Solvatochromic Absorbance Probe Behavior within Mixtures of the Ionic Liquid 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide + Molecular Organic Solvents

5 AUTHORS, INCLUDING:

Anwar Ali
Jamia Millia Islamia
155 PUBLICATIONS **1,130** CITATIONS

SEE PROFILE

Nisar Ahmad Malik
University of Kashmir
19 PUBLICATIONS **45** CITATIONS

SEE PROFILE

Sahar Uzair
Jamia Millia Islamia
14 PUBLICATIONS **30** CITATIONS

SEE PROFILE

Dr. Abbul Bashar Khan
Jamia Millia Islamia
20 PUBLICATIONS **167** CITATIONS

SEE PROFILE

Solvatochromic Absorbance Probe Behavior within Mixtures of the Ionic Liquid 1-Butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)imide + Molecular Organic Solvents

Anwar Ali,*,[†] Maroof Ali,[‡] Nisar Ahmad Malik,[†] Sahar Uzair,[†] and Abbul Bashar Khan[§]

[†]Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi 110025, India
[‡]Department of Chemistry, Aligarh Muslim University, Aligarh 202002, India
[§]Center for Interdisciplinary Research in Basic Sciences, Jamia Millia Islamia (Central University), New Delhi 110025, India

ABSTRACT: The solvent mixtures made up of ionic liquid and molecular solvents have potential applications in various fields such as chemical analysis and synthesis. Thus, in the present study, the role of the solvent microsphere in changing the behavior of the solvatochromic absorbance probe within binary solvent mixtures of ionic liquids with common molecular organic solvents is explored. Further, the behavior of the probes is explained with the help of solute−solvent and solvent−solvent interactions present in the mixtures. The binary mixtures of the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [bmim][Tf$_2$N], with molecular solvents, polar protic (methanol, 1-butanol) and polar aprotic (dimethyl sulfoxide, and N,N-dimethylformamide), have been selected for this investigation. The effect of the addition of molecular solvents to ionic liquid's polarity parameters, E_T^N, and Kamlet Taft parameters, the hydrogen bond donor ability (HBD) (α), hydrogen bond acceptor ability (HBA) (β), and dipolarity/polarizability (π^*), is investigated. The polarity parameters, E_T^N, and dipolarity/polarizability (π^*) of the mixtures indicate the "hyperpolarity" behavior on addition of molecular solvents to ionic liquid. The preferential solvation model has been used to provide insight on the solvent−solvent and/or solute−solvent interactions in the solvent mixtures.
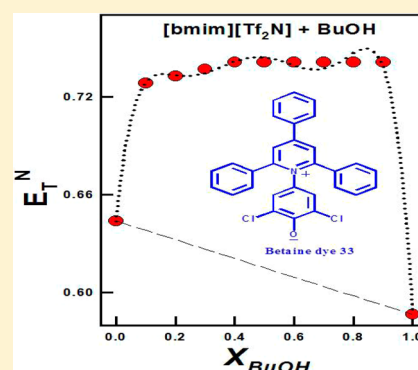
1. INTRODUCTION

Ionic liquids (ILs), the potentially green solvents, are a subject of main interest of the scientific and academic community due to their unusual features and vast range of applications in various fields.[1−10] ILs are made up of bulky organic cations and inorganic anions mainly and show a wide range of the physicochemical properties depending upon cations and anions and so are called tunable solvents. ILs have been used as solvents and as catalysts in many organic/inorganic/organometallic reactions.[10−15] ILs have also shown their importance in analytical chemistry and have been used in several analytical techniques such as in gas chromatography (GC), high-performance liquid chromatography (HPLC), or mass spectrometry and in electroanalysis, in separation techniques, and for sensing.[16−18] Recently, many research groups have demonstrated the effectiveness of the ILs in changing the photochemical and photophysical behavior of the solutes.[19−24] The importance of the ILs in biocatalysis and biotechnological fields has also been demonstrated by several groups.[25]

Besides the aforementioned chemical and biochemical applications of ILs, there are certain limitations also associated with these solvents. One crucial limitation is the limited solubility of many organic and inorganic solutes in these solvents which hampers the full utilization of these solvents in various important fields.[2,5−7] Thus, altering the physicochemical properties of ILs with molecular solvents is an area of

interest. The solute solubility may enhance in several cosolvent modified IL systems, and the addition of cosolvent may alter the physicochemical properties of solvent mixtures in a favorable manner. As a result, the researchers have started the use of IL + molecular solvent mixtures as solvent media for several chemical applications.[26−28] Toward this end, many research groups have studied the changes in the physicochemical properties and also explored solute−solvent and solvent−solvent interactions present in the IL + molecular solvent mixtures. Pandey and Fletcher reported the behavior of the solvatochromic probes in the [bmim][PF$_6$] + ethanol and + water/ethanol mixtures.[29,30] Kumar and Khupse studied the probe behavior in mixtures of ILs with methanol, water, and dichloromethane.[31] Gholami et al. explored the solvatochromic parameters for binary mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate with water, methanol, and ethanol.[32] In another study, Gholami et al. investigated probe behavior in the solvent mixtures of 2-hydroxyethylammonium formate with N,N-dimethylformamide, dimethyl amine, and dimethyl sulfoxide.[33] Moita et al. recently demonstrated the absorbance probe behavior of the IL + ethanol solutions.[34] Fortunato and Mancini et al. reported the molecular level behavior of the

mixtures made up of imidazolium-based IL and molecular organic solvents.[27,28] Brennecke et al. also explored the solvatochromism within the mixtures of the IL with molecular solvents.[35]

The IL [bmim][Tf$_2$N] is hydrophobic in nature and is immiscible with water and some of the polar and nonpolar organic solvents, e.g., hexane, toluene, ethyl acetate, butyl acetate, and diethyl ether, etc.[2] This limitation hampers the utilization of this IL as solvent media in many chemical applications. Thus, here, we report the solvatochromic absorbance probe behavior of the mixtures composed of IL, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide, [bmim][Tf$_2$N], and organic molecular solvents at ambient conditions. The addition of the protic polar (methanol), and aprotic polar (dimethyl sulfoxide, DMSO; and N,N-dimethylformamide, DMF) solvents alter the physicochemical properties of the [bmim][Tf$_2$N] in an unusual and favorable fashion, which is interesting and rare in the literature. The solute−solvent and solvent−solvent interactions present in the mixtures of the IL [bmim][Tf$_2$N] + molecular organic solvents are also explored with the help of the recovered solvatochromic parameters.

2. EXPERIMENTAL SECTION

**2.1. Materials.** 2,6-Diphenyl-4-(2,4,6-triphenyl-N-pyridino)phenolate [Betaine dye (30)] and 2,6-dichloro-4-(2,4,6-triphenyl-N-pyridino)phenolate [Betaine dye (33)] (highest purity) were obtained from Aldrich Chemical Co. and Fluka (≥ 99 %), respectively. 4-Nitroaniline (≥ 90 %) was purchased from Spectrochem Co. Ltd., and N,N-diethyl-4-nitroaniline was obtained from Frinton Laboratories. The IL [bmim][Tf$_2$N] was purchased from Sigma-Aldrich, USA, in the highest purity possible and was dried at 80 °C in inert atmosphere up to 24 h to minimize its water content. The water content in IL [bmim][Tf$_2$N] was 800 ppm, and IL was stored under anhydrous conditions to avoid the absorption of moisture. The water content in the sample was determined by the Karl Fischer method using a Karl Fischer titrator (model no. MA-101-13, SPECTRALAB, India). Dimethyl sulfoxide (DMSO), ethanol, 1-butanol (BuOH), and nitric acid were obtained from Merck. N,N-Dimethylformamide (DMF) and methanol (MeOH) were purchased from SD Fine-Chem. Ltd. and Rankem, respectively.

2.2. Methods. The stock solutions of probes were prepared in high purity ethanol and stored in ambered glass vials at 4 ± 1 °C. The Precisa XB-220A, Swiss make electronic balance with a precision of ± 0.1 mg, was used to weigh the desired amount of probe. The desired amount of the stock solution of probe was transferred to the quartz cuvette and was purged with pure and dry N$_2$ to remove the ethanol. The IL [bmim][Tf$_2$N] or other organic solutions were added to the cuvette to achieve the desired probe concentration. A Perkin Elmer Lambdabio EZ-201 double-beam spectrophotometer with a variable bandwidth was used for recording the UV−vis absorbance spectra. The 1 cm path length quartz cuvettes were used in the whole study. All of the measurements were recorded three times, and the average was taken. Microsoft Excel, Origin, and SigmaPlot 10.0 softwares were used for all data analysis.

