

SOLVATOCHROMIC AND FLUORESCENCE SPECTROSCOPIC STUDIES ON POLARITY OF IONIC LIQUID AND IONIC LIQUID-BASED BINARY SYSTEMS

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Abstract

Polarity behavior of a hydrophobic ionic liquid (IL) 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulphonylimide [EMI][TFSI] and binary mixtures of [EMI][TFSI] with ethanol, acetone and dichloromethane was investigated by solvatochromic method using Reichardt's betaine dye. Fluorescence spectroscopic method using pyrene as a probe was also used for estimation of polarity of [EMI][TFSI] and [EMI][TFSI]-based binary systems. The binary mixtures of [EMI][TFSI] with the molecular solvents interestingly showed increase in polarity with increasing [EMI][TFSI] for all compositions. The comparative and contrastive features of the results of two methods have been discussed to judge relative merit of one method over the other. Both of the methods collectively provided information to correlate specific interaction of the IL with molecular solvents and define polarity behavior.

Introduction

One of the most challenging tasks for the chemical industries is to incessantly deal with toxic, harmful, and flammable organic solvents on which the industries rely on greatly. Organic solvents used in most of the synthesis processes in chemical industries evaporate into the atmosphere with adverse effects on the environment as well as human health. Ionic liquids (ILs), on the other hand are composed entirely of ions and are liquid at ambient conditions with unique array of physico-chemical properties such as negligible vapor pressure and non-toxicity and offer the promises as environmentally benign solvent media for many industrially important chemical processes, which *inter alia* include: synthesis,¹ catalysis,^{2,3} polymerization,⁴ separation, and extraction processes⁵⁻⁹. However, a fundamental knowledge-base of ILs is still in its infancy, and an upsurge of interest is experienced to study the physicochemical properties of ILs in relation to their structures.

Addition of a conventional solvent to an IL system may significantly influence physicochemical properties of ILs to desirable chemistry to exploit them further for manifold applications. To explore the complete potential of ILs as solvent systems, a

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clearer understanding of the physicochemical properties of ILs as well as their binary systems with molecular solvents is very crucial. This may be achievable by analyzing viscosity, density, conductivity, thermal stability and other physicochemical properties to unveil interactive features in the binary systems. Polarity estimation can play a key role to understand specific interaction in such IL-based binary systems to evaluate other physicochemical properties. However, direct measurement of dielectric constant for IL-based system is not possible because of the high conductivity and alternative methods, such as, solvatochromic and fluorescence spectroscopic methods have been useful for estimation of polarity for such conducting systems.

In this study, we focused our attention on the effective employment of solvatochromic method using Reichardt's betaine dye (RBD) as solvatochromic probe and fluorescence method using pyrene as fluorescence probe to estimate the polarity of a hydrophobic IL, 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulphonylimide, [EMI][TFSI] (Fig. 1) and its binary mixture with several conventional molecular solvents e.g. ethanol, acetone and dichloromethane (DCM). Specific interaction of [EMI][TFSI] with the molecular solvents have been discussed to correlate change in physicochemical properties with composition. The comparative and contrastive features of the results obtained by two methods have also been analyzed to judge relative merit of one method over the other.

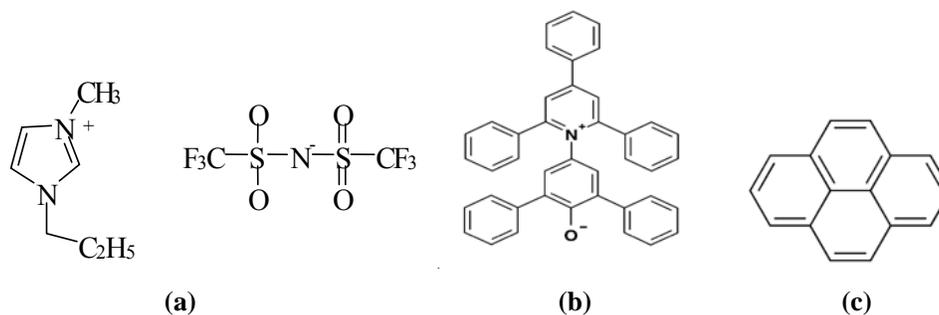


Fig. 1. Structures of (a) [EMI][TFSI] (b) RBD and (c) pyrene.

