parameters reported in Table 1. The deviation from ideal additive behavior is shown in inset.

solvatochromic probe behavior of Reichardt's dye is strongly affected by the hydrogen-bond donating acidity of the solvent; hydrogen-bond donating solvents stabilize the ground state more than the excited state [36]. Reichardt's dye is one of the most widely used probe of its kind; the empirical scale of solvent "polarity", $E_T(30)$, is defined as the molar transition energy of the dye in kcal mol^{-1} at room temperature and normal pressure according to the expression:

$$E_T(30) = \frac{28591.5}{\lambda_{\max}\ (\text{nm})} \tag{1}$$

Absorbance spectra of Reichardt's dye are collected in [bmim][PF$_6$] + propylene carbonate mixtures in the entire composition range, the corresponding $E_T(30)$ are converted into E_T^N using the following equation [37]:

$$E_T^N = \frac{E_T(30)_{\text{solvent}} - E_T(30)_{\text{TMS}}}{E_T(30)_{\text{water}} - E_T(30)_{\text{TMS}}} \tag{2}$$

Here, TMS stands for tetramethylsilane. From $E_T(30)_{\text{water}} = 63.1$ kcal mol^{-1} and $E_T(30)_{\text{TMS}} = 30.7$ kcal mol^{-1}, we obtain

$$E_T^N = \frac{E_T(30)_{\text{solvent}} - 30.7}{32.4} \tag{3}$$

E_T^N is easier to conceive as it is dimensionless and varies between 0 for TMS (extreme non-polar) and 1 for water (extreme polar). E_T^N in [bmim][PF$_6$] + propylene carbonate is plotted in Fig. 1. Our neat [bmim][PF$_6$] and propylene carbonate E_T^N are in agreement with those reported by many researchers earlier [1–10,12,14–18,36,38–46]. It is clear that in neat E_T^N [bmim][PF$_6$] is significantly higher than that in neat propylene carbonate indicating higher dipolarity/polarizability and/or hydrogen-bond donating acidity of [bmim][PF$_6$] relative to that of propylene carbonate. One would conceive that static dielectric constant of propylene carbonate being fairly high (~65.0), a higher in [bmim][PF$_6$] relative to that in E_T^N propylene carbonate may be a manifestation of the lack of HBD acidity of the later. Upon addition of 0.1 mole fraction [bmim][PF$_6$] to propylene carbonate, the E_T^N increases dramatically either due to the preferential solvation of Reichardt's dye by [bmim][PF$_6$] resulting in the introduction of HBD capability or as a result of solvent–solvent interactions between [bmim][PF$_6$] and propylene carbonate forming a more dipolar species in the solution resulting in enhanced dipolarity of the cybotactic region around the probe. As we put forth an effort to pin-point possible reason for this outcome, this exciting characteristic in our opinion will impart added importance and benefits to the [bmim][PF$_6$] + propylene carbonate system clearly increasing its future potential as solvent milieu.

3.2. *Empirical Kamlet–Taft parameters*

The proposition that addition of *small* amounts of [bmim][PF$_6$] to propylene carbonate may enhance the HBD acidity of the mixture to a significant degree can be easily tested by a separate assessment of empirical Kamlet–Taft solvatochromic indicators of solvent dipolarity/polarizability (π^*), HBD acidity (α), and HBA basicity (β) [26]. The π^* parameters are estimated from the absorption maximum (ν_{DENA}, in kK) of *N*,*N*-diethyl-4-nitroaniline (DENA), a non-hydrogen-bond donor solute, using:

$$\pi^* = 8.649 - 0.314\nu_{\text{DENA}} \tag{4}$$

α parameters were in turn calculated from $E_T(30)$ and π^* values:

$$\alpha = \frac{[E_T(30) - 14.6(\pi^* - 0.23\delta) - 30.31]}{16.5}; \quad \delta = \chi_{[bmim][PF_6]} \tag{5}$$

Finally, β values are determined from the enhanced solvatochromic shift of 4-nitroaniline (NA) relative to its homomorph *N*,*N*-diethyl-4-nitroaniline,$-\Delta\nu(\text{DENA} - \text{NA})$/kK:

$$\beta = -0.357\nu_{\text{NA}} - 1.176\pi^* + 11.12 \tag{6}$$

Experimentally obtained π^* are presented in Fig. 2. It is interesting to note that while the static dielectric constant of [bmim][PF$_6$] ($\varepsilon \sim 11.4$) [47] is significantly lower than that of propylene carbonate ($\varepsilon \sim 65.0$) [21], π^* of neat [bmim][PF$_6$] is observed to be higher than that of propylene carbonate, and as [bmim][PF$_6$] is added to propylene carbonate, the π^* increases drastically. To our convenience though, the trend of π^* within [bmim][PF$_6$] + propylene carbonate mixture has stark resemblance to that of E_T^N within the same