3. RESULTS AND DISCUSSION

3.1. Behavior of Reichardt's Dye and E_T^N. It is well-documented that betaine dye 30 (Scheme 1) shows interesting

Scheme 1. Chemical Structures of the Solvatochromic Probes Used in This Study

Betaine dye 30   Betaine dye 33

4-nitroaniline   N,N-diethyl-4-nitroaniline
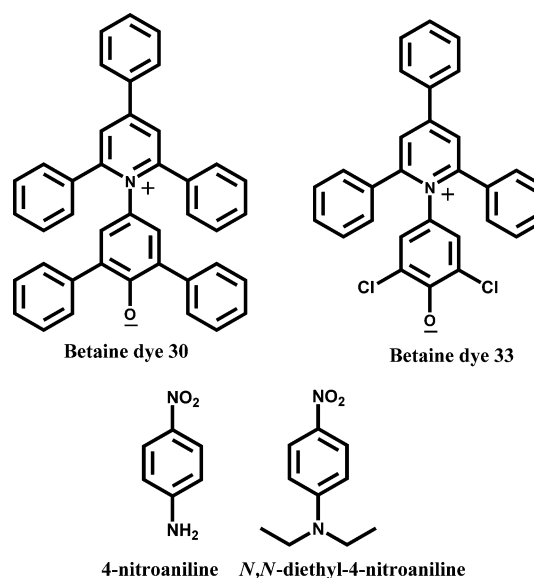
negative solvatochromism due to differential solvation of a more polar ground state and a less polar excited state.[36,37] Betaine dye 30 is zwitterionic in nature and hence shows charge transfer spectra which are highly sensitive to the hydrogen bond donating (HBD) ability of solvents. It is reported that the ground state is more stabilized than the excited state in the presence of solvents of those having a high HBD ability.[36,37] Betaine dye 30 has been routinely used for the determination of the polarity of the organic solvents, ionic liquids, and different kinds of the solvent mixtures. The solvatochromic behavior of betaine dye is measured by $E_T(30)$ scale, known as polarity scale. The $E_T(30)$ is known as the molar transition energy of Reichardt dye 30 in kcal/mol and can be calculated by $E_T(30)$ = 28591.5/λ_{max} (in nm). The betaine dye 33 (2,6-dichloro-4-(2,4,6-triphenylpyridinium-1-yl)phenolate) has several advantages over betaine dye 30 due to its low pK_a value; thus it is used in this study.[37] The $E_T(33)$ is calculated by equation[36,37]

$$E_T(33) = 28591.5/\lambda_{max} \text{ (in nm)} \tag{1}$$

Absorbance spectra of betaine dye 33 are recorded in [bmim][Tf$_2$N] + molecular organic solvents (methanol, 1-butanol, DMSO, and DMF) solutions over the whole mole fraction range; $E_T(33)$ values thus obtained are converted into E_T^N by the following equations:[38]

$$E_T(30) = 0.9953(\pm 0.0287)E_T(33) - 8.1132(\pm 1.6546) \tag{2}$$

$$E_T^N = \frac{[E_T(30)_{solvent} - E_T(30)_{TMS}]}{[E_T(30)_{water} - E_T(30)_{TMS}]} \tag{3}$$

Here, $E_T(30)_{water}$ and $E_T(30)_{TMS}$ (TMS = tetramethylsilane) values are (63.1 and 30.7) kcal/mol, respectively; eq 3 becomes

$$E_T^N = \frac{[E_T(30)_{solvent} - 30.7]}{32.4} \tag{4}$$

E_T^N is a dimensionless quantity, and its value varies from 0 (for TMS) to 1 (for water). E_T^N values of [bmim][Tf$_2$N] + organic solvents mixtures are given in Table 1. The E_T^N value of neat [bmim][Tf$_2$N] (0.60 ± 0.01) is comparable to that of benzyl

Table 1. E_T^N, π^* (Dipolarity/Polarizibility), α (HBD Ability), and β (HBA Basicity) within [bmim][Tf$_2$N] + Molecular Solvent (Methanol, 1-Butanol, DMSO, and DMF) Mixtures at Ambient Conditions[a]

| | [bmim][Tf$_2$N] + | | | | | | | | | | | | | | | |
| | methanol | | | | 1-butanol | | | | DMSO | | | | DMF | | | |
$X_{solvent}$	E_T^N	π^*	α	β	E_T^N	π^*	α	β	E_T^N	π^*	α	β	E_T^N	π^*	α	β
0	0.64	0.98	0.61	0.24	0.64	0.98	0.61	0.24	0.64	0.98	0.61	0.24	0.64	0.98	0.61	0.24
0.1	0.72	1.08	0.71	0.20	0.73	1.17	0.65	0.25	0.70	1.17	0.59	0.12	0.65	1.19	0.46	0.10
0.2	0.73	1.06	0.74	0.27	0.73	1.17	0.66	0.25	0.68	1.17	0.55	0.25	0.64	1.19	0.46	0.10
0.3	0.75	1.06	0.78	0.27	0.74	1.17	0.67	0.22	0.68	1.16	0.56	0.27	0.64	1.19	0.46	0.15
0.4	0.77	1.06	0.82	0.25	0.74	1.17	0.68	0.22	0.68	1.14	0.57	0.32	0.64	1.19	0.46	0.28
0.5	0.78	1.04	0.85	0.32	0.74	1.17	0.68	0.22	0.67	1.12	0.56	0.36	0.64	1.17	0.46	0.28
0.6	0.79	1.04	0.88	0.32	0.74	1.12	0.71	0.29	0.66	1.06	0.58	0.48	0.64	1.17	0.46	0.35
0.7	0.81	1.03	0.93	0.45	0.74	1.06	0.75	0.35	0.65	1.05	0.58	0.53	0.62	1.14	0.45	0.39
0.8	0.82	1.01	0.96	0.47	0.74	0.99	0.81	0.49	0.62	1.03	0.53	0.60	0.60	1.03	0.48	0.55
0.9	0.84	0.97	1.02	0.54	0.74	0.90	0.88	0.63	0.55	1.01	0.40	0.69	0.57	0.97	0.47	0.69
1.0	0.76	0.60	1.13	0.66	0.59	0.47	0.86	0.84	0.44	0.99	0.10	0.76	0.38	0.88	0.14	0.69

[a]The maximum errors associated with E_T^N, π^*, α, and β are $\leq \pm 0.01$, ± 0.01, ± 0.02, and ± 0.02, respectively.
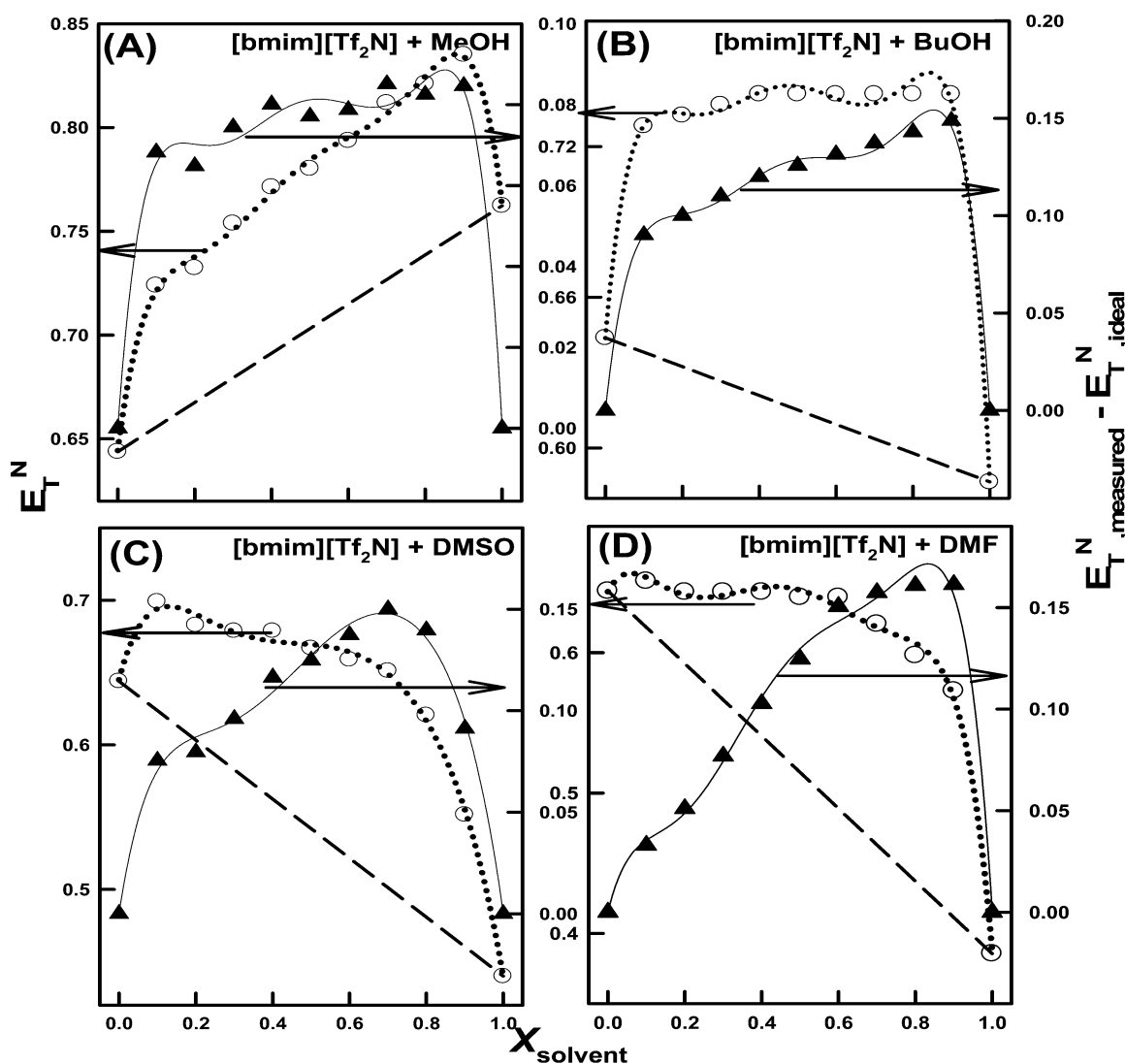