Experimental

Materials and Methods

The IL, [EMI][TFSI] was obtained from E. Merck and was used without any further purifications. RBD (2, 6-diphenyl-4-(2, 4, 6-triphenyl-*N*-pyridino) phenolate and pyrene were obtained from Sigma Aldrich and were used as received. Ethanol, acetone, DCM,

acetonitrile each were reagent grade materials and were used without further purifications.

Solvatochromic Method

Aliquots of a stock solution of RBD in ethanol were transferred to a volumetric flask and ethanol was allowed to evaporate at room temperature. Then water, ethanol, acetone, acetonitrile, DCM, [EMI][TFSI] and [EMI][TFSI]-ethanol mixture, [EMI][TFSI]-acetone mixture, [EMI][TFSI]-DCM mixture were added to the volumetric flask to prepare solutions with the desired concentration of the probe dye. For preparation of binary mixtures, volume percentage of [EMI][TFSI] was added to different solvents. The mixtures in all cases were sonicated (LU-2 Ultrasonic cleaner, Labnics, USA) for about 20 minutes to ensure homogeneity. The UV-visible spectra of RBD solutions in ethanol, acetone, DCM, [EMI][TFSI], mixtures of [EMI][TFSI] with ethanol, acetone and DCM in different composition was recorded by a double beam Shimadzu UV-visible spectrophotometer (model UV-1800 PC). The value of the λ_{\max} i.e. the wavelength maximum of the charge transfer band has been used to compare the polarity of different media based on the empirical scale of solvent polarity, the $E_T(30)$ scale.¹⁰

Fluorescence Spectroscopic Method

For preparation of solutions for fluorescence measurements, a known volume from a stock solution of 0.1 mM pyrene in ethanol was taken in a volumetric flask and ethanol was evaporated. Then ethanol, acetone, DCM and [EMI][TFSI] was added at required volume and mixtures of [EMI][TFSI]-ethanol, [EMI][TFSI]-acetone, [EMI][TFSI]-DCM were prepared by varying composition. The final concentration of pyrene in each solution was 1.0×10^{-6} M. The fluorescence emission spectra of pyrene in ethanol, acetone, DCM, [EMI][TFSI], mixtures of [EMI][TFSI] with ethanol, acetone and DCM by varying volume percentage of [EMI][TFSI] were recorded using a fluorescence spectrophotometer (Hitachi; Model no F-7000). Pyrene was excited at 337 nm. The intensity ratio data have been used to estimate the polarity of different systems.

Results and Discussion

Solvatochromism

Shift in wavelength corresponding to absorption maximum (λ_{\max}) of RBD in UV-visible absorption spectrum has been verified for water, ethanol, acetone, acetonitrile and DCM of different polarity. The concentration of RBD solutions in these solvents was 1.0×10^{-4} M. Fig. 2 represents the absorption spectra of RBD in different solvents. The absorption maxima (λ_{\max}) for the band 400-700 nm changed with change in the solvent.

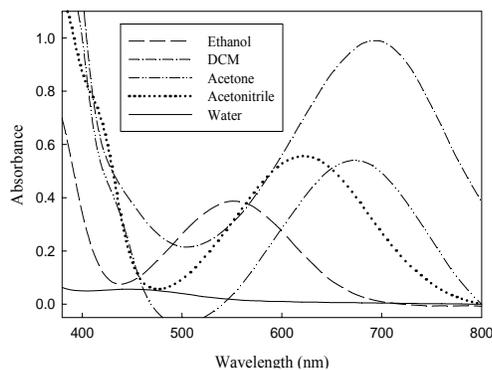


Fig. 2. Absorption spectra of 1.0×10^{-4} M RBD in different solvents.