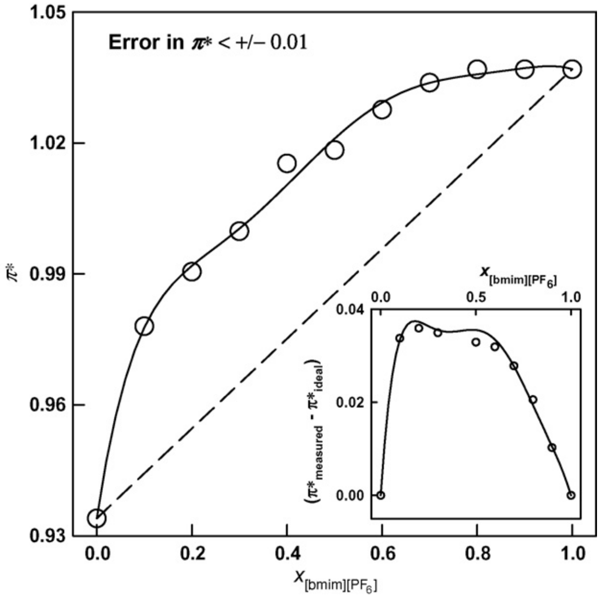


Fig. 2. Dipolarity/polarizability (π^*) *versus* $x_{[bmim][PF_6]}$ within [bmim][PF$_6$] + propylene carbonate at ambient conditions. Dashed line represents ideal additive π^*, while solid curve shows fit according to Redlich–Kister equation (Eq. (8)) with parameters reported in Table 1. The deviation from ideal additive behavior is shown in inset.

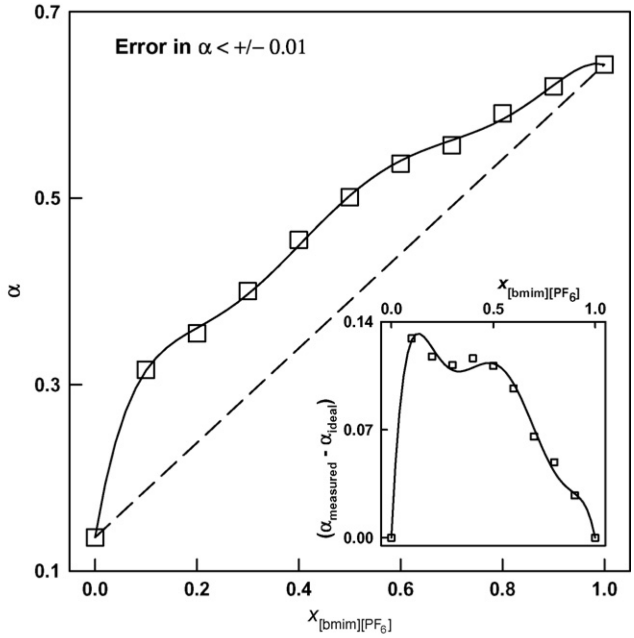


Fig. 3. Hydrogen-bond donating (HBD) acidity (α) *versus* $x_{\text{[bmim][PF}_6\text{]}}$ within [bmim][PF$_6$] + propylene carbonate at ambient conditions. Dashed line represents ideal additive α, while solid curve shows fit according to Redlich–Kister equation (Eq. (8)) with parameters reported in Table 1. The deviation from ideal additive behavior is shown in inset.