Figure 1. Variation in E_T^N with $X_{solvent}$ (—O—) in [bmim][Tf$_2$N] + different solvent mixtures at ambient conditions. The dashed line (- - -) shows the ideal additive E_T^N. The dotted line (···) shows fits according to the Redlich−Kister equation (eq 8). The deviation of experimentally observed E_T^N from ideality is given by (—▲—).

alcohol (0.60), 1-amino-2-propanol (0.599), 2-amino-1-butanol (0.602), furfuryl alcohol (0.605), 2-(hydroxymethyl)- tetrahydrofuran (0.605), and 2,4-dimethylphenol (0.605).[37] E_T^N of [bmim][Tf$_2$N] and other solvents studied in this work

are similar to the literature values.[39,40] Table 1 shows that E_T^N in neat $[bmim][Tf_2N]$ is higher than that of neat 1-butanol, DMF, and DMSO, indicating that $[bmim][Tf_2N]$ has more dipolarity/polarizability and/or hydrogen bond donating (HBD) ability in comparison to these solvents, while methanol has a higher E_T^N than that of $[bmim][Tf_2N]$. The higher E_T^N value of IL $[bmim][Tf_2N]$ in comparison to neat 1-butanol, DMF, and DMSO may be because the IL is ionic in nature, and the C2 hydrogen of the imidazolium cation contributes toward the HBD ability of $[bmim][Tf_2N]$.

Figure 1A, B, C, and D shows the behavior of E_T^N with the $X_{solvent}$ in binary mixtures of IL with methanol, 1-butanol, DMSO, and DMF, respectively. A cursory view of the data given in Table 1 and Figure 1 reveals that the E_T^N values deviate very much from the ideal additive values for all the four binary mixtures studied, indicating strong solvent-specific interaction between the IL and the molecular solvents. It is interesting to note that $[bmim][Tf_2N]$ + methanol (when $1 > X_{MeOH} > 0.2$), $[bmim][Tf_2N]$ + 1-butanol (over the entire composition range), and $[bmim][Tf_2N]$ + DMSO ($0 < X_{DMSO} < 0.8$) mixtures have unusual high E_T^N values indicating high dipolarity/polarizability and/or HBD ability of the mixtures. It is observed that the E_T^N value is higher than that of either of the neat component in the above-mentioned mixtures. This type of the behavior is known as "synergistic behavior".[41,42] This may be attributed to the favorable interaction between Reichardt dye 33 and the component having higher polarity. For the mixtures of IL + methanol and + 1-BuOH, E_T^N values are anomalously high. It clearly suggests the formation of new species around the probe as a result of the solvent–solvent interaction between IL $[bmim][Tf_2N]$ and MeOH/1-BuOH which have a higher dipolarity. Moreover, a sharp change in the E_T^N value at $X_{solvent} = 0.0$–0.1 and 0.9–1.0 is also observed. Such behavior of E_T^N was investigated by performing additional experiments between these ranges of $X_{solvent}$. The resulting data are given in Table 2. It is interesting to note that there is a

Table 2. E_T^N within $[bmim][Tf_2N]$ + Molecular Solvent (Methanol, 1-Butanol, DMSO, and DMF) Mixtures (at $X_{solvent} = 0.0$ to 0.1 and 0.9 to 1.0)[a]

	$[bmim][Tf_2N]$ +			
	methanol	1-butanol	DMSO	DMF
$X_{solvent}$	E_T^N	E_T^N	E_T^N	E_T^N
0	0.64	0.64	0.64	0.64
0.02	0.67	0.68	0.66	0.65
0.05	0.69	0.71	0.67	0.64
0.07	0.70	0.72	0.68	0.64
0.1	0.72	0.73	0.70	0.65
0.90	0.84	0.74	0.55	0.57
0.92	0.82	0.71	0.54	0.53
0.95	0.81	0.69	0.53	0.51
0.97	0.79	0.65	0.51	0.45
1.0	0.76	0.59	0.44	0.38

[a]The maximum error associated with E_T^N is $\leq \pm 0.01$.

gradual increase in E_T^N value from $X_{solvent} = 0.0$ to 0.1, while an opposite trend is observed from $X_{solvent} = 0.9$ to 1.0. The Pandey's group has coined the term "hyperpolarity" for such unusual behavior.[43–45] It appears that the interaction of $[bmim][Tf_2N]$ with 1-BuOH or methanol gives rise to the hyperpolarity in these mixtures. Pandey et al. have reported

such unusual behavior of E_T^N in the case of $[bmim][PF_6]$ + tetraethylene glycol (TEG) and $[bmim][PF_6]$ + poly(ethylene glycol)s (PEG) mixtures. Recently, this group also reported such unusual behavior in the case of $[bmim][PF_6]$ + 2,2,2-trifluoroethanol mixtures. They proposed that the possible cause of such synergy in solvation may be the favorable interactions (especially hydrogen bond interaction) of $[bmim]$-$[PF_6]$ with TEG and PEGs, which give rise to hyperpolarity (high dipolarity/polarizability and/or hydrogen bond donating ability). While in the case of $[bmim][Tf_2N]$ + DMF mixtures a regular decrease in the E_T^N value is observed with increase in X_{DMF}; thus, no synergistic behavior in this case is observed (Figure 1D). We believe that this useful physicochemical property inherent to these hybrid $[bmim][Tf_2N]$ + molecular solvent systems will definitely increase the importance of ILs as solvent media for several chemical applications.

3.2. Empirical Kamlet–Taft Parameters. To get full insight of such anomalous behavior of the $[bmim][Tf_2N]$ + molecular solvent mixtures, we calculated empirical Kamlet–Taft parameters (dipolarity/polarizability (π^*), hydrogen-bond donating (HBD) ability (α), and hydrogen-bond accepting (HBA) basicity (β)) of the binary mixtures.[46–49] The π^* is determined from the absorption behavior (λ_{max}) of N,N-diethyl-4-nitroaniline using eq 5, where ν_{DENA} in kK:

$$\pi^* = 8.649 - 0.314\nu_{DENA} \tag{5}$$

The values of β are estimated from the absorbance behavior (λ_{max}) of 4-nitroaniline (NA) by eq 6:

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

and, α are calculated from $E_T(30)$ and π^* by the following eq:

$$\alpha = \frac{[E_T(30) - 14.6(\pi^* - 0.23\delta) - 30.31]}{16.5} \tag{7}$$

(where δ is 1.0 for aromatics, 0.5 for polychlorinated aliphatic, and 0.0 for all other aliphatic solvents).[36] The values of π^*, α, and β of molecular solvent + $[bmim][Tf_2N]$ binary mixtures are given in Table 1. π^* is a measure of dipolarity/polarizability within the cybotactic region which can be probed by solute–solvent interaction of DENA with solvent molecules.[39,40] The ideal additive π^* with experimental values is given in Figure 2. The π^* values for methanol, 1-butanol, and DMF are less than that for neat $[bmim][Tf_2N]$ show that reduced dipolarity/polarizability of the milieu made up of these solvents, while the DMSO has a π^* value similar to $[bmim][Tf_2N]$. It is remarkable that, similar to E_T^N, the experimental π^* are higher than the ideal values calculated by $X_{solvent}$ over all compositions for all $[bmim][Tf_2N]$ + molecular solvent mixtures (Figure 2). Most importantly, π^* for all the binary mixtures are even higher than that either of the neat component. Similar behavior is observed for E_T^N (vide supra). It is worth to note that the E_T^N parameter represents both the dipolarity/polarizability and the HBD ability effect of the solvation sphere. Thus, it is concluded from the solvatochromic behavior of independent probe DENA that all $[bmim][Tf_2N]$ + molecular solvent mixtures show high dipolarity/polarizability, thereby showing a "synergistic or hyperpolarity effect". This useful characteristic (dipolarity/polarizability) of the IL−solvent mixtures may help to lend them as favorable media for several chemical applications.