One of the most widely used empirical scales of solvent polarities is the $E_T(30)$ scale based on

$$E_T(30) \text{ (kcal/mol)} = 28591 / \lambda_{\max} \quad (1)$$

where, λ_{\max} is the wavelength for absorption maxima for intramolecular charge-transfer $\pi-\pi^*$ absorption band of the zwitterionic RBD. This zwitterionic compound exhibits one of the largest observed solvatochromic effects of any known organic molecule and a large shift in λ_{\max} in going from a polar solvent to a nonpolar solvent. According to $E_T(30)$ scale the value of $E_T(30)$ increases with increasing solvent polarity. The $E_T(30)$ for different solvents has been evaluated and plotted against dielectric constant of the solvents¹¹ in Fig. 3.

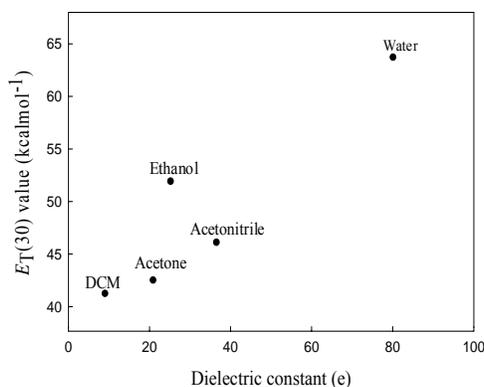


Fig. 3. $E_T(30)$ value of the solvents as a function of dielectric constant.

The results in Fig. 3 indicate higher $E_T(30)$ values for polar solvent water and ethanol (i.e. lower λ_{\max}) compared to less polar solvents acetone and DCM (i.e. higher λ_{\max}). This agrees well with the concept of solvatochromism of RBD. If the ground state is more polar than excited state it is better stabilized by polar solvent and its energy is lowered. Therefore, the energy gap between ground state and excited state becomes larger (Fig. 4). Thus the charge transfer transition will occur at a shorter wavelength. Consequently, there will be hypsochromic shift (blue shift) with increasing solvent polarity.

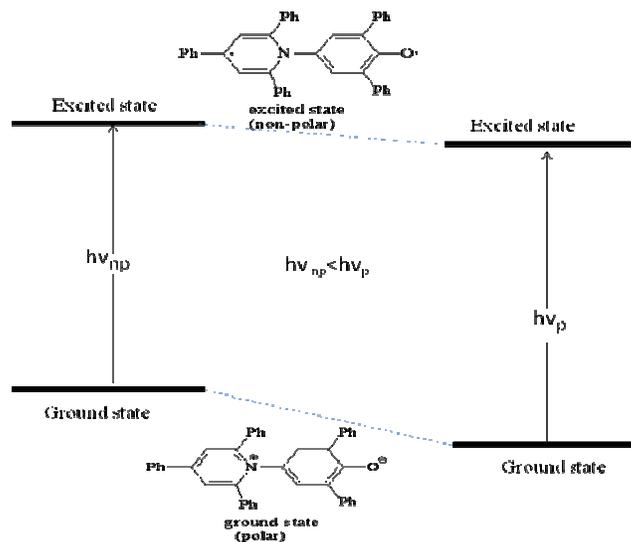


Fig. 4. Solvatochromic shift of RBD.

Since RBD is polar in ground state, it follows the negative solvatochromism and blue shift occurs. Thus water is the most polar and DCM is the least polar among the solvents studied in this work. The $E_T(30)$ value is quite consistent with the value of dielectric constant (Fig. 3) and an increase in dielectric constant of the solvent caused expected increase in the $E_T(30)$ value which is consistent with available literature¹². Polarity scale based on $E_T(30)$ values may therefore serve the purpose of estimation of polarity of a wide variety of solvents and in fact, this is considered to be reliable method for the determination of solvent polarity of most of the solvents.

