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Solvatochromic Parameters and Preferential Solvation Behavior for Binary Mixtures of 1,3-Dialkylimidazolium Ionic Liquids with Water

Shan Ding, Li-gang Wei*, Kun-lan Li, Ying-chong Ma

School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian 116034, China

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Binary mixtures of 1,3-dialkylimidazolium based ionic liquids (ILs) and water were selected as solvent systems to investigate the solute-solvent and solvent-solvent interactions on the preferential solvation of solvatochromic indicators at 25 °C. Empirical solvatochromic parameters, dipolarity/polarizability (π^*), hydrogen-bond donor acidity (α), hydrogen-bond acceptor basicity (β), and Reichardt's polarity parameters (E_T^N) were measured from the ultraviolet-visible spectral shifts of 4-nitroaniline, 4-nitroanisole, and Reichardt's dye. The solvent properties of the IL-water mixtures were found to be influenced by IL type and IL mole fraction (x_{IL}). All these studied systems showed the non-ideal behavior. The maximum deviation to ideality for the solvatochromic parameters can be obtained in the x_{IL} range from 0.1 to 0.3. For most of the binary mixtures, the π^* values showed the synergistic effects instead of the E_T^N , α and β values. The observed synergy extent was dependent on the studied systems, such as the dye indicator and IL type. A preferential solvation model was utilized to gather information on the molecular interactions in the mixtures. The dye indicator was preferentially solvated on the following trend: IL>IL-water complex>water.

Key words: Solvatochromic parameters, Preferential solvation, Ionic liquid, Water

I. INTRODUCTION

Ionic liquids (ILs), as potential environment-friendly solvents, have gained a great deal of interest with a wide range of applications because of their insignificant vapor pressure, high thermal and chemical stabilities, good solvating capabilities, and excellent recyclability [1, 2]. To expand the application field of ILs, recent researchers have been focusing on the mixed systems of IL and other solvent, such as alcohols [3] and dimethyl sulfoxide [4]. These mixed systems have been credited with special physicochemical properties in comparison with pure IL. However, the study of physicochemical properties is more complex in the mixed solvent than that in pure IL [5]. Intermolecular interactions occur between IL and other solvent in the mixture, as well as intramolecular interactions between the cation and anion of IL [6, 7].

Investigating solvent-solvent interactions using solvatochromic indicators is simple and effective because the transition energy of the indicator depends on the solvating sphere composition and properties [8]. Solvatochromic indicator studies offer direct information on solvent properties, such as polarity, dipolarity/polarizability (π^*), and hydrogen-bond donating/accepting capabilities. Reichardt proposed the sol-

vatochromic zwitterionic pyridinium *N*-phenolate betaine dyes, which depended on the observed changes in the ultraviolet-visible (UV-Vis) spectral band shift, to indicate solvent polarity [8–10]. Reichardt's parameter $E_T(30)$ and its dimensionless normalized solvent polarity parameter E_T^N quantify the polarity and acidity, but are not dependent on polarizability. On this basic finding, Kamlet and Taft [11–14] exploited a multi-parameter polarity system, solvatochromic parameters, consisting of hydrogen-bond donor (HBD) acidity (α) [12], hydrogen-bond acceptor (HBA) basicity (β) [13], and π^* [14], to study solute-solvent and solvent-solvent interactions. Solvatochromism has been proven to be successful in correlating intermolecular interactions in the binary mixtures [15]. Beniwal *et al.* [16] explored the polarity parameters in both hydrophilic and hydrophobic ILs. The results revealed that synergistic effects were generated as a result of high β values of alcohols compared with those of the ILs. A strong correlation was observed in the β values and hydrophobicities of pure ILs, suggesting that β values can play a role in describing synergism. Similarly, Ali *et al.* investigated the role of the solvent microsphere in changing the behavior of the solvatochromic absorbance probe within binary solvent mixtures of ILs with common molecular organic solvents [17]. The polarity parameters, E_T^N , and π^* of the mixtures, indicated the "hyperpolarity" behavior on addition of molecular solvents to ILs.

The binary mixtures of IL and water (IL-water) have been widely used in separation [18], organic reaction

* Author to whom correspondence should be addressed. E-mail: wei_ligang@hotmail.com, Tel.: +86-411-86323726

[19], material synthesis [20], pretreatment and delignification of lignocellulosic biomass [21, 22]. Solvent properties of IL-water mixtures have also been studied using solvatochromic indicator [23–26]. Adam *et al.* explored the solvatochromic response of dipolarity micro-sensors based on Reichardt's $E_T(30)$ and Kamlet-Taft solvent parameters and the application of the solvent exchange model [25]. The results confirmed the formation of different intersolvent complexes in the binary mixtures of water and 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4C_1IM]BF_4$)/1-butyl-3-methylimidazolium bromide ($[C_4C_1IM]Br$). These complexes provided hydrogen-bonds or electron pairs to the polar network, respectively. Nayak *et al.* investigated the solvatochromic characterization of the mixtures of a series of ILs and water aimed to describe the changes in the solvent environment as a function of composition [26]. They found that the critical solution behavior of poly(*N*-isopropyl acrylamide) in IL-water mixtures was correlated to the values of α and β . These specific properties of IL-water mixtures make them more advantageous for a number of technical processes and then reduce the effect of the ILs on environment. To profit from IL-water mixtures, their solvent properties should be fully understood. Sorting out, organizing, and analyzing the solvatochromic parameters of various IL-water binary mixtures systematically are crucial.

In this study, the empirical solvatochromic parameters (E_T^N , α , β , and π^*) of the binary mixtures of water and 1,3-dialkylimidazolium based ILs with different cations and anions were measured over the entire range of IL mole fractions (x_{IL}) at room temperature (25 °C), aiming to ascertain the discrepancies in mixed solvent properties. The dyes used in this study were Reichardt's dye (RD), 4-nitroaniline, and 4-nitroanisole, as shown in Fig.1. Preferential solvation model that measures the deviation in $E_T(30)$ from linearity with the addition of water in ILs was applied to fit the parameters as well.