The hydroxyl (OH) contributes toward the HBD ability to methanol and 1-butanol,[32] and the HBD ability of $[bmim]$-$[Tf_2N]$ is due to the C2 hydrogen of the 1,3-dialkylimidazolium cation.[29,30] The α value of $[bmim][Tf_2N]$ is found to be lower
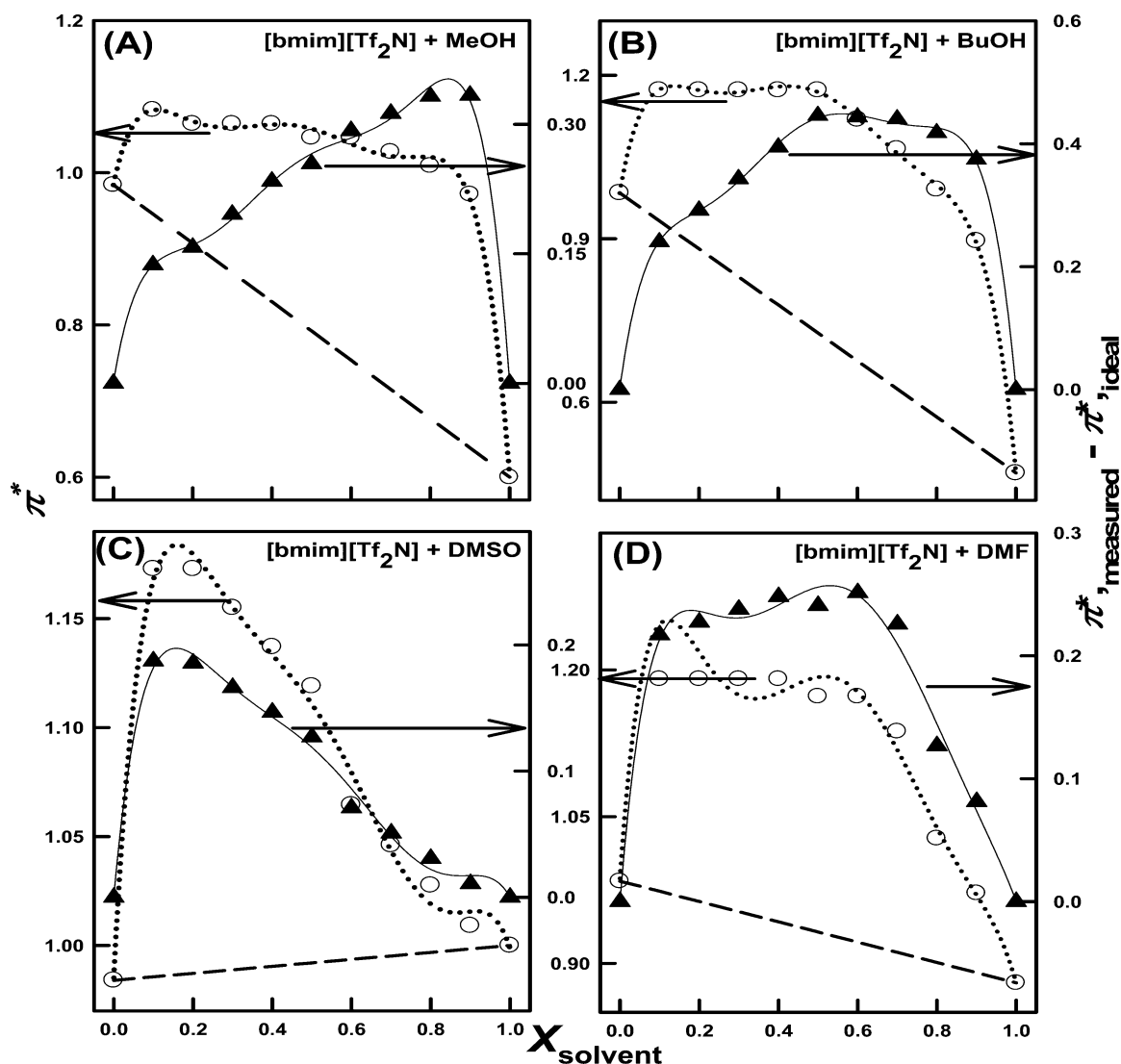
Figure 2. Variation in π^* with $X_{solvent}$ (−O−) in [bmim][Tf$_2$N] + different solvent mixtures at ambient conditions. The dashed line (- - -) shows the ideal additive π^*. The dotted line (···) shows fits according to the Redlich−Kister equation (eq 8). The deviation of experimentally observed π^* from ideality is given by (−▲−).

than that of methanol and 1-butanol. The DMSO and DMF have no HBD sites and hence have α values close to zero. The HBD ability (α) of the binary mixtures along with ideal additive α is plotted in Figure 3. The α of [bmim][Tf$_2$N] + molecular solvents furnishes much useful information regarding the investigated binary mixtures. Contrary to what we found for E_T^N and π^*, the experimentally observed α for binary mixtures shows different behavior for different binary mixtures. The α values for [bmim][Tf$_2$N] + methanol and [bmim][Tf$_2$N] + 1-butanol mixtures slightly deviate from the ideal additive values, and negative as well as positive deviations are observed (Figure 3A and B). Meanwhile in the case of [bmim][Tf$_2$N] + DMSO and in [bmim][Tf$_2$N] + DMF ($X_{DMF} > 0.3$) binary mixtures a positive deviation from ideal additive values is observed. The positive deviations in these cases may be attributed to the solvation of the probe by IL or by the new species formed by the interaction of IL with molecular solvents. However, the negative deviation of α in [bmim][Tf$_2$N] + DMF ($X_{DMF} < 0.3$) indicates solvation of the probe by DMF. It is interesting to note that the addition of small amounts of [bmim][Tf$_2$N] to

DMSO or DMF result in an unusually high HBD ability of the solvent mixture.

Figure 4 shows the plot of experimentally observed β with ideal β values estimated using $X_{solvent}$. All of the molecular solvents have a higher β value than [bmim][Tf$_2$N]. The contributor to the HBA basicity (β) of methanol and 1-butanol is the −OH group. The DMSO has one lone pair of electron on the =O group, while DMF has (−NH$_2$ and =O) as hydrogen bond accepting (HBA) sites. The Tf$_2$N$^-$ is the only contributor to the HBA basicity of [bmim][Tf$_2$N]. An increase in the β values of [bmim][Tf$_2$N] + molecular solvent mixtures is observed with an increase in $X_{solvent}$, and a negative deviation from ideal additive values is observed for all of the binary mixtures (Figure 4). The behavior of the solvatochromic parameter β also shows the anomalous physicochemical properties of [bmim][Tf$_2$N] + molecular solvent binary mixtures. Finally, it is concluded that three solvatochromic absorbance dyes, betaine dye 33, DENA, and NA, exhibit anomalous solvatochromism within binary mixtures of [bmim]-[Tf$_2$N] and molecular solvents.
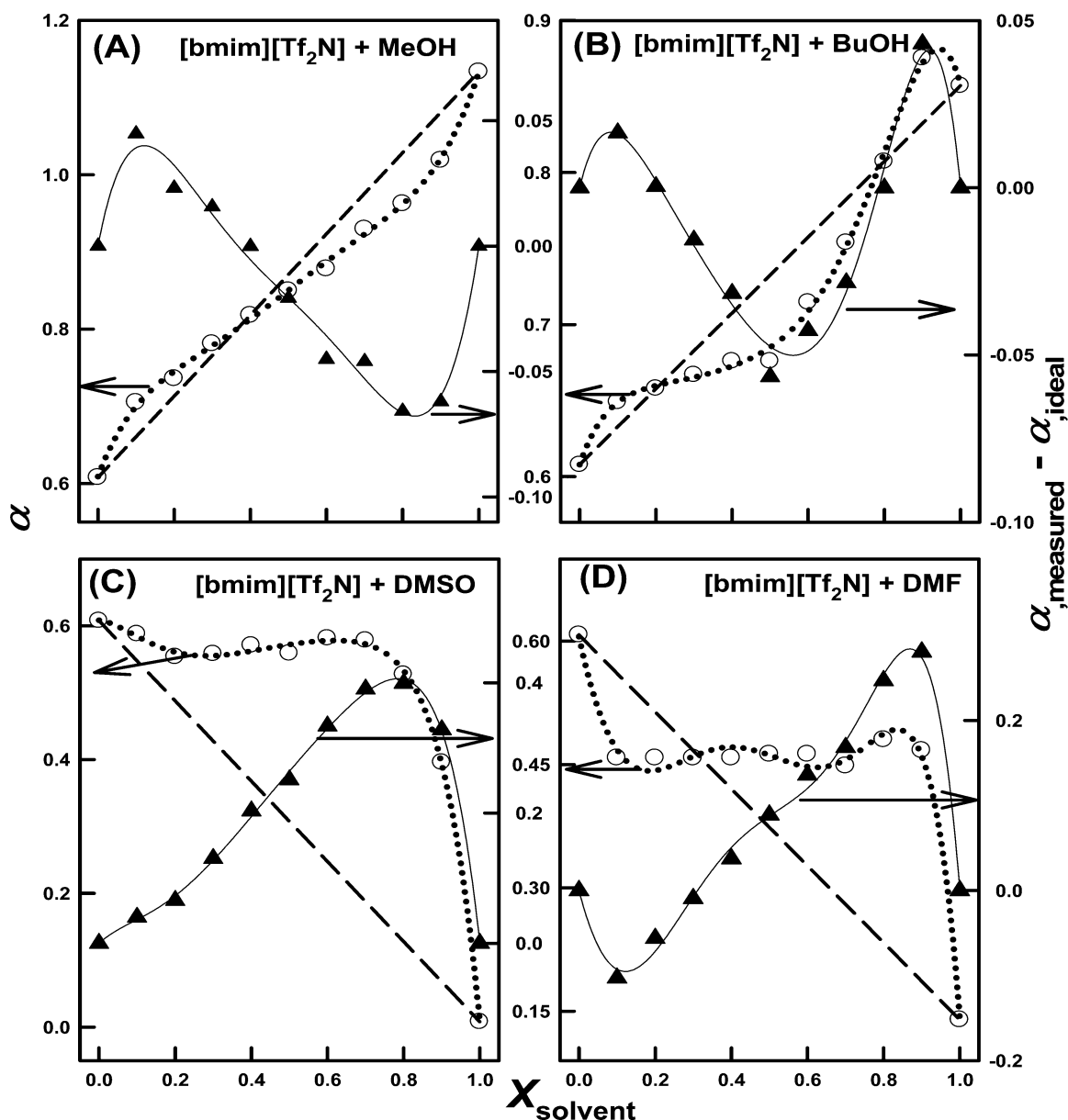
Figure 3. Variation in α with $X_{solvent}$ (−O−) in $[bmim][Tf_2N]$ + different solvent mixtures at ambient conditions. The dashed line (- - -) shows the ideal additive α. The dotted line (···) shows fits according to the Redlich−Kister equation (eq 8). The deviation of experimentally observed α from ideality is given by (−▲−).