Solvatochromic shift in λ_{\max} of RBD in UV-visible absorption spectrum has also been checked for pure [EMI][TFSI] where the concentration of RBD was 1.0×10^{-4} M. In the absorption spectrum of RBD in [EMI][TFSI], surprisingly no significant change in absorption can be marked in the visible range, although [EMI][TFSI] is also expected to exhibit intramolecular charge-transfer $\pi-\pi^*$ transition band. To clarify, excess amount RBD was added in [EMI][TFSI] and absorption spectrum was recorded again. Interestingly, the charge transfer band appears in the absorption spectrum with excess

RBD. This may correspond to the presence of silver ions¹³ or other species in [EMI][TFSI], which coordinate with RBD to prevent the [EMI][TFSI] intramolecular charge transfer $\pi-\pi^*$ transition. The presence of silver species in [EMI][TFSI] is not surprising. In fact, during synthesis of [EMI][TFSI], metathesis of a halide salt with silver salt of the desired anion is carried out and silver ions, even in the trace amount, can remain as residue in the IL after purifications. Upon addition of large excess of RBD, all of the silver species present in the IL form coordination complexes and excess RBD becomes available for solvatochromic interaction with [EMI][TFSI] resulting in the appearance of the band to estimate polarity of the IL. The dye is zwitterionic in the ground state; upon excitation electron transfer occurs from the oxygen atom to the centre of the aromatic system. In the presence of silver ions electron transfer can occur from the oxygen to the Ag^+ by the formation of a complex of RBD-Ag which hinders the intermolecular $\pi\rightarrow\pi^*$ charge transfer (CT) excitation, thus lowering absorbance at the λ_{max} value of RBD in the presence of the IL. The $E_{\text{T}}(30)$ has been calculated 52.13 kcal/mol for [EMI][TFSI] from the λ_{max} value from the absorption spectrum (Fig. 5) and the value is close to that of ethanol which indicates that they are of similar polarities. Thus solvatochromic method may be successfully used for the estimation of the polarity of conventional solvents as well as ILs.

The study of physicochemical properties that depend on solute-solvent interactions is much more complex in mixed solvent systems than in pure solvents. Not only the solute can be preferentially solvated by any of the solvents present in the mixture but also solvent-solvent interactions can strongly affect solute-solvent interactions. Studying solute-solvent interactions by means of solvatochromic probes is both simple and convenient. In addition, solvatochromic probe studies offer direct information about solvent properties such as polarity and hydrogen-bond-donating/accepting capabilities¹⁴.

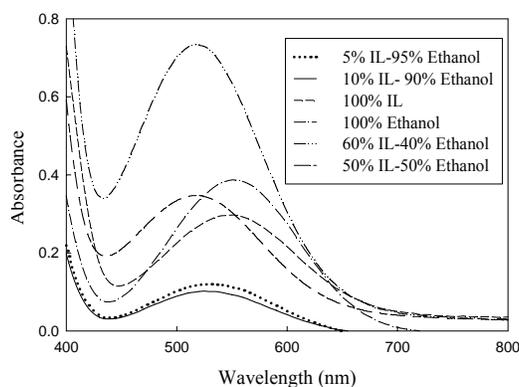


Fig. 5. Absorption spectra of RBD in [EMI][TFSI]-ethanol system with varying volume % of [EMI][TFSI].

In analogous to the RBD solution in IL, IL-based binary mixtures did not show any λ_{\max} in the visible range at low RBD concentrations and excess RBD had to be added in the systems. Fig. 5 presents observed λ_{\max} values for RBD in binary [EMI][TFSI]-ethanol mixtures where [EMI][TFSI] was added gradually in ethanol.

A careful examination of the λ_{\max} reveals an extremely unusual behavior. While λ_{\max} values are similar in pure ethanol and [EMI][TFSI], observed λ_{\max} decreases from 548.03 nm to 515.06 nm in moving from pure [EMI][TFSI] to the binary solution of composition 60% [EMI][TFSI]-40% ethanol with a consequent increase in the $E_T(30)$ value (Table 1).