II. EXPERIMENTS

A. Materials

The ILs used in this work were as follows: 1-ethyl-3-methylimidazolium acetate ($[C_2C_1IM]OAc$), 1-butyl-3-methylimidazolium acetate ($[C_4C_1IM]OAc$), 1-hexyl-3-methylimidazolium acetate ($[C_6C_1IM]OAc$), 1-octyl-3-methylimidazolium acetate ($[C_8C_1IM]OAc$), 1-butyl-3-ethylimidazolium acetate ($[C_4C_2IM]OAc$), 1-butyl-3-propylimidazolium acetate ($[C_4C_3IM]OAc$), 1-butyl-3-methylimidazolium chloride ($[C_4C_1IM]Cl$), 1-butyl-3-methylimidazolium dibutylphosphate ($[C_4C_1IM](C_4H_9O)_2PO_2$), $[C_4C_1IM]Br$, and $[C_4C_1IM]BF_4$. Molecular structures of the used ILs are indicated in Fig.2. These ILs (purity >98.5%) were obtained from Lanzhou Greenchem ILs, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. These ILs were characterized by 1H NMR spectroscopy and the

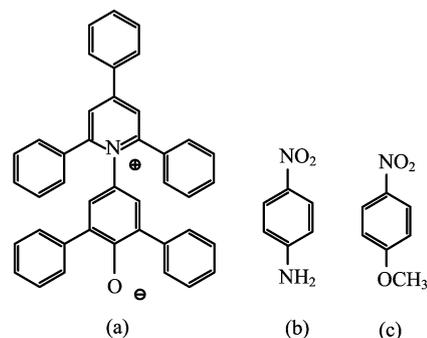


FIG. 1 Dyes used: (a) Reichardt's dye (RD), (b) 4-nitroaniline, and (c) 4-nitroanisole.

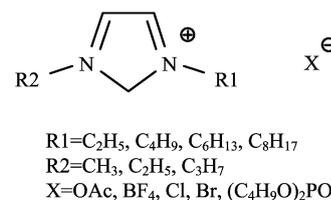


FIG. 2 Molecular structures of ILs used in this work.

spectra were consistent with reported data. The water content of the ILs was measured using a Karl Fischer moisture titrator (MKS-500), which didn't exceed 47 ppm for the used ILs. The residual content of chloride or bromide ions in the ILs was determined to be less than 50 ppm by using the Volhard titration method. The details about the impurities in the ILs are shown in Table S1 in supplementary materials.

The RD dye was purchased from Sigma-Aldrich (>90%) and used without additional purification. The dyes of 4-nitroaniline (>99.5%) and 4-nitroanisole (>98%) were purchased from Aladdin Chemistry Co., Shanghai, China. All reagents were kept out of light and stored at a desiccator. Deionized water with conductivity of 0.056 $\mu S/cm$ was used in this work.

B. Methods

UV-Vis spectroscopic measurements were performed with a Perkin-Elmer Lambda 35 spectrophotometer (USA). Polarity measurements were implemented in accordance with the recognized process [23–26]. An appropriate concentration of acetone solution of indicators was added to IL and mixed adequately. The mixed reagents were dried under vacuum at 80 °C for 5 h to remove the acetone. Various IL-water binary mixtures were prepared by weight, with a systematic change in the x_{IL} from 0 to 1.0. All the indicators were dissolved in a concentration range of 0.5 mmol/L to 1.0 mmol/L. Temperature was maintained at 25 ± 1 °C. After 12 h standing to ensure that the mixtures were stable, all samples were tested for UV-Vis spectra with a mean

value of three times in duplicate. The absorption spectra of the indicator were collected with scopes of $\lambda=250$ nm to 400 nm for the 4-nitroanisole, 300 nm to 450 nm for the 4-nitroaniline, and 420 nm to 600 nm for the RD.

C. Solvatochromic polarity analyses

Solvatochromic polarity parameters were determined as follows. $E_T(30)$ polarity was defined as the electronic transition energy of the RD indicator in a particular solvent, which can be obtained from the spectroscopic shift according to Eq.(1). The value was always normalized using water and tetramethylsilane (TMS) as references, as defined by Eq.(2).

$$E_T(30) = \frac{28591}{\lambda_{\max, \text{RD}}} \quad (1)$$

$$\begin{aligned} E_T^N &= \frac{E_T(30) - E_T(\text{TMS})}{E_T(\text{water}) - E_T(\text{TMS})} \\ &= \frac{E_T(30) - 30.7}{32.4} \end{aligned} \quad (2)$$

Laurence *et al.* proposed to use 4-nitroanisole (OMe) as the indicator dye for determining π^* [27], in accordance with Eq.(3).

$$\pi^* = 14.57 - \frac{4270}{\lambda_{\max, \text{OMe}}} \quad (3)$$

Hydrogen bond acceptor (HBA) basicity (β) was measured using the spectroscopic shift of the dye 4-nitroaniline (NH_2) and can be calculated using Eq.(4).

$$\beta = 11.134 - \frac{3580}{\lambda_{\max, \text{NH}_2}} - 1.125\pi^* \quad (4)$$

Hydrogen-bond donor (HBD) acidity (α) was derived from Reichardt's scale and can be calculated using Eq.(5) in relation to $E_T(30)$ and π^* .

$$\alpha = 0.0649E_T(30) - 2.03 - 0.72\pi^* \quad (5)$$

Ideal mixtures show a linear relationship among the solvatochromic parameter, the solvent composition, and the indicator that are equally solvated by the constituents of mixtures. The experiments performed for predicting the solvatochromic parameters of binary mixtures of ILs and water indicated the measured values didn't follow the expected ideal behavior. The measured values of solvatochromic parameters for binary mixtures derive from the predicted for linear mixing. Thus, the excess solvatochromic parameters (ΔSP) was defined as follows.

$$\Delta\text{SP} = \text{SP}_{\text{mixture}} - (x_{\text{IL}}\text{SP}_{\text{IL}}^0 + x_{\text{water}}\text{SP}_{\text{water}}^0) \quad (6)$$

Where $\text{SP}_{\text{mixture}}$, SP_{IL}^0 , $\text{SP}_{\text{water}}^0$, x_{IL} and x_{water} are the solvatochromic parameter of the mixture, pure IL, pure water, mole fraction of IL and water in the binary mixture, respectively. The ΔSP can be employed to evaluate the deviations from the ideality.

III. RESULTS AND DISCUSSION

Given that the RD is almost insoluble in pure water [24, 28], the solvatochromic polarities for pure water ($E_T^N=1.0$, $\beta=0.14$, $\alpha=1.17$, $\pi^*=1.09$) were adopted in this study according to well-accepted values [2, 15]. The values of solvatochromic parameters (π^* , β , α , E_T^N) for the binary mixtures of ILs and water at 25 °C over the entire range of x_{IL} , are given in Fig.3–Fig.6 and Table S2 in the supplementary materials. The polarity values of the some pure ILs and IL-water mixtures basically conformed to the values reported in the literatures [23, 25, 29–33], as shown in Table S3 in the supplementary materials.