mixture. As proposed in the previous section, the HBD acidity may not be the only contributor to unusually enhanced E_T^N, the dipolarity/polarizability obtained from an independent probe, DENA, also increases dramatically upon addition of [bmim][PF$_6$] to propylene carbonate. An assessment of HBD acidity (α) using Eqs. (1), (4) and (5) indicates the trend in α within [bmim][PF$_6$] + propylene carbonate to be almost identical to the trends in E_T^N and π^* as [bmim][PF$_6$] is added to propylene carbonate (please refer to Fig. 3). While propylene carbonate has no functionality which may give rise to HBD acidity, the well-established HBD acidity of 1-alkyl-3-methylimidazolium ILs stems from the ring hydrogens located on the imidazolium ring hydrogen on C2 being the most acidic [36]. It may be inferred that both π^* and α show unusually enhanced values within [bmim][PF$_6$] + propylene carbonate mixture; and this manifests itself in the behavior of Reichardt's dye (i.e., in E_T^N values). Contrary to E_T^N, π^* and α, HBA basicity (β) of propylene carbonate is observed to be significantly higher than that of [bmim][PF$_6$] (Fig. 4). While it is easy to identify the HBA sites on propylene carbonate (the two –O– as well as =O to some extent; see structure in Scheme 1), the low-HBA basicity associated to [bmim][PF$_6$] is due to PF$_6{}^-$. HBA basicity of [bmim][PF$_6$] + propylene carbonate mixture is observed to be unusually lower (Fig. 4); β decreases drastically as [bmim][PF$_6$] (the component with lower HBA basicity) is added to propylene carbonate (the component with higher HBA basicity). All in all, unusual solvatochromism is observed in [bmim][PF$_6$] + propylene carbonate mixture.

3.3. Preferential solvation or solvent–solvent interaction?

The study of physicochemical properties that depend on solute–solvent interactions is much more complex in mixed solvent systems than in pure solvents [32]. On one hand, the solute can be preferentially solvated by any of the solvents present in the mixture; on the other, solvent–solvent interactions can strongly affect solute–solvent interactions. Preferential solvation arises whenever the bulk mole fraction solvent composition is different from the solvation microsphere solvent composition. The response of spectroscopic probes is dependent upon the composition of the solvation microsphere and therefore provides a convenient means to measure the extent of preferential solvation. Most spectroscopic probe techniques assume an idealized situation where solvent–solvent interactions can be neglected and the measured spectral response, R, in a binary solvent mixture is given by [14–16,32]

$$R = Y_A R_A^0 + (1 - Y_A) R_B^0 \tag{7}$$

a weighted local mole fraction of the probe's spectral response in the two pure solvents, R_A^0 and R_B^0. Here Y_A and $(1 - Y_A)$ refer to the solvation sphere composition, which, in the case of preferential solvation, may be quite different from the overall bulk liquid-phase composition. The reason for preferential solvation, in most cases, is the favorable interactions that may exist between the solute and *one* of the solvents (or components) in the mixture [31,32]. The mole fraction weighed ideal additive parameters E_T^N, π^*, α, and β are represented by dashed lines in Figs. 1–4 (the deviation from ideal additive behavior is depicted in insets). It is clear that all four solvatochromic parameters within [bmim][PF$_6$] + propylene carbonate show significant deviation from ideal additive behavior.

A careful examination of Figs. 1–4 reveals that at every mixture composition investigated measured E_T^N, π^*, and α are always higher than their corresponding ideal additive values. This may suggest the possibility of preferential solvation of the probes by [bmim][PF$_6$], the component having higher E_T^N, π^*, and α of the two. In further support of this, the β of the mixture is lower than the ideal additive β at all compositions suggesting preferential solvation by the component having lower of the two β values, which is again [bmim][PF$_6$]. The calculated mole fractions using Eq. (7) of [bmim][PF$_6$] (i.e., $x_{\text{[bmim][PF}_6\text{],calculated}}$) around the probe from spectral responses of Reichardt's dye and DENA further support this hypothesis. Fig. 5 presents $x_{\text{[bmim][PF}_6\text{],calculated}}$ *versus* mole fraction [bmim][PF$_6$] in the bulk ($x_{\text{[bmim][PF}_6\text{],bulk}}$) for Reichardt's dye (panel A) and DENA (panel B) within [bmim][PF$_6$] + propylene carbonate mixture. It is clear that $x_{\text{[bmim][PF}_6\text{],calculated}} > x_{\text{[bmim][PF}_6\text{],bulk}}$ for Reichardt's dye and DENA at all compositions investigated. It is important to men-