3.3. Solvatochromic Parameters and the Redlich–Kister Model.

In the past few decades, computational chemistry has shown its importance in correlating/predicting of physicochemical properties/solvatochromic parameters of binary mixtures by using experimental results. Empirical solvatochromic parameters have been proven useful in predicting/correlating different physicochemical properties of solvents.[50−52] In the present study, the combined nearly ideal binary solvent/Redlich−Kister (CNIBS/R-K) equation is used to explore the role of solute−solvent and/or solvent−solvent interaction on various solvatochromic parameters and for the prediction of the excess solvatochromic properties.[53−55] The solvatochromic parameter (SP) of a binary mixture, according to the CNIBS/R-K model, can be given as

$$SP_m = x_1 SP_1^0 + x_2 SP_2^0 + x_1 x_2 \sum_{j=0}^{k} A_j (x_1 - x_2)^j \qquad (8)$$

where SP_m, SP_1^0, and SP_2^0 represent the values of solvatochromic parameters of the binary systems and pure solvents 1 and 2, respectively, and x_1 and x_2 represent the mole fractions of the neat solvents in the binary system. A_j represents the equation coefficients, and j is the degree of the polynomial expansion. The values of j may change for a particular system.

The analysis of physicochemical properties with respect to the mole fraction by CNIBS/R-K theory gives useful information regarding the solvation behavior of the probes. Further, the solute−solvent/solvent−solvent interactions present in the mixtures can be explored with the help of this model. The positive values of ΔE_T^N, $\Delta\alpha$, and $\Delta\pi^*$ (Figures 1 to 4) indicate that the probes are mainly solvated by the more polar solvent, IL, or by a new entity (IL−solvent complex) with
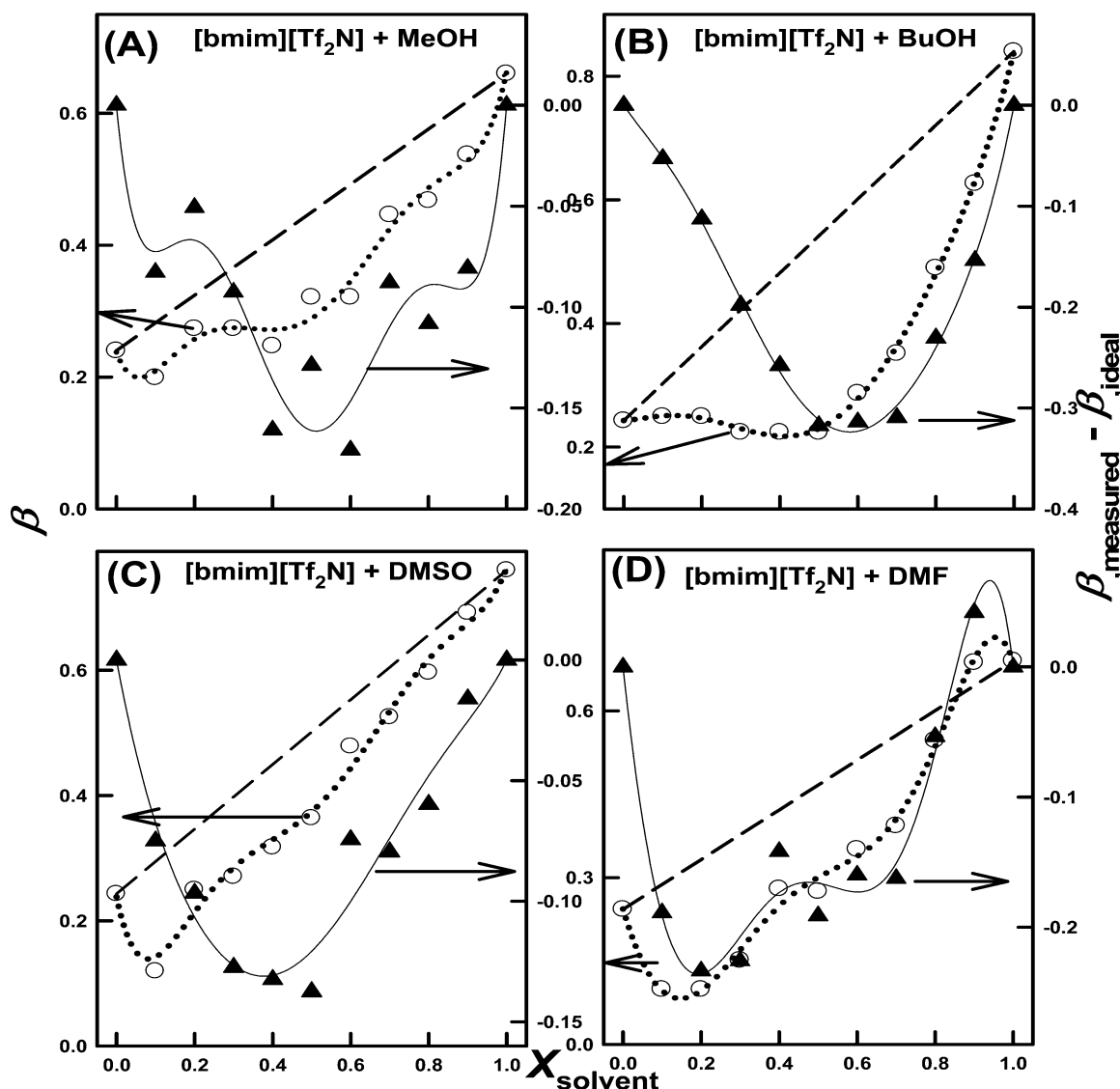
Figure 4. Variation in β with $X_{solvent}$ (−O−) in $[bmim][Tf_2N]$ + different solvent mixtures at ambient conditions. The dashed line (- - -) shows the ideal additive β. The dotted line (···) shows fits according to the Redlich−Kister equation (eq 8). The deviation of experimentally observed β from ideality is given by (−▲−).

a higher polarity. It is well-documented that the cation and anion of IL strongly interact with the molecular solvents and form a IL−solvent complex. The solvation of the probes with this IL−solvent complex may be a reason for "hyperpolarity" of the solvent mixtures, vide supra. While, the negative value of $\Delta\beta$ shows that the probe is mainly solvated by IL $[bmim]$-$[Tf_2N]$ initially at lower solvent mole fraction, and the solvation of probe is governed by the molecular solvent molecules at higher $X_{solvent}$.

The results of the regression analysis of experimental data according to eq 8 are given in Table 3 where the standard deviation (σ) is determined by eq 9

$$\sigma = \left(\frac{\sum_{i=1}^{n} (SP_i^{exp} - SP_i^{cal})^2}{n} \right)^{1/2}$$

(9)

where n represents data points, and SP_i^{exp} and SP_i^{cal} indicate the measured and calculated solvatochromic parameters of the binary mixtures of $[bmim][Tf_2N]$ with molecular organic solvents. The value of $\sigma = 0.0093$ (for $j = 4$) indicates that the

CNIBS/R K (eq 8) model fairly predicts the solvatochromic parameters of binary mixtures. The cross-validation approach is very helpful and reliable to test the predictive significance of any model.[56] Figure 5 shows the plot of the calculated values of solvatochromic parameters $[E_T^N, \pi^*, \alpha,$ and $\beta]$ derived from the CNIBS/R K model (eq 8) against the experimental values for all of the studied mixtures, the following linear equation indicates good agreement between calculated and experimental values:

$$SP_m^{cal} = 1.008(\pm 0.0119)SP_m^{exp} - 0.0007(\pm 0.0103)$$

$$n = 176 \qquad (R^2 = 0.9987) \qquad \sigma = 0.0093 \qquad (10)$$

The dotted lines linking $E_T^N, \pi^*, \alpha,$ and β in Figures 1, 2, 3, and 4, respectively, represent the goodness of fit of the experimental data values with the CNIBS/R-K model (with $j = 4$). Finally, it is proposed that the CNIBS/R-K equation is fairly good enough to correlate/predict the solvatochromic parameters value within $[bmim][Tf_2N]$ + molecular organic solvent mixtures at ambient conditions.