A. The E_T^N parameter

Reichardt's polarity parameter E_T^N reflects the charge transfer from the phenolate to the pyridinium part of zwitterionic molecule and is affected by polarizability, dipole moment, and hydrogen-bonding. As shown in Fig.3 (a) and (c), for the pure ILs ($x_{\text{IL}}=1.0$), the trends for E_T^N values were as follows: $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4$ (0.67) > $[\text{C}_4\text{C}_1\text{IM}]\text{Br}$ (0.65) > $[\text{C}_2\text{C}_1\text{IM}]\text{OAc}$ (0.61) > $[\text{C}_4\text{C}_2\text{IM}]\text{OAc}$ (0.60) > $[\text{C}_4\text{C}_1\text{IM}]\text{Cl}$ (0.60) > $[\text{C}_4\text{C}_1\text{IM}]\text{OAc}$ (0.59) = $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}$ (0.56) = $[\text{C}_6\text{C}_1\text{IM}]\text{OAc}$ (0.56) > $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}$ (0.55) > $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2$ (0.54).

The trends of E_T^N values for binary mixtures of ILs and water were similar to that for the pure ILs. The presence and position of alkyl substitutes do not affect the variations to a very great extent in the E_T^N parameters of binary systems. It should be noted that the E_T^N parameters didn't show a synergistic behavior. It was apparently opposite to the trend observed in the binary mixtures of ILs and alcohol [16, 17], suggesting that the IL-water mixtures provided a different microenvironment for the RD indicator in comparison with IL-alcohol mixtures.

Figure 3 (a) and (c) show that the E_T^N values largely decreased at low x_{IL} region (0–0.2) by adding small quantities of the IL. The RD dye has a highly dipolar ground state in comparison with its excited state and therefore exhibits a significant permanent dipole moment, a large polarizable π electron system, a substantial negative charge on the phenoxide O, and a positive charge on the pyridinium N. The strong negative charge on the phenoxide O of RD dye in the electronic ground state can acquire additional solvent stabilization by hydrogen-bonding interactions with the IL, which decreased E_T^N values. This suggested that the RD dye is much more preferentially solvated by the IL than water. It was also observed in Fig.3 (a) and (c) that the E_T^N values varied smoothly in the region of x_{IL} from 0.2 to 1.0, indicating that there wasn't the nonspecific solvation effects due to the formation of the dye-IL complex. As shown in Fig.3 (b) and (d), the E_T^N param-

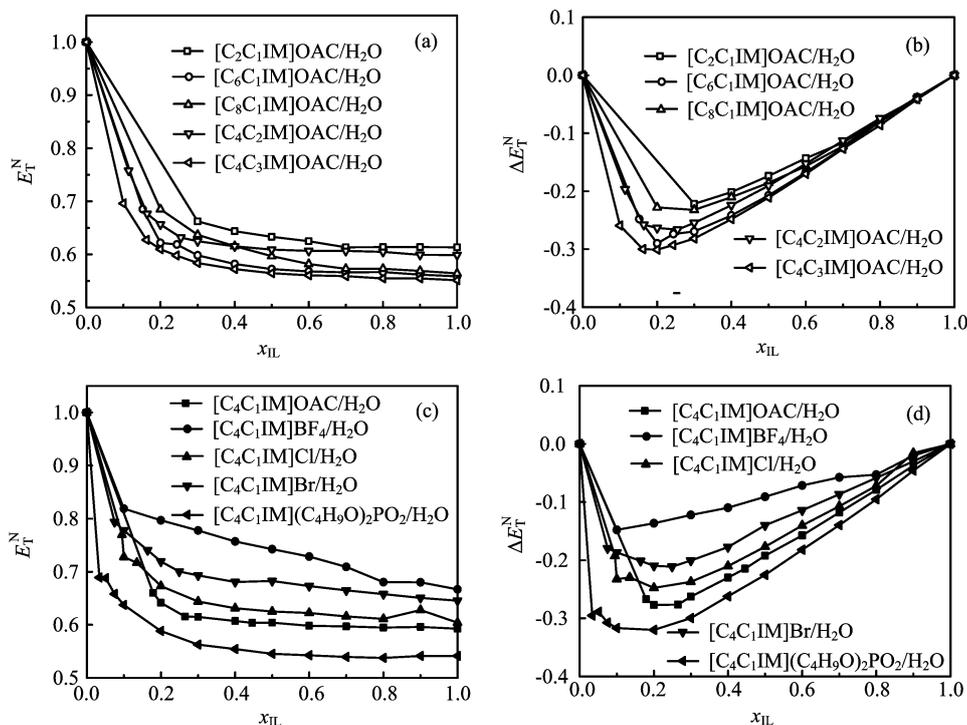


FIG. 3 The E_T^N parameters (a, c) and ΔE_T^N values (b, d) for binary mixtures of ILs and water at 25 °C. The maximum ΔE_T^N of $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$ was ± 0.006 .

eters showed negative deviation. The reason for this nonlinear behavior (nonideal behavior) is “preferential solvation” of the indicator by one component of the binary mixtures. Preferential solvation arises whenever the bulk mole fraction solvent composition is different from the solvation microsphere [25]. In principle, this phenomenon includes the contribution of specific (*e.g.* hydrogen-bonding) and non-specific indicator-solvent interactions. It was worthwhile to note that the maximum ΔE_T^N was obtained at $x_{\text{IL}}=0.1-0.3$ for all the binary mixtures of ILs and water, suggesting that there were the strongest interactions between IL and the RD dye in this x_{IL} region.

B. The α and β parameter

As shown in Fig.4 (a) and (c), for the pure ILs ($x_{\text{IL}}=1.0$), the order of α values was as follows. $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4$ (0.66) $>$ $[\text{C}_4\text{C}_2\text{IM}]\text{OAc}$ (0.48) $>$ $[\text{C}_4\text{C}_1\text{IM}]\text{Br}$ (0.46) $>$ $[\text{C}_2\text{C}_1\text{IM}]\text{OAc}$ (0.44) $=$ $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}$ (0.44) $>$ $[\text{C}_4\text{C}_1\text{IM}]\text{OAc}$ (0.43) $>$ $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2$ (0.42) $>$ $[\text{C}_6\text{C}_1\text{IM}]\text{OAc}$ (0.40) $>$ $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}$ (0.39) $>$ $[\text{C}_4\text{C}_1\text{IM}]\text{Cl}$ (0.38).