Table 1. $E_T(30)$ value for different composition of [EMI][TFSI]-solvent binary mixtures

System containing excess RBD	$E_T(30)$ value(kcal/mol)		
	ethanol	acetone	DCM
100% solvent	51.88	42.48	41.20
5%[EMI][TFSI]-95% solvent	53.84	48.17	46.98
10%[EMI][TFSI]-90% solvent	53.95	48.80	47.41
50%[EMI][TFSI]-50% solvent	55.30	52.46	50.96
60%[EMI][TFSI]-40% solvent	55.51	52.17	51.98
100% [EMI][TFSI]	52.17	53.04	52.17

It is clear that the addition of [EMI][TFSI] causes a significant increase in polarity. The polarity of the binary mixtures is very interestingly much higher than the corresponding values for the constituent IL and the solvent. This indicates stronger interaction between [EMI][TFSI] and ethanol. The zwitterionic solvatochromic probe, RBD is strongly affected by hydrogen-bond donating (HBD) ability of the solvent. In general, hydrogen bond donating solvents stabilize the ground state more than the excited state and thus lower the value of λ_{\max} for an apparent increase in the polarity of the medium. Thus it may be assumed that in the binary mixtures, HBD ability increases as the volume % of [EMI][TFSI] in the mixtures is increased; as a result λ_{\max} value decreases to indicated increase in polarity of the system.

The binary mixtures of [EMI][TFSI]-acetone and [EMI][TFSI]-DCM systems show that [EMI][TFSI] is more polar ($E_T(30)$ value=52.17) than acetone ($E_T(30)$ value=42.48) (Table 1) and DCM ($E_T(30)$ value=41.20) but when we added [EMI][TFSI] in acetone and DCM respectively, the observed λ_{\max} value shifts to lower wavelength (Fig. 6) indicating that polarity of the binary system is increased.

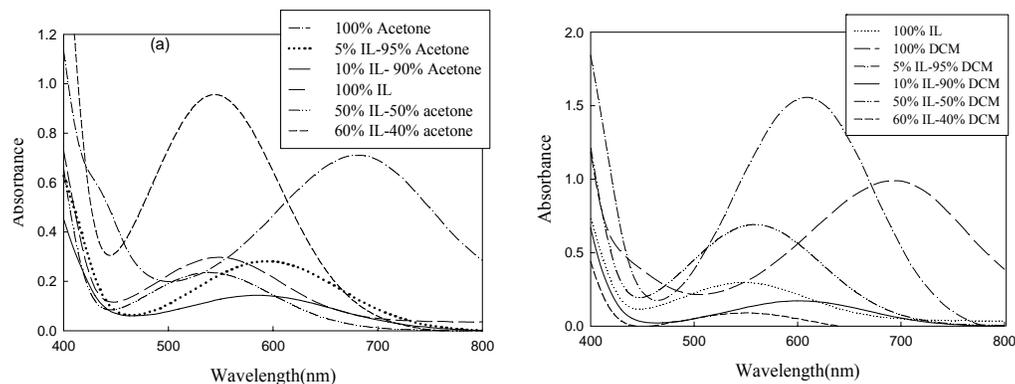


Fig. 6. Absorption spectra of RBD in (a) [EMI][TFSI]-acetone and (b) [EMI][TFSI]-DCM system with varying volume % of [EMI][TFSI].

In [EMI][TFSI]-acetone system, the polarity of the binary system increases as volume % of [EMI][TFSI] increases and the value is much higher than acetone at all compositions; but lower than that of [EMI][TFSI] (Table 1). Thus it may be presumed that HBD ability of the [EMI][TFSI]-acetone binary system is higher compared to acetone. In the binary mixture, the oxygen in carbonyl group may hydrogen bond with the imidazolium cation of [EMI][TFSI]; but as [EMI][TFSI] is more polar than acetone, the neat HBD ability increases. Polarity is thereby increased.

In resemblance to the [EMI][TFSI]-acetone system, the polarity of [EMI][TFSI]-DCM system is higher than the molecular solvent, pure DCM (Table 1). Increase in polarity in the binary mixture indicates that there is significant interaction between [EMI][TFSI] and DCM. [EMI][TFSI] enhances the polarity of the medium since ground state of RBD is more stabilized possibly due to higher HBD ability of [EMI][TFSI] in the binary system.