Table 3. Average of Redlich−Kister Parameters, Standard Deviation, and R^2 for the Solvatochromic Parameters (E_T^N, π^*, α, and β) According to eq 8 for [bmim][Tf$_2$N] + Molecular Solvents (Methanol, 1-Butanol, DMSO, and DMF) Mixtures at Ambient Conditions

| SP	A_0	A_1	A_2	A_3	A_4	σ	R^2
			[bmim][Tf$_2$N] + MeOH				
E_T^N	0.3250	0.0265	0.0275	0.1558	1.1866	0.0032	0.9960
π^*	1.0630	0.4824	0.2122	1.3124	3.3662	0.0064	0.9976
α	−0.0824	−0.2917	−0.0950	−0.6176	0.0697	0.0051	0.9987
β	−0.6445	−0.107	1.5187	−0.0242	−3.006	0.0180	0.9832
			[bmim][Tf$_2$N] + BuOH				
E_T^N	0.5155	0.0750	0.0776	0.4851	1.8224	0.0026	0.9972
π^*	1.7690	0.4477	−0.2747	0.7013	4.4083	0.0044	0.9995
α	−0.1899	−0.1645	0.3610	0.5157	0.6574	0.0042	0.9976
β	−1.2461	−0.6086	0.6045	−0.1108	−0.6465	0.0064	0.9989
			[bmim][Tf$_2$N] + DMSO				
E_T^N	0.5092	0.3614	0.3662	−0.3009	0.4244	0.0042	0.9965
π^*	0.4751	−0.5574	−0.0255	−0.9165	1.5808	0.0067	0.9903
α	1.0560	1.3724	0.8640	0.9948	0.9817	0.0060	0.9986
β	−0.5095	0.0653	0.8767	1.1879	−2.6454	0.0199	0.9897
			[bmim][Tf$_2$N] + DMF				
E_T^N	0.5189	0.3605	−0.0583	0.7458	1.4212	0.0044	0.9964
π^*	1.0236	0.1540	−0.0922	−1.7559	1.5367	0.0098	0.9918
α	0.3505	0.6049	0.0759	3.0311	1.4832	0.0091	0.9925
β	−0.6647	−0.1054	−1.5012	2.7595	2.0298	0.0149	0.9946
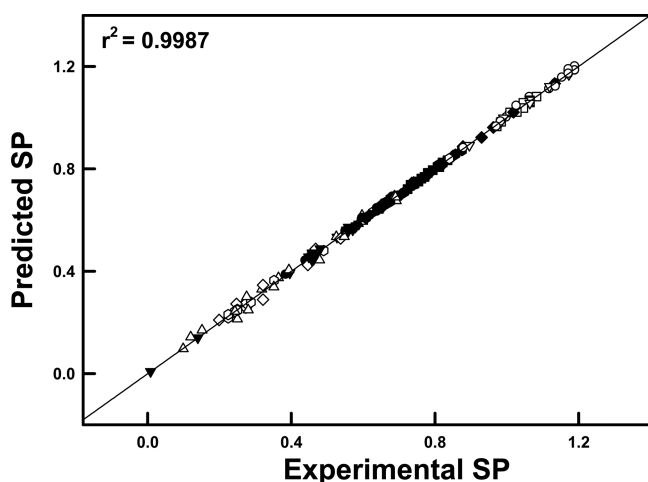
Figure 5. Predicted values of solvatochromic parameters from the correlation equation versus its experimental values for [bmim][Tf$_2$N] + molecular solvent mixtures (results of the fit are provided in eq 10).

3.4. Solvation Model. In past decades, the utility of the solvation models to delineate the behavior of the solvatochromic probes in solvent mixtures has increased noticeably.[13,18] These simple models have shown their importance in describing the solvation behavior of probes and the structure−property relationship of the mixed solvent systems. The solute−solvent and solvent−solvent interaction present in the solvent mixtures can also be explored with the help of solvation models. In addition, these models are also helpful to describe the synergism of the solvent mixtures. Buhvestov et al.[57] and Skwierczynsi and Connors[58] used the preferential solvation model first time; later other researchers applied this model for describing the solvation phenomena in solvent mixtures.[31−34] According to this model, the solvent exchange phenomena of the two solvents can be given by eqs 11 and 12

$$I(S1)_2 + 2S2 \leftrightarrow I(S2)_2 + 2S1 \tag{11}$$

$$I(S1)_2 + S2 \leftrightarrow I(S12)_2 + S1 \tag{12}$$
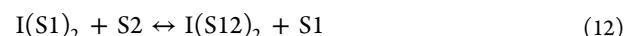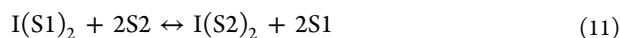
where I, (S1 and S2), and S12 indicate the probe, for pure solvents, and for the mixed solvent, respectively. I(S1), I(S2), and I(S12) correspond the probe microsphere made up of predominately by the S1 solvent, by the S2 solvent, and by the S12 mixed solvent complex, respectively. The exchange phenomena of solvent S1 by solvent S2 within the solvation microenvironment of the probe are represented by eq 11, while eq 12 represents the exchange of solvent S1 by the S12 species.[33] The constants $f_{2/1}$ and $f_{12/1}$ corresponding to the phenomena described by eq 11 and eq 12, respectively, can be estimated using eqs 13−15.

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \tag{13}$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \tag{14}$$

$$f_{12/2} = \frac{f_{12/1}}{f_{2/1}} \quad \text{or} \quad f_{12/2} = \frac{x_{12}^s/x_2^s}{x_2^0/x_1^0} \tag{15}$$

where x_i^s and x_i^0 represent the solvent mole fractions in the cybotactic milieu of the probe and in the bulk, respectively; $f_{12/2}$ corresponds to the ratio of $f_{12/1}$ to $f_{2/1}$ in cybotactic milieu.[33]

With the help of pure solvent properties (Y_1 and Y_2), the solvatochromic property of binary mixture (Y_{12}) can be estimated by eq 16. The ΔY is the correction term (eq 17), where k is called the proportionality constant.

$$Y = \frac{Y_1(1 - x_2^0)^2 + Y_2 f_{2/1}(x_2^0)^2 + Y_{12}f_{12/1}(1 - x_2^0)x_2^0}{(1 - x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1 - x_2^0)x_2^0}$$
$$+ \Delta Y \tag{16}$$

Table 4. Parameters Obtained by Application of the Preferential Solvation Model (eq 16) to the Experimental Wave Numbers (cm^{-1}) of Indicators Betaine Dye 33, *N,N*-Diethyl-4-nitroaniline, and 4-Nitroaniline in the Selected Binary Mixtures

probe	solvent	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	R^2	k
Betaine dye 33	IL/MeOH	20.96	22.42	22.09	4.04	24.25	6.00	0.9953	6.91
	IL/BuOH	20.96	20.32	22.08	0.57	50.81	89.14	0.9996	3.64
	IL/DMSO	20.88	18.76	21.57	3.32	61.45	18.50	0.9928	−5.84
	IL/DMF	20.95	18.08	21.05	26.83	1094.76	40.80	0.9920	−6.02
N,N-diethyl-4-nitroaniline	IL/MeOH	24.12	25.59	25.24	0.014	0.084	6.00	0.9863	−4.44
	IL/BuOH	24.41	26.03	23.67	4.36	46.37	10.63	0.9956	−0.01
	IL/DMSO	24.41	24.34	23.54	13.72	27.98	2.03	0.9926	1.82
	IL/DMF	24.40	24.53	23.59	2.37	33.89	14.29	0.9790	4.38
4-nitroaniline	IL/MeOH	27.45	27.54	27.24	32.75	316.12	9.65	0.9563	−5.82
	IL/BuOH	27.56	27.60	26.87	5.76	111.71	19.39	0.7377	−3.18
	IL/DMSO	27.47	25.96	24.51	1.77	1.38	0.78	0.9997	6.67
	IL/DMF	27.46	26.32	25.63	27.42	4.39	0.16	0.9784	5.83

$$\Delta Y = \frac{kf_{2/1}(x_2^0)^2[(1-x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0/2]}{[(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0]^2} \quad (17)$$

The wave numbers of the betaine dye 33, DENA, and NA at whole composition range have been fitted to the proposed eq 16, and the parameters obtained are given in Table 4.