It was found that the parameter α was mainly affected by cation, but with an anion influence as well. The parameter β is a measure of the HBA basicity of a solvent. As shown in Fig.5 (a) and (c), for the pure ILs, the order of β values was as follows. $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}$ (1.14) $>$ $[\text{C}_4\text{C}_1\text{IM}]\text{OAc}$ (1.13)

$=$ $[\text{C}_4\text{C}_2\text{IM}]\text{OAc}$ (1.13) $>$ $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2$ (1.08) $>$ $[\text{C}_6\text{C}_1\text{IM}]\text{OAc}$ (1.07) $>$ $[\text{C}_2\text{C}_1\text{IM}]\text{OAc}$ (1.04) $=$ $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}$ (1.04) $>$ $[\text{C}_4\text{C}_1\text{IM}]\text{Cl}$ (0.79) $>$ $[\text{C}_4\text{C}_1\text{IM}]\text{Br}$ (0.70) $>$ $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4$ (0.51).

Given uniform cation with 1-butyl-3-methyl imidazolium ($[\text{C}_4\text{C}_1\text{IM}]^+$), β values obviously changed with different anions. Conversely, given uniform anion with acetate (OAc^-), β values were relatively stable. The β values for $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}$, $[\text{C}_4\text{C}_1\text{IM}]\text{OAc}$ and $[\text{C}_4\text{C}_2\text{IM}]\text{OAc}$ were slightly higher than that for the other ILs with acetate anions. The phenomenon mainly stemmed from the fact that the butyl substituent made the imidazolium rings highly symmetric. Generally, the parameter β of pure IL was largely affected by the nature of the anion, but there was a small cation effect. The polarity of solvent depends on both cations and anions of ILs.

Water is a good HBD because of its fairly high α value ($\alpha=1.17$) and relatively low β scale ($\beta=0.14$). On the contrary, an opposite phenomenon of α and β scales for pure ILs was observed. ILs, as HBA, made it easy to build hydrogen-bond with water. Variation in Fig.4 and Fig.5 of solvatochromic parameters for all IL-water binary systems provides valuable information that the solvent properties of binary mixtures can be affected by solvent composition (water content) distinctly.

The α and β scales changed dramatically as IL was initially added in water. The β values increased by almost 0.5 unit, while the α values decreased signifi-

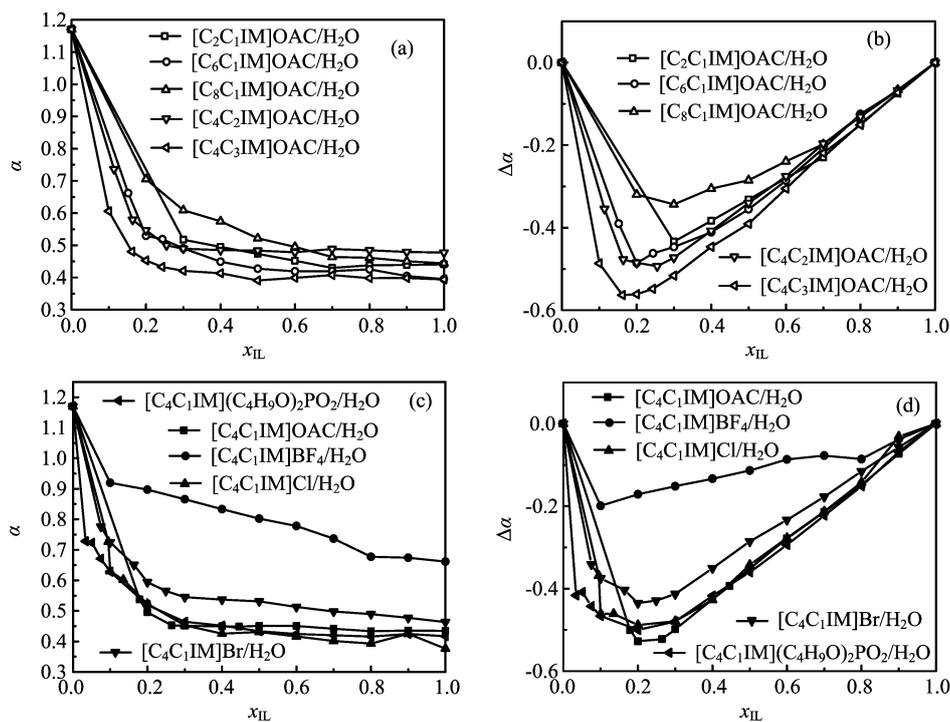


FIG. 4 The parameters α (a, c) and $\Delta\alpha$ values (b, d) for binary mixtures of ILs and water at 25 °C. The maximum $\Delta\alpha$ of $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$ was $\leq \pm 0.021$.

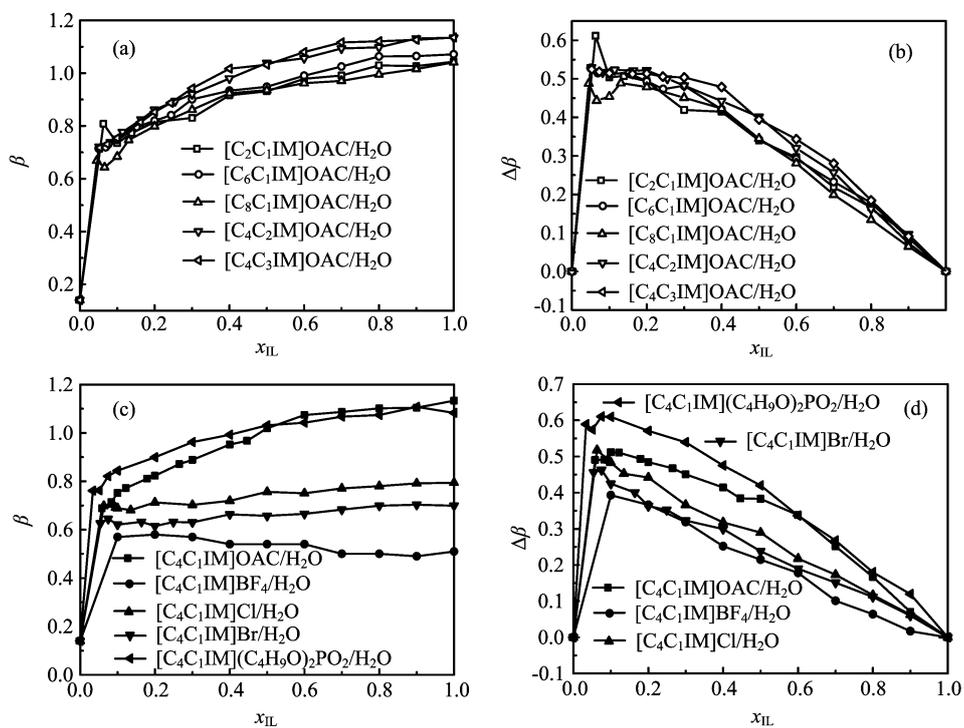


FIG. 5 The parameter β (a, c) and $\Delta\beta$ values (b, d) for the binary mixtures of ILs and water at 25 °C. The maximum $\Delta\beta$ of $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$ was $\leq \pm 0.022$.