Fluorescence Emission Spectra

Pyrene, constituted of four fused benzene rings and no functional group otherwise, is a neutral fluorescence probe and shows significant fine structure (vibronic band) in its monomer fluorescence spectra in solution phase. Figure 7 represents the fluorescence emission spectra of pyrene in ethanol, acetone, and DCM shows four characteristic bands in agreement with literature¹⁵. Band I and III (numbering based on increasing wavelength) provide useful information regarding solvent polarity. Band I corresponds to an S_1 ($v=0$) to S_0 ($v=0$) transition, while band III is an S_1 ($v=0$) to S_0 ($v=1$) transition.¹⁶ The I_I/I_{III} emission intensity ratio of pyrene has been used to define polarity and an increase in the I_I/I_{III} indicates an increase in the solvent polarity.

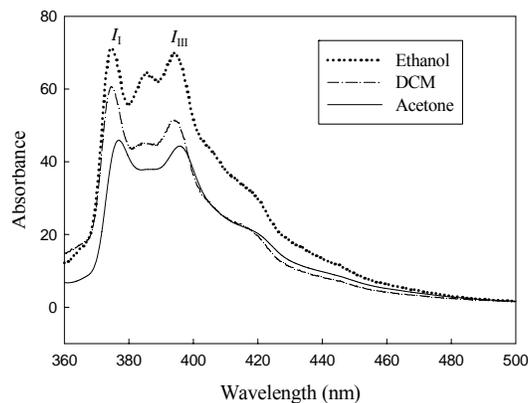


Fig. 7. Fluorescence emission spectra of 1×10^{-6} M pyrene in ethanol, acetone and DCM.

The I_I/I_{III} did not change appreciably with change in solvent. Beyond experimental error, the change in the ratio can provide no significant information regarding change in polarity. However, Fig. 3 shows clear difference in the dielectric constants of the solvent, in other words the solvent polarity. The anomaly observed is not surprising. Literature reports clearly indicate that fluorescence probe may not always quantitatively provide useful information regarding polarity for a wide variety of solvent. For instance, Street and Acree¹⁷ reported several problems associated with the correct determination of the I_I/I_{III} emission intensity ratio. However, the importance of the technique for qualitative estimation of polarity for a binary mixture, especially for IL systems cannot be overruled.

Fluorescence emission spectrum of 1.0×10^{-6} M pyrene for [EMI][TFSI] has been shown in Fig. 8. Although, band II is convoluted, bands I and III have been very clearly distinguishable. Therefore, the I_I/I_{III} emission intensity ratio could be easily evaluated from the spectrum (Table 2). The measured pyrene I_I/I_{III} value in [EMI][TFSI] clearly indicates a completely different microenvironment sensed by excited-state pyrene. The pyrene I_I/I_{III} value in [EMI][TFSI] is significantly higher than those measured in ethanol, acetone and DCM. It is worth mentioning that a comparison of the pyrene I_I/I_{III} values measured in the present study to the values reported by Dong and Winnik¹⁸ and Fletcher et al.¹⁹ shows some discrepancies. The pyrene I_I/I_{III} values depend on several experimental variables²⁰. Although quantitative description of polarity for a wide variety of solvents has not been possible by fluorescence spectroscopic method, the technique still offers the possibility of use for specific solvents, like ILs. The neutral fluorescence probe, pyrene avoids any interference from probe-probe interaction because of the extreme low concentration used. Therefore, for a binary mixture of IL, the composition dependence on polarity may be best described by this method (*vide infra*).

Fluorescence emission spectra of 1×10^{-6} M pyrene in [EMI][TFSI]-ethanol system are also shown in Fig. 8. The composition of the binary mixtures has been varied by adding different amount of [EMI][TFSI] in ethanol. Table 2 presents measured pyrene I_V/I_{III} in neat [EMI][TFSI], neat solvent (ethanol, acetone and DCM) and their binary mixtures.