Betaine dye 33 is the negative solvatochromic probe, and its spectral response changes with the dipolarity/polarizability and HBD ability of medium.[36] The Y_1, Y_2, and Y_{12} corresponds to the wavenumbers of probe in IL, solvent, and IL−solvent complex, respectively. The Y_{12} values are higher than the Y_1 and Y_2 values, except in the case of the IL−MeOH mixture, which indicate a higher dipolarity/polarizability of the IL−solvent complex, made up by solvent−solvent interactons of IL [bmim][Tf$_2$N] with solvent molecules. In the case of the IL−MeOH mixture $f_{2/1}$ and $f_{12/1}$ is higher than unity, which indicate that the solvation of the Reichardt dye 33 by MeOH and IL−MeOH complexes. While, in the case of IL+ 1-BuOH mixture, the $f_{2/1}$ < 1 and $f_{12/1}$ >1 indicate the solvation of Reichardt dye 33 with [bmim][Tf$_2$N] and the IL−BuOH complex. The [bmim][Tf$_2$N] + DMSO, and + DMF mixtures also show that $f_{2/1}$ and $f_{12/1}$ values are higher than unity which clearly indicate the solvation of probe by solvent (DMSO or DMF) and hydrogen-bonded IL−molecular solvent complex. *N,N*-Diethyl-4-nitroaniline is a positive solvatochromic indicator, and its spectral response is changed with the dipolarity/polarizability of the solvent. Because of the positive solvatochromism of DENA, a decrease in the solvatochromic property with an increase in the wavenumber of maximum absorption is observed. Table 4 shows that, except for the IL−MeOH mixture, the wavenumbers of maximum absorptions of all mixed solvent S12 (Y_{12}) are lower than Y_1 and Y_2 values, indicating stronger dipolarity/polarizability of the IL−molecular solvent complex (S12) than that of IL and molecular solvents. The $f_{2/1}$ and $f_{12/1}$ are < 1 for the IL+ MeOH mixture, while greater than unity for all mixtures studied, which indicates that the probe is preferentially solvated by the IL [bmim]-[Tf$_2$N] in the IL + MeOH mixture, while by solvent and IL-solvent complex (S12) in all the other mixtures. Hence, high dipolarity/polarizability (hyperpolarity behavior) as shown in Table 1 and Figure 2 is primarily due to the solvent−solvent interaction between IL and other solvents. 4-Nitroaniline also shows positive solvatochromism, and its spectral response depends upon both the solvent dipolarity/polarizability and the solvent HBA basicity. In all of the studied mixtures $f_{2/1}$ and $f_{12/1}$ values are greater than unity, indicating preferential solvation of

the indicator by solvents and the IL−solvent complex, which is the cause of a gradual increase in the β values of the mixtures.

Thus, the model clearly shows that the solvent−solvent interaction is the main reason for the hyperpolarity in polarity parameters; however, the role of solute−solvent interaction within the mixture cannot be neglected.

On the whole, the solvation model applied here clearly corroborates the formation of the new IL−molecular solvent complex in the mixture which gives rise to the synergistic behavior of the [bmim][Tf$_2$N] + molecular solvent mixtures.

4. CONCLUSIONS

In summary, we conclude that the behavior of the solvatochromic absorbance probe greatly deviates from ideality in IL + molecular solvent binary mixtures. The solvent mixtures made up of [bmim][Tf$_2$N] and molecular solvents (MeOH, BuOH, DMSO, and DMF) show interesting and unusual solvatochromism, termed as "hyperpolarity". The values of E_T^N and π^* parameters are found to be higher even than that of neat [bmim][Tf$_2$N] and molecular solvents. This synergistic behavior in E_T^N and π^* indicates strong solute−solvent and solvent−solvent interaction present in the systems. The interaction of C2 hydrogen of the [bmim$^+$] cation with lone pair electrons of the molecular solvents and attraction of [Tf$_2$N$^-$] with hydrogen of the protic solvent forms a HBD−HBA network in the mixture, which may impart synergistic behavior to these IL−molecular solvent systems. We believe these favorable physicochemical properties of the binary solvent mixtures will help to expose ILs as favorable solvents in several chemical and biochemical applications.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail address: anwarali.chem@gmail.com; aali2@jmi.ac.in.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Baker, G. A.; Baker, S.; Pandey, S.; Bright, F. V. An analytical view of ionic liquids. *Analyst* **2005**, *130*, 800−808.

(2) *Ionic Liquids in Synthesis*; Wasserscheid, P., Welton, P., Eds.; Wiley-VCH: Weinheim, Germany, 2003.

(3) Hallett, J. P.; Welton, T. Room temperature ionic liquids: Solvents for synthesis and catalysis 2. *Chem. Rev.* **2011**, *111*, 3508−3576.

(4) Pandey, S. Analytical applications of ionic liquids: A review of recent efforts. *Anal. Chim. Acta* **2006**, *556*, 38−45.

(5) *Ionic Liquids: Industrial Applications for Green Chemistry*; Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 818; American Chemical Society: Washington, DC, 2002.

(6) *Ionic Liquids as Green Solvents: Progress and Prospects*, Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series 856; American Chemical Society: Washington, DC, 2003.

(7) *Ionic Liquids III: Fundamentals, Challenges, and Opportunities*, Rogers, R. D., Seddon, K. R., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2005.

(8) *Electrochemical Aspects of Ionic Liquids*; Ohno, H., Ed.; Wiley-Interscience: New York, 2005.

(9) Poole, C. F. Chromatographic and spectroscopic methods for the determination of solvent properties of room temperature ionic liquids. *J. Chromatogr., A* **2004**, *1037*, 49−82.

(10) Liu, J. F.; Jonsson, J. A.; Jiang, G. B. Application of ionic liquids in analytical chemistry. *Trends Anal. Chem.* **2005**, *24*, 20−27.

(11) Wu, H.-H.; Yang, F.; Cui, P.; Tang, J.; He, M.-Y. An efficient procedure for protection of carbonyls in Brønsted acidic ionic liquid [Hmim]BF₄. *Tetrahedron Lett.* **2004**, *45*, 4963−4965.

(12) Palimkar, S. S.; Siddiqui, S. A.; Daniel, T.; Lahoti, R. J.; Srinivasan, K. V. Ionic liquid-promoted regiospecific Friedlander Annulation: Novel synthesis of quinolines and fused polycyclic quinolines. *J. Org. Chem.* **2003**, *68*, 9371−9378.

(13) Muchowski, J. M.; Maddox, M. L. Concerning the mechanism of the Friedländer quinoline synthesis. *Can. J. Chem.* **2004**, *82*, 461−478.

(14) Morrison, D. W.; Forbes, D. C.; Davis, J. H., Jr. Base promoted reactions in ionic liquid solvents. The Knoevenagel and Robinson Annulation reactions. *Tetrahedron Lett.* **2001**, *42*, 6053−6055.

(15) Forbes, D. C.; Law, A. M.; Morrison, D. W. The Knoevenagel Reaction: Analysis and recycling of the ionic liquid medium. *Tetrahedron Lett.* **2006**, *47*, 1699−1703.

(16) Sun, P.; Armstrong, D. Ionic liquids in analytical chemistry. *Anal. Chim. Acta* **2010**, *661*, 1−16.

(17) Xu, Y.; Wang, E. Ionic liquids used in and analyzed by capillary and microchip electrophoresis. *J. Chromatogr., A* **2009**, *1216*, 4817−4823.

(18) Tholey, A.; Heinzle, E. Ionic (liquid) matrices for matrix-assisted laser desorption/-ionization mass spectrometry-Applications and perspectives. *Anal. Bioanal. Chem.* **2006**, *386*, 24−37.

(19) Ali, M.; Kumar, V.; Pandey, S. Unusual fluorescein prototropism within aqueous acidic 1-Butyl-3-methylimidazolium tetrafluoroborate solution. *Chem. Commun.* **2010**, *46*, 5112−5114.

(20) Kumar, V.; Baker, G. A.; Pandey, S. Ionic liquid-controlled J-versus H-aggregation of cyanine dyes. *Chem. Commun.* **2011**, *47*, 4730−4732.

(21) Sarkar, A.; Ali, M.; Baker, G. A.; Tetin, S. Y.; Ruan, Q.; Pandey, S. Multiprobe spectroscopic investigation of molecular-level behavior within aqueous 1-Butyl-3-methylimidazolium tetrafluoroborate. *J. Phys. Chem. B* **2009**, *113*, 3088−3098.

(22) Mondal, T.; Das, A. K.; Sasmal, D. K.; Bhattacharya, K. Excited state proton transfer in ionic liquid mixed micelles. *J. Phys. Chem. B* **2010**, *114*, 13136−13142.

(23) Bhattacharya, B.; Samanta, A. Excited-state proton-transfer dynamics of 7-Hydroxyquinoline in room temperature ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 10101−10106.