cantly. $[\text{C}_6\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$, $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$, and $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$ systems decreased initially, whereas others were the exact contrary. This phenomenon was reasonable because the addition of ILs induced competitions in molecular interactions among ILs and water. A commonly increasing trend of β values and a moderately decreasing trend of α values were observed with increasing x_{IL} . In IL-rich regions (in the x_{IL} range of 0.4 to 1.0), similar trends for the parameters α and β were followed; all values began to flatten and were basically steady, which can be due to the approximate composition of binary mixture by the time. This behavior was exactly in line with what was observed by Moita *et al.* [34], who considered that the competitions in molecular interactions of transition energies for pairs depended on composition range.

The values α and β (ILs-water) were between that of pure ILs and water. This result demonstrated no synergistic effect in these imidazolium-based IL-water binary systems. The trends of parameter α for binary mixtures of water and ILs with acetate anion were tanglesome on the whole, as depicted in Fig.4 (a) and (c). $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$ system is on the high side, and $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}/\text{H}_2\text{O}$ system is the least. Sarkar *et al.* [24] deemed that the HBD acidity of $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4/\text{H}_2\text{O}$ system stemmed from the strong acidity for H on the two positions of imidazolium ring, which is in accordance with our results. The entire imidazolium ring protons are acidic, which provides a possibility to hydrogen-bonding with anions and dye indicator-solute as HBD. In microstructural perspective, a highly symmetric cation leads to a high hydrophobicity degree of the cation cluster. As a result, this phenomenon is less likely to provide a proton to form hydrogen-bond. The α values for binary mixtures are determined by the nature of cations and anions together, but cation is the main factor.

Considering that basicity is dominated by the characteristic of anions, the tendency of β values for the binary mixtures of water and ILs with different anions was specifically distinct as shown in Fig.5 (a) and (c). For 1-butyl-3-methylimidazolium ILs-water mixtures, $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$ and $[\text{C}_4\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$ systems show high HBA basicity because of the presence of oxyanions. The β values generally have a close relationship with the capability of IL-water mixtures to dissolve lignin [35, 36]. However, the order of β values can't exactly explain this dissolving behavior.

As shown in Fig.4 and Fig.5, the β values displayed a positive deviation ($\Delta\beta>0$), whereas the α values expressed a negative deviation ($\Delta\alpha<0$). Such a difference revealed preferential solvation of the indicator by the most polar constituent. Harifi-Mood *et al.* studied the solvatochromic behavior among water, methanol, ethanol and $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4$, and found a similar trend of solvent properties for IL-water mixtures [23]. As depicted in Fig.4 (b) and (d), the α values of $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}/\text{H}_2\text{O}$ showed large negative deviation

in the case of $x_{\text{IL}}=0.2$, which was due to high symmetric cation of $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}$. As shown in Fig.5 (b) and (d), the β values of $[\text{C}_2\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$ and $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$ presented large positive deviations in the case of around $x_{\text{IL}}=0.1$, which indicated that the basic character of these ILs resembled more different from that of water than other ILs. The reason for this finding can be that the IL with small size of cation or large size of anion can donate their protons easier than other used ILs.

It should be noted that the binary mixtures of $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4/\text{H}_2\text{O}$ owned the highest HBD acidity and the smallest deviations from the ideality, as shown in Fig.4. The solvatochromic parameters of $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4/\text{H}_2\text{O}$ measured in this work were similar to the data reported by Harifi-Mood *et al.* [23]. However, Freire *et al.* [37] proposed that the hydrolysis of BF_4^- was observed under even at room temperature and the hydrolysis extent was increased with increasing time and temperature. Thus, in this work, the $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4/\text{H}_2\text{O}$ mixtures were measured for a short time for reducing the influence of the hydrolysis of BF_4^- . Even so, the influence of the hydrolysis of BF_4^- on the solvatochromic parameters should be further investigated. Here, the $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4/\text{H}_2\text{O}$ were only used in theoretically comparing the solvatochromic parameters of the binary mixtures, as did in other researches [16, 25].

C. Net basicity ($\beta-\alpha$)

Hauru *et al.* discussed the relationship between solvent parameters and cellulose regeneration from IL solutions and found that the capability of IL-water system to dissolve cellulose can be interpreted by net basicity ($\beta-\alpha$) rather than β alone [38]. Shi *et al.* reported a similar conclusion that the ILs with high net basicity could dissolve cellulose more efficiently [35].

Net basicity ($\beta-\alpha$) for all 1,3-dialkylimidazolium-based IL-water binary mixtures over the entire range of mole fractions is presented in Table I. For these ILs, while trace water was added, the value increased only from 0.1 unit to 0.4 unit. By contrast, with the addition of trace ILs, the value increased by almost 1.8 units at maximum. This phenomenon revealed that severe intermolecular interactions occurred in solution, which fitted with the former discussion.

For pure IL, the cellulose dissolution located in a region is roughly defined by $0.35<(\beta-\alpha)<0.9$ and $0.80<\beta<1.20$ [21]. Shi *et al.* reported that cellulose can still be dissolved in the mixture of $[\text{C}_2\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$ (IL content of 20wt%) [35]. Table I indicates that most of ($\beta-\alpha$) values of 1,3-dialkylimidazolium-based IL-water systems are within the range of the solvent window, which gave a relatively unsophisticated account of the solvation behavior. Wang *et al.* reported that lignin could be dissolved in a series of 1,3-

TABLE I Net basicity ($\beta-\alpha$) for all IL-water binary mixtures.