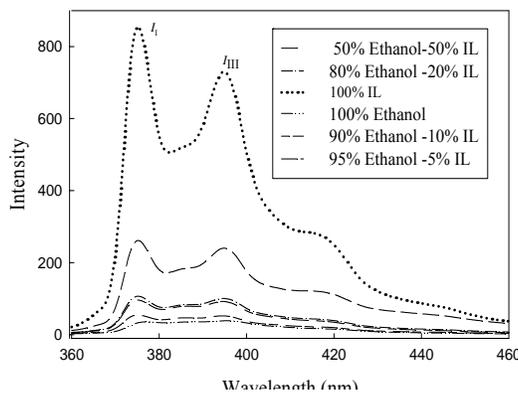


Fig. 8. Fluorescence emission spectra of 1×10^{-6} M pyrene in [EMI][TFSI]-ethanol system with varying volume % of [EMI][TFSI].

Table 2. Fluorescence intensity ratio of 1×10^{-6} M pyrene in [EMI][TFSI]- solvent systems

Systems	I_V/I_{III}		
	ethanol	acetone	DCM
100% [EMI][TFSI]	1.18	1.18	1.18
5%[EMI][TFSI]-95% solvent	1.05	1.07	1.07
10%[EMI][TFSI]-10% solvent	1.05	1.07	1.08
20%[EMI][TFSI]-80% solvent	1.06	1.11	1.08
50%[EMI][TFSI]-50% solvent	1.09	1.12	1.11
100% solvent	1.02	1.04	1.06

The I_V/I_{III} of pyrene in neat [EMI][TFSI] is higher than ethanol but the ratio increases as [EMI][TFSI] is added progressively (Table 2 and Fig. 8). These results clearly indicate a strong preferential solvation of the excited state pyrene moieties in the binary mixture. There may be some interaction between the π -electrons on the pyrene and the ones on the 1-ethyl-3-methylimidazolium cation. The I_V/I_{III} value in 50% [EMI][TFSI]-50% ethanol system is higher than the other compositions to indicate higher polarity at this composition.

Similar investigations have also been made for estimation of polarity of the binary systems, [EMI][TFSI]-acetone and [EMI][TFSI]-DCM. In both systems, polarity has been found to increase with increasing amount of [EMI][TFSI] in the mixtures (Table 2).

Comparative Study of Polarity of [EMI][TFSI]Based Binary System by Solvatochromism and Fluorescence Spectroscopy

To have a realistic comparison of polarity of [EMI][TFSI]-based binary systems and envisage interaction between the IL and the molecular solvents with change in composition and type of the solvents, the experimental results of solvatochromic and fluorescence spectroscopic methods have been summarized in Fig. 9.