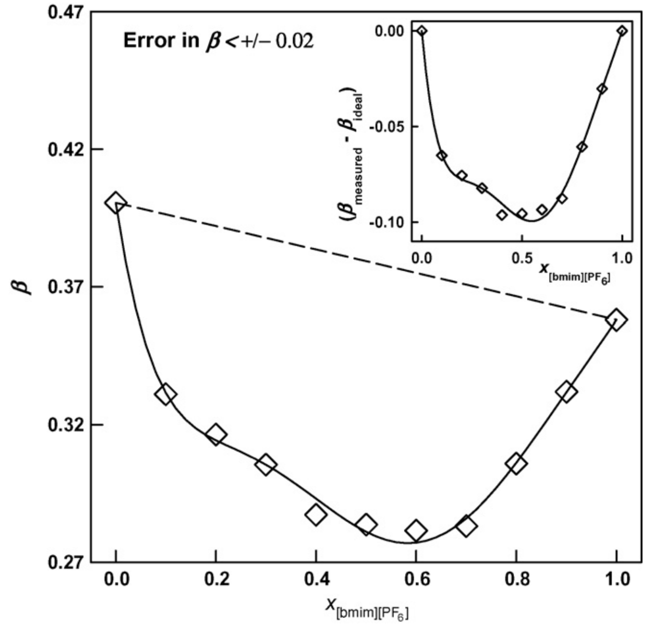


Fig. 4. Hydrogen-bond accepting (HBA) basicity (β) *versus* $x_{\text{[bmim][PF}_6\text{]}}$ within [bmim][PF$_6$] + propylene carbonate at ambient conditions. Dashed line represents ideal additive β, while solid curve shows fit according to Redlich–Kister equation (Eq. (8)) with parameters reported in Table 1. The deviation from ideal additive behavior is shown in inset.

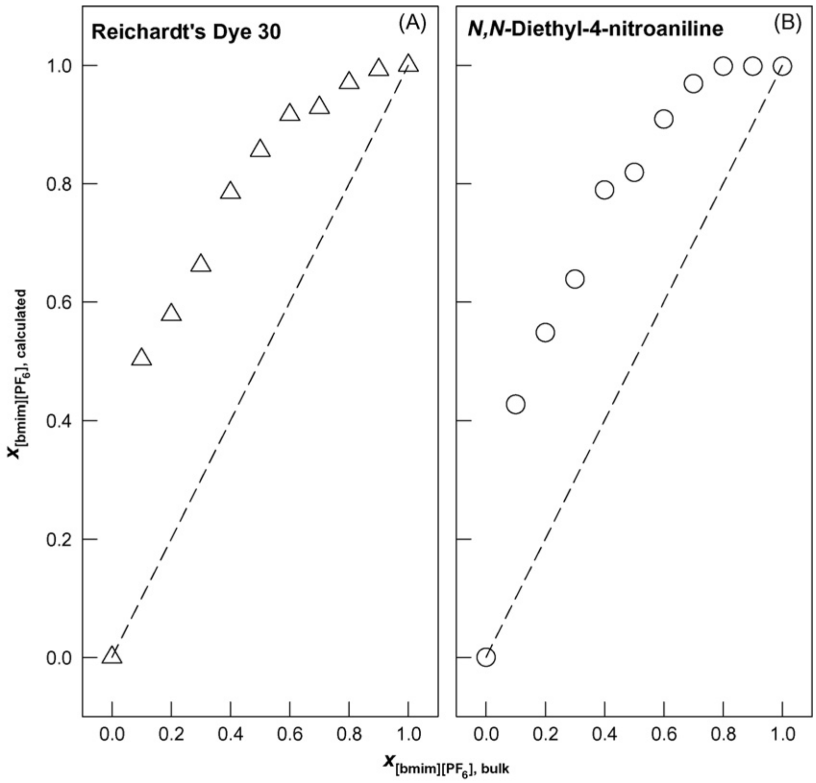


Fig. 5. Comparison of calculated [bmim][PF_6] mole fraction from Eq. (7) (i.e., $x_{[bmim][PF_6],calculated}$) *versus* bulk [bmim][$PF_6$] mole fraction in the solution (i.e., $x_{[bmim][PF_6],bulk}$) for Reichardt's dye (panel A) and DENA (panel B) within [bmim][PF_6] + propylene carbonate at ambient conditions.

tion here that Eq. (7) could not be used to carry out such analysis for NA as a minima in β renders it not possible. It is inferred from this analysis that Reichardt's dye and DENA may be preferentially solvated by the IL [bmim][PF_6] within [bmim][PF_6] + propylene carbonate mixture. It is easy to conceive a microenvironment around Reichardt's dye rich in [bmim][PF_6] perhaps due to the structural similarities between zwitterionic dye and [bmim][PF_6] along with the HBD ability of $bmim^+$. Similarly, the HBD ability of $bmim^+$ may render the DENA cybotactic region also rich in [bmim] [PF_6].