x_{IL}	OAc ⁻ /H ₂ O						[C ₄ C ₁ IM] ⁺ /H ₂ O			
	[C ₂ C ₁ IM] ⁺	[C ₄ C ₁ IM] ⁺	[C ₆ C ₁ IM] ⁺	[C ₈ C ₁ IM] ⁺	[C ₄ C ₂ IM] ⁺	[C ₄ C ₃ IM] ⁺	BF ₄ ⁻	Cl ⁻	Br ⁻	(C ₄ H ₉ O) ₂ PO ₂ ²⁻
0.1	0.73	0.75	0.75	0.68	0.75	0.15	-0.35	0.06	-0.10	0.22
0.2	0.81	0.33	0.29	0.09	0.31	0.40	-0.32	0.19	0.02	0.38
0.3	0.31	0.44	0.41	0.25	0.43	0.52	-0.29	0.25	0.09	0.50
0.4	0.42	0.50	0.48	0.35	0.47	0.60	-0.30	0.29	0.13	0.54
0.5	0.46	0.57	0.52	0.41	0.56	0.64	-0.26	0.33	0.13	0.60
0.6	0.53	0.62	0.57	0.47	0.58	0.68	-0.24	0.33	0.15	0.62
0.7	0.56	0.64	0.61	0.51	0.61	0.71	-0.24	0.37	0.18	0.65
0.8	0.59	0.67	0.64	0.53	0.61	0.72	-0.17	0.39	0.21	0.66
0.9	0.59	0.67	0.66	0.57	0.65	0.73	-0.19	0.37	0.23	0.68
1.0	0.60	0.70	0.68	0.60	0.66	0.74	-0.15	0.42	0.24	0.67

Note: $(\beta-\alpha)_{\text{water}}=-1.03$. The maximum error associated with net basicity ($\beta-\alpha$) was $\leq\pm 0.012$.

alkylimidazolium-based IL-water mixtures except for [C₄C₁IM]BF₄/H₂O [36]. As shown in Table I, $\beta-\alpha$ values of [C₄C₁IM]BF₄/H₂O were negative, whereas those of most of IL-water mixtures were positive. Hence, the lignin dissolution capacity of [C₄C₁IM]BF₄/H₂O was weaker than that of other IL-water mixtures.

The preceding results indicated that the net basicity can be used to predict the dissolution behavior of cellulose and lignin in IL-water mixtures. Net basicity was considered as an important solvatochromic parameter for the binary mixtures of IL and water.

D. Dipolarity/polarisability (π^*)

The parameter π^* is a measure of dipolarity/polarisability of the solvent, which is derived from the variation of energy corresponding to the dye OMe maximum absorption. It is induced by the local electric field generated by the solvent. The π^* values of pure ILs are depicted in Fig.6 (a) and (c). The order of these π^* was as follows: [C₄C₁IM]Cl (1.19)=[C₄C₁IM]Br (1.19) > [C₂C₁IM]OAc (1.13) > [C₄C₁IM]OAc (1.08) > [C₆C₁IM]OAc (1.03)=[C₄C₂IM]OAc (1.03) > [C₄C₃IM]OAc (1.01) > [C₈C₁IM]OAc (0.98)=[C₄C₁IM]BF₄ (0.98) > [C₄C₁IM](C₄H₉O)₂PO₂ (0.95).

For 1,3-dialkylimidazolium acetate, the π^* values decreased with increasing length of alkyl chain of R1 (C3–C8) or R3 (C1–C3) (Fig.6 (a) and (c)), suggesting that the π^* can be affected by the position and size of substituent. The π^* value for pure water (1.07) was higher than for some pure ILs, such as [C₄C₁IM]BF₄ and [C₄C₁IM](C₄H₉O)₂PO₂, whereas was lower than that for [C₄C₁IM]Cl and [C₄C₁IM]Br (Fig.6(b)). The π^* values were related to the size of the anion of ILs. With increasing in the size of the anion, the π^* values decreased for the used ILs.

The π^* values for these IL-water mixtures are also shown in Fig.6 (a) and (c). It was not surprising that π^*

parameter was greatly influenced by increasing solute-solvent interactions when the x_{IL} was increased. It was noted that the dramatic change of π^* values occurred in the x_{IL} range from 0 to 0.2, suggesting that the micro environment of binary mixtures substantially changed due to the molecular interactions between IL and water. The π^* values kept relative steady with increasing x_{IL} from 0.2 to 1.0. It was worthwhile to be noted that binary mixtures of [C₄C₁IM]OAc/H₂O, [C₄C₂IM]OAc/H₂O and [C₄C₃IM]OAc/H₂O showed strong synergistic effects, in which π^* values of the mixture is higher than that of either of the pure solvents. This synergistic effect was attributed to the formation of hydrogen-bond complexes, whose properties were different from either of the solvents. Very small levels of synergism were observed in the binary mixtures of [C₂C₁IM]OAc/H₂O, [C₄C₁IM]Cl/H₂O and [C₄C₁IM]Br/H₂O, which was due to strong intramolecular interactions between anions and cations of these ILs. For [C₆C₁IM]OAc/H₂O, [C₈C₁IM]OAc/H₂O and [C₄C₁IM](C₄H₉O)₂PO₂/H₂O systems, small levels of synergism were also found, which was probably due to the very large size of the cations and anions, suggesting that steric hindrance restricts interactions between the ILs and the dye. No synergistic effects were found for the binary mixtures of [C₄C₁IM]BF₄/H₂O. This finding was consistent with other reports [23, 24]. The synergistic behavior in case of some π^* scales validated the existence of complex S12 (displaying a mixed solvent formed by the interaction of pure solvents 1 and 2) with a higher polarity than pure components have. This phenomenon didn't necessarily indicate that no S12 existed in other systems, but S12 was not significant.

The E_{T}^{N} , α and β values didn't present the synergy with varying x_{IL} (Fig.3–Fig.5), whereas the values showed the synergistic effects for most of binary mixtures (Fig.6). It suggested that the synergy weren't entirely characteristic of the studied mixtures but determined by the systems employed to study the mixtures.