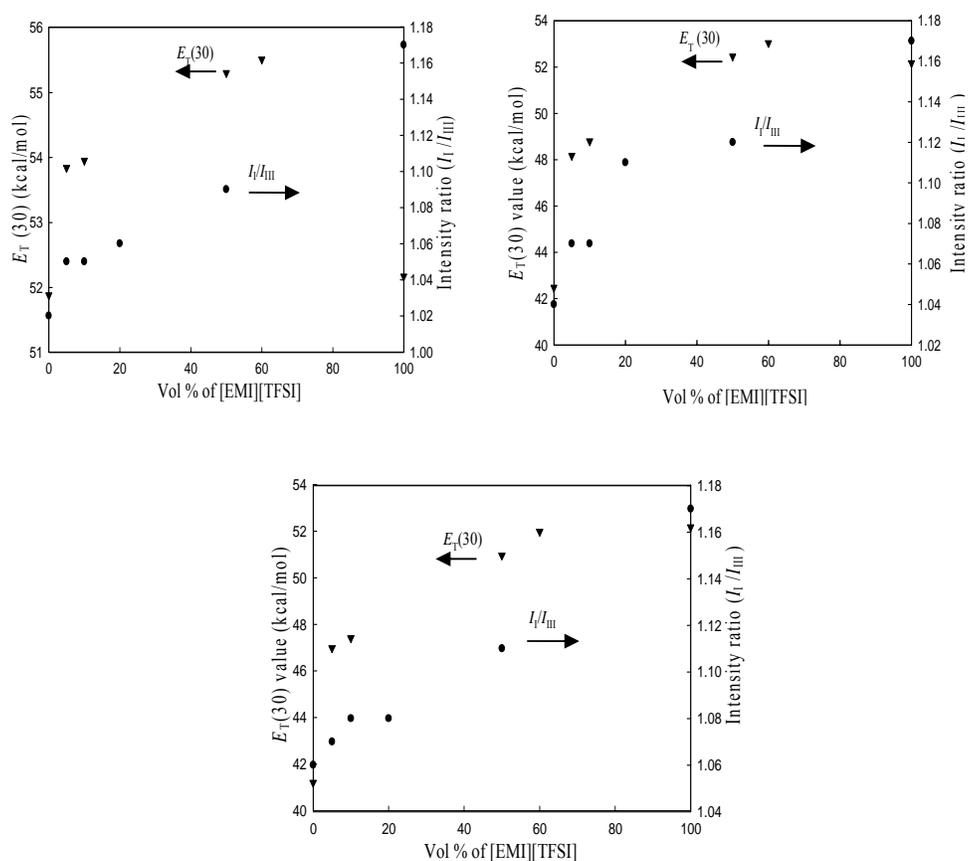


Fig. 9. $E_T(30)$ value for RBD and intensity ratio of pyrene versus volume % of [EMI][TFSI] in (a)[EMI][TFSI]-ethanol (b) [EMI][TFSI]-acetone and (c) [EMI][TFSI]-DCM systems.

It is apparent that irrespective of the methods used, the polarity of the molecular solvents in all cases increases upon addition of EMITFSI (Fig. 9). For [EMI][TFSI]-acetone and [EMI][TFSI]-DCM systems, both of the techniques estimate polarity lower than the neat IL. However, anomalous behavior could be marked for [EMI][TFSI]-ethanol system. The solvatochromic method shows significant increase in polarity of the binary mixtures than neat IL and ethanol. However, fluorescence spectroscopic method, gives relatively lower polarity of the binary mixtures compared to neat IL. Though pyrene monomer fluorescence spectra show solvent dependency, but interaction of pyrene with solvents involve interactions different from those in the solvatochromic method. Pyrene polarity scale has the drawback that it does not provide information about specific interactions such as hydrogen bonding, dipolarity, and dispersion to be identified and only give an overall indication of the overall polarity of the probe environment. Therefore it is not surprising that fluorescence spectroscopic method cannot completely define polarity of a wide variety of molecular solvents and ILs. In contrast, solvatochromic method gives much more information about polarity and can cover a very broad range of solvents in polarity scale. Solvatochromism can therefore be a reliable robust method for determination of polarity of many solvents as well as many ILs and IL-based binary systems. However, since fluorescence spectroscopic method used a neutral fluorescence probe, it can efficiently correlate change in polarity behavior of ionic substances, especially ILs upon addition of molecular solvents. Combination of both the techniques may provide useful information on polarity and mutual interaction of ILs with other solvents and help in tuning suitable binary mixtures with desirable chemistry for task-specific applications.

Conclusion

RBD can be used as a solvatochromic probe for study of polarity of solvents including IL and IL-based binary mixtures of molecular solvents with wide difference in polarity. Fluorescence spectroscopic study using pyrene as a probe can also provide qualitative information regarding polarity of IL-based systems. Solvatochromic results show that the polarity of [EMI][TFSI] is similar to that of ethanol. Irrespective of the polarity of the molecular solvent, addition of the IL in a solvent (polar, nonpolar or intermediate polar) brings about an apparent increase in the polarity of the system due to enhancement of HBD ability. A systematic study is now underway to study solvent-probe interaction for IL-based binary systems to correlate polarity behavior with physicochemical properties for task specific ILs for versatile applications.

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