(24) Ali, M.; Kumar, V.; Baker, S. N.; Baker, G. A.; Pandey, S. J-aggregation of ionic liquid solutions of Meso-tetrakis(4-sulfonatophenyl)porphyrin. *Phys. Chem. Chem. Phys.* **2010**, *12*, 1886−1894.

(25) Naushad, Mu.; Al-Othman, Z.; Khan, A. B.; Ali, M. Effect of ionic liquid on activity, stability, and structure of enzymes: A Review. *Int. J. Biol. Macromol.* **2012**, *51*, 555−560.

(26) Ali, M.; Sarkar, A.; Tariq, M.; Ali, A.; Pandey, S. Dilute aqueous 1-Butyl-3-methylimidazolium hexafluorophosphate: Properties and solvatochromic probe behavior. *Green Chem.* **2007**, *9*, 1252−1258.

(27) Mancini, P. M.; Fortunato, G. G.; Adam, C. G.; Vottero, L. R. Solvent effects on chemical processes: New solvents designed on the basis of the molecular−microscopic properties of (Molecular Solvent + 1,3-Dialkylimidazolium) binary mixtures. *J. Phys. Org. Chem.* **2008**, *21*, 87−95.

(28) Fortunato, G. G.; Mancini, P. M.; Bravo, M. V.; Adam, C. G. New solvents designed on the basis of the molecular-microscopic properties of binary mixtures of the type (Protic molecular solvent + 1-Butyl-3-methylimidazolium-based ionic liquid). *J. Phys. Chem. B* **2010**, *114*, 11804−11819.

(29) Fletcher, K. A.; Pandey, S. Solvatochromic probe behavior within ternary room-temperature ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate + ethanol + water Solutions. *J. Phys. Chem. B* **2003**, *107*, 13532−13539.

(30) Fletcher, K. A.; Pandey, S. Solvatochromic probe behavior within binary room temperature ionic liquid 1-Butyl-3-Methyl Imidazolium hexafluorophosphate plus ethanol solutions. *Appl. Spectrosc.* **2002**, *56*, 1498−1503.

(31) Khupse, N. D.; Kumar, A. Delineating solute-solvent interactions in binary mixtures of ionic liquids in molecular solvents and preferential solvation approach. *J. Phys. Chem. B* **2011**, *115*, 711−718.

(32) Harifi-Mood, A. R.; Habibi-Yangjeh, A.; Gholami, M. R. Solvatochromic parameters for binary mixtures of 1-(1-Butyl)-3-methylimidazolium tetrafluoroborate with some protic molecular solvents. *J. Phys. Chem. B* **2006**, *110*, 7073−7078.

(33) Salari, H.; Khodadi-Moghaddam, M.; Harifi-Mood, A. R.; Gholami, M. R. Preferential solvation and behavior of solvatochromic indicators in mixtures of an ionic liquid with some molecular solvents. *J. Phys. Chem. B* **2010**, *114*, 9586−9593.

(34) Moita, M. C. J.; Santos, A. F. S.; Silva, J. F. C. C.; Lampreia, I. M. S. Polarity of some [NR₁R₂R₃R₄]⁺[Tf2N]⁻ ionic liquids in ethanol: Preferential solvation versus solvent−solvent interactions. *J. Chem. Eng. Data* **2012**, *57*, 2702−2709.

(35) Mellein, B. R.; Aki, N. V. K.; Ladewski, R. L.; Brennecke, J. F. Solvatochromic studies of ionic liquid/organic mixtures. *J. Phys. Chem. B* **2007**, *111*, 131−138.

(36) *Solvents and Solvent Effects in Organic Chemistry*; Reichardt, C.; Wiley-VCH: Weinheim, Germany, 2003.

(37) Reichardt, C. Solvatochromic dyes as solvent polarity indicators. *Chem. Rev.* **1994**, *94*, 2319−2358.

(38) Singh, P.; Pandey, S. Solute−solvent interactions within aqueous poly(ethylene glycol): Solvatochromic probes for empirical determination and preferential solvation. *Green Chem.* **2007**, *9*, 254−261.

(39) Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. Investigations of solvent-solute interactions in room temperature ionic liquids using solvatochromic dyes. *J. Chem. Soc., Perkin Trans.* **2001**, *2*, 433−435.

(40) Crowhurst, L.; Mawdsley, P. R.; Perez-Arlandis, J. M.; Salter, P. A.; Welton, T. Solvent-solute interactions in ionic liquids. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2790−2794.

(41) *Solvatochromism*; Suppan, P., Ghoneim, N., Eds.; Royal Society of Chemistry: Cambridge, 1997.

(42) *Solvent Mixtures: Properties and Selective Solvation*; Marcus, Y.; Marcel Dekker: New York, 2002, and references therein.

(43) Sarkar, A.; Trivedi, S.; Baker, G. A.; Pandey, S. Multi-Probe spectroscopic evidence for 'Hyperpolarity' within 1-Butyl-3-methylimidazolium hexafluorophosphate mixtures with tetraethylene glycol. *J. Phys. Chem. B* **2008**, *112*, 14927−14936.

(44) Sarkar, A.; Trivedi, S.; Baker, G. A.; Pandey, S. Unusual solvatochromism within 1-Butyl-3-methylimidazolium hexafluorophosphate + poly(Ethylene Glycol) mixtures. *J. Phys. Chem. B* **2008**, *112*, 9042−9049.

(45) Trivedi, S.; Baker, G. A.; Pandey, S. Pronounced hydrogen bonding giving rise to apparent probe hyperpolarity in ionic liquid mixtures with 2,2,2-trifluoroethanol. *J. Phys. Chem. B* **2012**, *116*, 1360−1369.

(46) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. The solvatochromic comparison method. 6. The π* scale of solvent polarities. *J. Am. Chem. Soc.* **1977**, *99*, 6027−6038.

(47) Taft, R. W.; Kamlet, M. J. The solvatochromic comparison method. 2. The α-scale of solvent hydrogen-bond donor (HBD) acidities. *J. Am. Chem. Soc.* **1976**, *98*, 2886−2894.

(48) Kamlet, M. J.; Taft, R. W. The solvatochromic comparison method. I. The β scale of solvent hydrogen-bond acceptor (HBA) basicities. *J. Am. Chem. Soc.* **1976**, *98*, 377−383.

(49) Kamlet, M. J.; Abboud, J. L.; Abraham, M. H.; Taft, R. W. Linear solvation energy relationships. 23. A comprehensive collection of the solvatochromic parameters, π*, α, and β, and some methods for simplifying the generalized solvatochromic equation. *J. Org. Chem.* **1983**, *48*, 2877−2887.

(50) Redlich, O. J.; Kister, A. T. Thermodynamics of non-electrolyte solutions, x−y−t relations in a binary system. *Ind. Eng. Chem.* **1948**, *40*, 341−345.

(51) Hernandez, C. E.; Coym, K. S.; Roy, L. E.; Powell, J. R.; Acree, W. E. Solubility of pyrene in binary (alkane + 2-butanol) solvent mixtures. *J. Chem. Thermodyn.* **1998**, *30*, 37−42.

(52) Al-Sharrah, G. K.; Ali, S. H.; Fahim, M. A. Solubility of anthracene in two binary solvents containing toluene. *Fluid Phase Equilib.* **2002**, *193*, 191−201.

(53) Wold, S.; Sjostrom, M.; Eriksson, L. PLS-regression: a basic tool of chemometrics. *Chemom. Intell. Lab. Syst.* **2001**, *58*, 109−130.

(54) Wang, J.; Tian, Y.; Zhao, Y.; Zhou, K. A volumetric and viscosity study for the mixtures of 1-n-butyl-3-methylimidazolium tetrafluoroborate ionic liquid with acetonitrile, dichloromethane, 2-butanone and N,N-dimethylformamide. *Green Chem.* **2003**, *5*, 618−622.

(55) Rodriguez, H.; Brennecke, J. F. Temperature and Composition Dependence of the Density and Viscosity of Binary Mixtures of Water + Ionic Liquid. *J. Chem. Eng. Data* **2006**, *51*, 2145−2155.

(56) Gonzalez, E. J.; Alonso, L.; Dominguez, A. Physical Properties of Binary Mixtures of the Ionic Liquid 1-Methyl-3-octylimidazolium Chloride with Methanol, Ethanol, and 1-Propanol at T = (298.15, 313.15, and 328.15) K and at P = 0.1 MPa. *J. Chem. Eng. Data* **2006**, *51*, 1446−1452.

(57) Buhvestov, U.; Rived, F.; Rafols, C.; Bosch, E.; Roses, M. Solute−solvent and solvent−solvent interactions in binary solvent mixtures. Part 7. Comparison of the enhancement of the water structure in alcohol−water mixtures measured by solvatochromic indicators. *J. Phys. Org. Chem.* **1998**, *11*, 185−192.

(58) Skwierczynsi, R. D.; Connors, K. A. Solvent effects on chemical processes. Part 7. Quantitative description of the composition dependence of the solvent polarity measure ET(30) in binary aqueous-organic solvent mixtures. *J. Chem. Soc., Perkin Trans.* **1994**, *2*, 467−472.