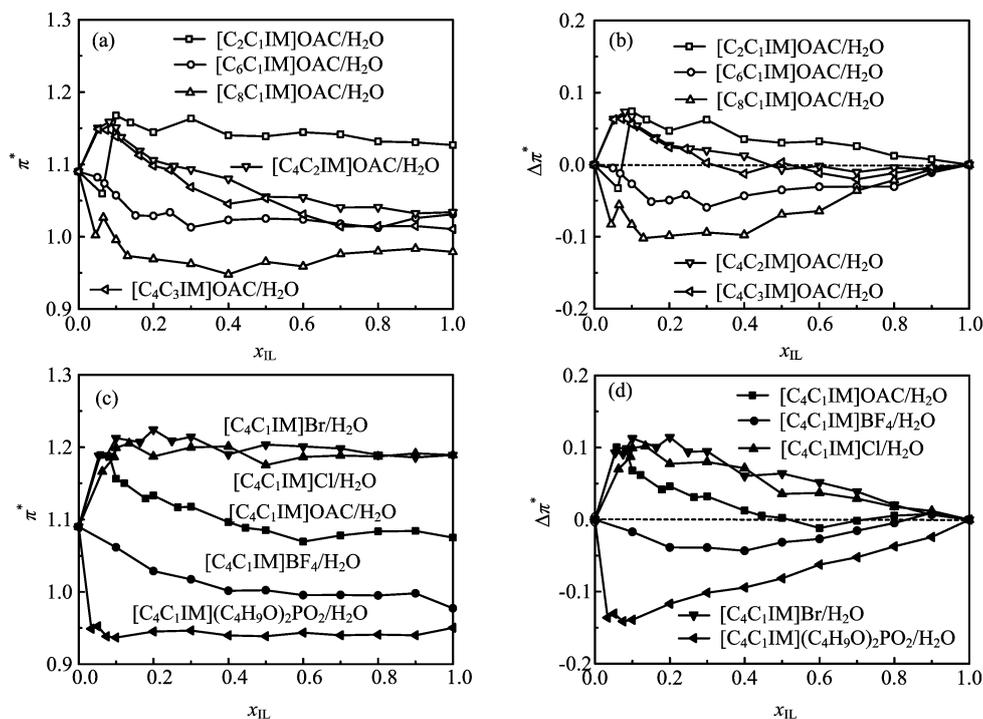


FIG. 6 The π^* parameter (a, c) and $\Delta\pi^*$ values (b, d) for the binary mixtures of ILs and water at 25 °C. The maximum error associated with π^* of $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$ was $\leq \pm 0.026$, and the details can be found in Table S2 in supplementary materials.

The selection of the systems, for example the polarity indicator, was decisive in determining the nature of the molecular interactions and the extent of synergy occurred. In this work, the π^* parameters measured using the dye 4-nitroanisole could reflect the synergy. It was difficult to speculate about the nature of interactions between the solvent and the dye in this stage. But such difference in synergy in these same IL-water mixtures emphasized the requirements for more extensive studies in the future.

As illustrated in Fig.6 (b) and (d), the π^* values measured for all the binary mixtures didn't follow the expected ideal behavior. The π^* values produced a negative deviation for the binary mixtures of $[\text{C}_6\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$, $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$, $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4/\text{H}_2\text{O}$, $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O}$. For $[\text{C}_6\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$ and $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$, asymmetrical cation and anion of the IL came into being clusterization, which was not conducive to deformability. Containing a tetrahedral structure anion group, the deformability of $(\text{C}_4\text{H}_9\text{O})_2\text{PO}_2^-$ and BF_4^- is poor, which directly led to a negative deviation of π^* values. It may be attributed to the specific interactions between the IL and water. As shown in Fig.6 (b) and (d), the π^* values produced a positive deviation for the binary mixtures due to their high electronegativity anions and sphere microstructure.

As depicted in Fig.3–Fig.6, the maximum deviation to ideality for the solvatochromic parameters can be ob-

tained in the x_{IL} range from 0.1 to 0.3. Its origin must be some interesting molecular interactions. Thermodynamic studies of imidazolium-based IL-water systems have revealed that cation and counterion seem completely dissociated only below x_{IL} of 0.013 to 0.015. At higher x_{IL} than this threshold, ions begin to interact with each other and organize themselves by mutual attraction. At a higher concentration, such as $x_{\text{IL}} > 0.5$ to 0.6, IL molecules form clusters as the pure state, and water molecules interact with IL clusters without forming a high hydrogen-bond network among themselves [39]. As indicated in Fig.3–Fig.6, the solvatochromic parameters dramatically changed in a range of low x_{IL} (0–0.3) and kept the stable stage in a range of high x_{IL} (0.3–1.0). The solvatochromic parameters seemed to be closely related to the microstructure of the binary mixtures.

E. Preferential solvation model

Considering that indicator dye can be preferentially solvated by either binary mixtures, water or IL, the selection must be made with the help of a preferential solvation model. Skwierczynski and Connors [40] proposed a phenomenological model of solvent effects, which were based on a simple two-step solvent exchange according to Eq.(7) and Eq.(8), to quantitatively describe solvent-solvent (the general medium effect), solvent-solute (the solvation effect), and solute-solute (the intersolute ef-

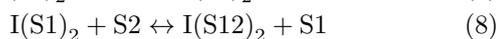
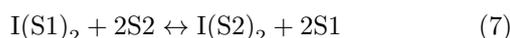
TABLE II Fitting parameters obtained from the preferential solvation models in the selected binary mixtures at 25 °C.

Solvents	E_{T2}^N	E_{T12}^N	$f_{2/1}$	$f_{12/1}$	R^2
[C ₂ C ₁ IM]OAc/H ₂ O	0.61	0.805	11.994	3.124	0.9948
[C ₄ C ₁ IM]OAc/H ₂ O	0.59	0.795	70.014	2.986	0.9949
[C ₆ C ₁ IM]OAc/H ₂ O	0.56	0.78	61.57	2.237	0.9954
[C ₈ C ₁ IM]OAc/H ₂ O	0.56	0.78	30.382	0.035	0.9851
[C ₄ C ₂ IM]OAc/H ₂ O	0.60	0.8	67.097	1.766	0.9974
[C ₄ C ₃ IM]OAc/H ₂ O	0.55	0.775	114.798	2.003	0.9942
[C ₄ C ₁ IM]BF ₄ /H ₂ O	0.67	0.835	4.34	1.923	0.7658
[C ₄ C ₁ IM]Cl/H ₂ O	0.60	0.8	119.505	1.084	0.9628
[C ₄ C ₁ IM]Br/H ₂ O	0.65	0.825	72.323	2.238	0.9625
[C ₄ C ₁ IM](C ₄ H ₉ O) ₂ PO ₂ /H ₂ O	0.54	0.77	199.861	3.127	0.9946

Note: $E_{T1}^N=1$.

fect) interactions in aqueous-organic binary mixtures. Bosch *et al.* developed the model for a wide application successfully [41, 42]. Nevertheless, this model can't explain synergistic behavior [43].