Possibility of solvent–solvent interaction(s) giving rise to a solution structure with enhanced dipolarity/polarizability and HBD acidity, and diminished HBA basicity may in part or fully be responsible for the unusual solvatochromism within [bmim][PF_6] + propylene carbonate system as well. In this context, the formation of HBD–HBA complex due to hydrogen bonding interactions between C2-H of $bmim^+$ and –O– and/or =O of propylene carbonate within [bmim][PF_6] + propylene carbonate may produce a third 'species' in the solution possessing enhanced dipolarity/polarizability and HBD acidity and diminished HBA basicity. One may seek support for this possibility from a non-invasive technique where no external probe is used. For this purpose, we chose to use FTIR absorbance of [bmim][PF_6] + propylene carbonate mixture to assess if C2-H of $bmim^+$ is involved in specific hydrogen bonding with –O– and/or =O of propylene carbonate. In this context, we examined $bmim^+$ C2-H stretching (i.e., NC(H)NCH stretching) frequency as propylene carbonate is added to [bmim][PF_6]. For neat [bmim][PF_6], this stretching frequency appears at $3125\,cm^{-1}$, which is in good accord with the literature value [48]. The stretching frequency is observed to shift to 3124, 3123, and $3120\,cm^{-1}$ for $x_{[bmim][PF_6]} = 0.8$, 0.5, and 0.2, respectively. It is important to mention that not much change in the spectral profile of this stretching band results as propylene carbonate is added to [bmim][PF_6] (data not shown). A meager shift of $\sim 5\,cm^{-1}$ in going from $x_{[bmim][PF_6]} = 1$ to $x_{[bmim][PF_6]} = 0.2$ along with unchanged spectral profile may hint against the presence of significant solvent–solvent interaction(s) within [bmim][PF_6] + propylene carbonate mixture. Though it may not be completely ruled out, the contribution of solvent–solvent interaction(s) towards dramatic deviation of probe responses from ideal additive behavior may be considered negligible.

3.4. Solvatochromic parameters and Redlich–Kister model

Empirical solvatochromic parameters are shown to be useful in correlating a wide range of physicochemical properties [49–55]. The prediction of solvatochromic parameters of mixtures, using a minimum number of experiments may provide a useful computational tool. In order to demonstrate the effect of solution composition on different empirical solvatochromic parameters in mixtures, we applied the combined nearly ideal binary solvent/Redlich–Kister (CNIBS/R–K) equation to the experimental data for these parameters [56–61]. The CNIBS/R–K model provides a method to predict the excess molar properties of a solute dissolved in a multicomponent solvent mixture in terms of a weighted mole fraction average of solute properties in neat components and contributions of solute–solvent and solvent–solvent interactions [56–61]. According to CNIBS/R–K model, the empirical solvatochromic parameters (SP) in a binary solvent mixture at a constant temperature can be expressed as

$$\mathrm{SP}_m = x_1\mathrm{SP}_1^0 + x_2\mathrm{SP}_2^0 + x_1x_2\sum_{j=0}^{k}A_j(x_1 - x_2)^j \tag{8}$$

where SP_m, SP_1^0, and SP_2^0 are solvatochromic parameters determined in mixture and neat components 1 and 2, respectively, and x_1 and x_2 are the mole fractions of the components in the mixture. A_j and j are the equation coefficients and the degree of the polynomial

Table 1
Average of Redlich–Kister parameters (A_j's), standard deviation (σ), and R^2 for the solvatochromic parameters (SP) according to Eq. (8) for [bmim][PF$_6$] + propylene carbonate at ambient conditions.

SP	A_0	A_1	A_2	A_3	A_4	σ	R^2
E_T^N	0.2470	−0.0390	0.4218	−0.6008	–	0.0562	0.9592
	0.2942	−0.0390	−0.2064	−0.6008	0.9560	0.0224	0.9948
π^*	0.1311	−0.0087	0.1632	−0.2345	–	0.0172	0.9727
	0.1421	−0.0087	0.0175	−0.2345	0.2218	0.0135	0.9864
α	0.3689	−0.0692	0.6835	−0.9713	–	0.0972	0.9542
	0.4517	−0.0692	−0.4195	−0.9713	1.6784	0.0348	0.9953
β	−0.3743	−0.0993	−0.2188	0.5268	–	0.0267	0.9665
	−0.3929	−0.0993	0.0285	0.5268	−0.3763	0.0189	0.9866

expansion, respectively. The numerical values of j can be varied to find an accurate mathematical representation of the experimental data. Regression analysis was performed to fit the polynomials to our experimental data, and the results of the fit are reported in Table 1 where the standard deviation (σ) is calculated according to the following equation:

$$\sigma = \left(\frac{\sum_{i=1}^{n} (\mathrm{SP}_i^{\mathrm{exp}} - \mathrm{SP}_i^{\mathrm{cal}})^2}{n} \right)^{1/2} \tag{9}$$

where n, $\mathrm{SP}_i^{\mathrm{exp}}$, and $\mathrm{SP}_i^{\mathrm{cal}}$ are the number of the experimental data points, the experimental and calculated solvatochromic parameter within [bmim][PF$_6$] + propylene carbonate mixtures, respectively. An overall $\sigma = 0.0032$ (for $j = 4$) shows reasonably good agreement between the experimental solvatochromic parameters and the ones calculated using parameters in Table 1 obtained according to CNIBS/R–K model (Eq. (8)). It is convenient to use a cross-validation method which is a practical and reliable way to test the predictive significance when little data are available [62]. In Fig. 6, the predicted values of solvatochromic parameters [E_T^N, π^*, α, and β] obtained by the cross-validation method for various [bmim][PF$_6$] + propylene carbonate mixtures from Eq. (8) with $j = 4$ have been plotted against the corresponding experimental values, and the following simplistic equation depicting an excellent linear correlation is obtained:

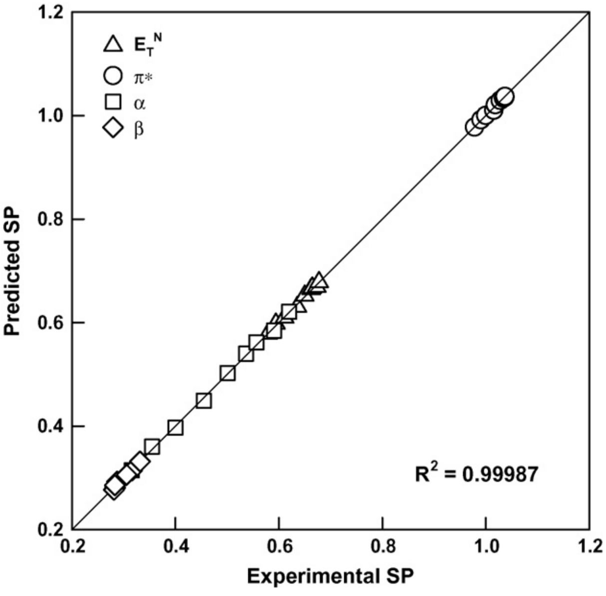


Fig. 6. Predicted values of solvatochromic parameters from the correlation equation *versus* its experimental values for [bmim][PF$_6$] + propylene carbonate mixture (results of the fit are provided in Eq. (10)).

$$\mathrm{SP}_m^{\mathrm{cal}} = 0.99998(\pm 0.00200)\mathrm{SP}_m^{\mathrm{exp}} - 1.5059(\pm 0.0013) \times 10^{-5}$$
$$n = 36, \quad R^2 = 0.9999, \quad \sigma = 0.0032 \tag{10}$$

The solid lines connecting each of the solvatochromic parameters [E_T^N, π^*, α, and β] in Figs. 1–4, respectively, at all proportions are obtained from the CNIBS/R–K model fit (with $j = 4$) which also strongly support the good correlation between the predicted and the experimentally obtained values. To conclude, the CNIBS/R–K model shows a good correlation between predicted and experimentally measured values at ambient conditions; no proportional and systematic errors were observed. It may be proposed that the CNIBS/R–K model is a reasonable one to predict solvatochromic parameters within [bmim][PF$_6$] + propylene carbonate mixtures.

4. Conclusions

Solvatochromic absorbance probes – Reichardt's dye, DENA, and NA – show unusual behavior within [bmim][PF$_6$] + propylene carbonate mixture. Empirical parameters E_T^N, π^*, and α within the mixture are observed to be higher than those expected from mole fraction weighed ideal additive values suggesting enhanced dipolarity/polarizability as well as HBD acidity of the mixture. HBA basicity (β) is observed to be diminished within the mixture. It is demonstrated that Redlich–Kister type mathematical formulation can adequately predict these solvatochromic parameters with acceptable accuracy. Spectral behavior of solvatochromic absorbance probes hint at solute-specific preferential solvation; specific solvent–solvent interaction(s) are observed to be negligible within [bmim][PF$_6$] + propylene carbonate mixture.

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