As stated previously, all IL-water binary mixtures show a non-synergistic effect on the solvatochromic parameters of E_T^N , α , and β . The generalized model below is applied in this work to IL-water binary systems investigated.



where S1 and S2 indicate two pure solvents, and S12 displays a mixed solvent formed by the interaction of solvents 1 and 2. I represents the corresponding RD indicator. I(S1)₂, I(S2)₂, I(S12)₂ stand for the RD solvated by S1, S2, and S12 components, respectively. The equilibrium constants for two solvent-exchange processes, $f_{2/1}$ and $f_{12/1}$, measure the tendency of the probe to be solvated by solvent S2 and "mixed solvent" S12 with reference to solvent S1.

$$f_{2/1} = \frac{x_2^s/x_1^s}{(x_2^0/x_1^0)^2} \quad (9)$$

$$f_{12/1} = \frac{x_{12}^s/x_1^s}{x_2^0/x_1^0} \quad (10)$$

where x_1^s , x_2^s , and x_{12}^s are the mole fractions of solvents S1, S2, and S12 in the sphere of solvation of the indicator, respectively. x_1^0 and x_2^0 are the mole fractions of the two solvents in the bulk mixed solvent.

According to this model, Reichardt's polarity E_T of binary mixtures as a function of mole fraction x_2 can be calculated.

$$E_T = E_{T1} + \frac{a(x_2^0)^2 + c(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0} \quad (11)$$

$$E_{T12} = \frac{E_{T1} + E_{T2}}{2} \quad (12)$$

In Eq.(11), a and c are the regression coefficients that minimize the square residuals of E_T values. For the convenience of calculation, Skwierczynski and Connors [40] assumed E_T polarity of solvent S12 to be the average of E_{T1} and E_{T2} , as presented in Eq.(12).

To understand the unique natures of IL-water at the molecular-level aspect, two parameters, $f_{2/1}$ and $f_{12/1}$, were measured by fitting the wavenumbers of maximum absorptions of the RD at different compositions of S1 (water) and S2 (ILs) to the proposed Eq.(11). The results are listed in Table II. For all IL-water binary mixtures, $f_{2/1}$ was generally greater than 1, which reflected that the indicator was more solvated by IL rather than water, and the solvation sphere was substantiated with IL. Similarly, $f_{12/1}$ commonly exceeds 1, except for system [C₈C₁IM]OAc/H₂O. $f_{2/1} > f_{12/1}$ exhibited that IL built a closer solute-solvent interaction with the indicator in comparison with the mixture. Macrocosmically, the difference in the values of $f_{2/1}$ and $f_{12/1}$ demonstrated that the nature of anions and cations played an important role in the preferential solvation study. [C₄C₁IM]BF₄/H₂O system, however, was not suitable for this preferential solvation model.

The parameters $f_{2/1}$ and $f_{12/1}$ differed from each other for acetate-based IL-water mixtures, which can affirm that the alkyl substitution on the imidazolium ring greatly affected the solute-solvent interactions of solvation sphere. With increasing alkyl chain of cation on one position, the value of $f_{2/1}$ first increased sharply and then decreased, whereas $f_{12/1}$ decreased continuously. Given that RD dye molecule is large, the phenomenon can be attributed to the steric-hindrance effect and symmetry of the large substitution on one position of the ring. Therefore, [C₂C₁IM]OAc/H₂O system held lower $f_{2/1}$ and higher $f_{12/1}$ than others do, which reflected that "mixed solvent", combination of water and [C₂C₁IM]OAc, was easier to form and more active to interact with the indicator than other IL-water

mixtures. On the contrary, the parameter $f_{12/1}$ for $[\text{C}_8\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O}$ mixture was inferior to 1, which might be ascribed to the fact that large asymmetric cation putted a brake on the formation of the “mixed solvent” that directly led to a weak solute-solvent interaction. As for substituting proton on three positions, the values of $f_{2/1}$ and $f_{12/1}$ for $[\text{C}_4\text{C}_3\text{IM}]\text{OAc}/\text{H}_2\text{O}$ system were higher than those for the two other systems. Hence, the symmetry of different alkyl group of cation tied the solute-solvent interactions up. From another aspect, the parameters $f_{2/1}$ and $f_{12/1}$ for the systems with butyl substitute on one position of cation were higher than the others.

The preferential parameters $f_{2/1}$ and $f_{12/1}$ for 1-butyl-3-methylimidazolium-based IL-water systems were determined. The overall values followed $f_{2/1} > f_{12/1} > 1$, which reflected that the dye is strongly preferentially solvated by pure ILs in comparison with the mixture with reference to water. Danten *et al.* [44] reported that an almost symmetric structure of anion $\cdots\text{H}-\text{O}-\text{H}\cdots$ anion is formed by hydrogen-bonds in IL-water mixtures. When solute was added, similar to the dye indicator, a competition existed between anion and dye indicator, thereby indicating that the solvent-solvent interaction always strongly influenced solute-solvent interaction. For systems that shared the same cations, the observed trend for preferential solvation was $[\text{C}_4\text{C}_1\text{IM}](\text{C}_4\text{H}_9\text{O})_2\text{PO}_2/\text{H}_2\text{O} > [\text{C}_4\text{C}_1\text{IM}]\text{Cl}/\text{H}_2\text{O} > [\text{C}_4\text{C}_1\text{IM}]\text{OAc}/\text{H}_2\text{O} > [\text{C}_4\text{C}_1\text{IM}]\text{Br}/\text{H}_2\text{O}$. This trend was closely related to the electronegativity and magnitude of anions.

IV. CONCLUSION

The empirical solvatochromic parameters (E_{T}^{N} , α , β , and π^*) of the binary mixtures of 1,3-dialkylimidazolium ILs and water were investigated. This result indicated that solvent properties of IL-water mixtures were influenced by both the x_{IL} and IL type. The behavior of the solvatochromic absorbance indicator obviously deviated from ideality in these mixtures. The maximum deviation to ideality was obtained in the x_{IL} range from 0.1 to 0.3. Net basicity ($\beta - \alpha$) for these IL-water mixtures can predict the capacity of dissolving lignin. For most of IL-water mixtures (except for $[\text{C}_4\text{C}_1\text{IM}]\text{BF}_4/\text{H}_2\text{O}$), the π^* parameters were found to be higher than that of pure ILs and water instead of other parameters (E_{T}^{N} , α and β). The synergy in π^* parameters indicated interesting and strong solute-solvent and solvent-solvent interactions in these studied systems. With the preferential solvation model, the dye probe is preferentially solvated in the following order: pure IL > mixtures > water. This work will help to understand the physicochemical properties of these IL-water mixtures and facilitate their practical applications.

Supplementary materials: The impurities contents in the used ILs, the measured solvatochromic parameters of the binary mixtures of ILs and water, and comparison between reference data and the measured values in this work are given.

V. ACKNOWLEDGMENTS

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