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Research Article

Quantification of Ionic Liquids Concentration in Water and Qualification of Conjugated and Inductive Effects of Ionic Liquids by UV Spectroscopy

The determination of the concentrations of ionic liquids (ILs) in water by UV spectroscopy was proposed. The effects of alkyl chain length, anion, cation, and C2 methylation of ILs were systematically investigated. The concentration detection limit ranges from 0.625 to 80 mg/L, and can be extended by changing the path length of the UV cuvette. In addition, the conjugated and inductive effects of ILs were analyzed by the maximum absorption wavelength λ_{max} . Cations without conjugated effect (e.g., pyrrolidium, tetraammonium, and tetraphosphonium) show no UV spectra peak, while cations with conjugated effects (e.g., imidazolium, and pyridinium) present UV spectra peaks. Electron-donating substitute groups (e.g., alkyl, C2 methylation) induce a larger value of maximum absorption wavelength λ_{max} than the electron-withdrawing substitute groups (e.g., amine, non-C2 methylation). These findings are helpful to detect and quantify the concentration of ILs in water.

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1 Introduction

Ionic liquids (ILs) are liquid salts with an organic cation and an organic or inorganic anion at or below 100°C. ILs have unique properties such as non-volatility, non-flammability, and high thermal stability compared to conventional organic solvent [1]. The physicochemical properties (e.g., viscosity, density, conductivity, mp, basicity and acidity, hydrophobicity and hydrophilicity) of ILs can be tuned by an appropriate selection of the cation or anion or both [2, 3]. Since then, ILs have been paid much attention in catalyzed reactions, metal electrodeposition, gas separation, cellulose dissolution, materials fabrication, and so on [4–12].

Most of the ILs are hygroscopic [13, 14]. Even the "hydrophobic" ILs (e.g., [BMIM][Tf₂N]) can absorb significant amounts of water from air [15]. ILs with anions halides, nitrate, acetate have good miscibility with water, whereas anions such as hexafluorophosphate, cholate, bis(trifluoromethylsulfonyl)imide hinder water miscibility [16, 17]. Cations also have influence on the interactions between water and ILs. For example, pyridinium and pyrrolidinium ILs have poorer solubility in water than imidazolium salts [16, 18, 19]. A longer chain or C2 methylation at the cation of ILs may reduce water solubility [16, 20]. The high hydrophilicity of ILs is partially due to their strong hydrogen-bonding interaction [21–23], or high polarity [24].

The presence of water could dramatically affect the physicochemical properties of ILs and affect the rate and selectivity of chemical reactions [25]. Variability of experimental results for the same ILs might partially be caused by water contamination [15]. Water can also serve as a co-solvent or anti-solvent to alter the solvation of solutes in ILs [26, 27].

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On the other side, water is also the most common impurity in ILs because exposure to ubiquitous water can hardly be avoided. Solubility of ILs in water is also a concern for environmental impact, such as toxicity [28]. Release of ILs to aquatic environments could lead to water contamination because of their potential toxicity and limited biodegradability [18, 29–32].

Therefore, the determination of the concentrations of ILs in water is important. Karl Fischer titration, thermogravimetric analysis (TGA) [33], MS [34], cathodic stripping voltammetry [35], and redox probe [36] have been used for the determination of the concentrations of ILs in water. Karl Fisher titration is one of the most common methods to measure water content, while it has a large uncertainty of measurement. Thermogravimetric analysis and MS are relatively accurate while time-consuming. Cathodic stripping voltammetry and redox probe methods are also expensive and inconvenient. The abovementioned methods are used to determine the content of water first and then deriving the content of ILs.

In this study, UV–Vis spectroscopy is proposed as a favorable way to determine the concentrations of ILs in water directly. This method is convenient, accurate, and cheap because no other chemicals needed for the measurement. For example, Wu et al. [37, 38] has used UV to measure the content of ILs (i.e., [BMIM][BF₄] and [BMIM][PF₆]) in their mixtures with supercritical CO_2 and organic co-solvents. Note that using of UV to quantify the concentration of ILs in water must make sure that nearly no UV light absorption impurities exists.

Here, the concentrations of 23 ILs in water were determined by UV spectroscopy. Those ILs vary in alkyl chain length, anion, cation, C2

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Abbreviation: IL, ionic liquid

methylation (Table 1). A linear equation was fitted, the absorption coefficient ε was derived from the concentrations of ILs (ranging from 0.625 to 10 mg/L) and its corresponding absorbance measured by UV spectroscopy with the path length of the cuvette d = 1 cm (Table 2). The concentration detection limit of ILs could be expanded to as much as 80 mg/L by decreasing the path length of the cuvette to 1 mm (Table 3). Meanwhile, the conjugated and inductive effects of ILs in water were also analyzed.

2 Materials and methods

The ILs (\geq 99%) were purchased from Lanzhou Greenchem ILs, LICP, CAS (Lanzhou, China). The ILs were dried at 50°C for 96 h in vacuum drying oven with P₂O₅ desiccant nearby before use. The ¹H- and ¹³C-NMR analysis (Bruker AM 400 MHz spectrometer) indicated no detectable impurities in the ILs. Inductively coupled plasma optical emission spectrometry (ICP-OES) with a Varian Vista MPX gave the content of Li and Na (<40 ppm), and the content of Cl (<50 ppm) except for [BMIM][Cl], and the content of Br (<45 ppm)

except for [BPy][Br], [aEMIM][Br], [ABIM][Br], [P_{666,14}][Br], and [BMPyrr][Br].

The relative low concentration of ILs (0.625–10 mg/L) was measured by UV spectroscopy (Carry 5.0, Varian) with the longer path length quartz cuvette (d = 1 cm). The relative high concentration of ILs (2.5– 80 mg/L) was measured with a shorter path length d = 1 mm. Both the value of absorbance and maximum absorption wavelength could be read directly from the UV spectra. All the experiments were conducted for three times, with deviations <3%.

3 Results and discussion

3.1 Quantifying the concentration of ILs in water by UV spectroscopy

The molar absorption coefficient (ε_{mol}), mass absorption coefficient (ε_{mg}), and maximum absorption wavelength (λ_{max}) of 23 ILs (Table 1) were investigated with a path length of cuvette d = 1 cm. Results show that 18 ILs present λ_{max} while the remaining 5 ILs ([BMIM][Ac],

Table 1. Name, structure, and molecular weight of the 23 ILs investigated

| No. | Full name | Abbreviated name | Structure | MW $(g mol^{-1})$ |
|-----|--|--------------------------|--|-------------------|
| 1 | 1-Ethyl-3-methyl-imidazolium tetrafluoroborate | [EMIM][BF ₄] | N F F F F F F F F | 197.97 |
| 2 | 1-Butyl-3-methyl-imidazolium tetrafluoroborate | [BMIM][BF ₄] | N F F F F F F F | 226.02 |
| 3 | 1-Hexyl-3-methyl-imidazolium tetrafluoroborate | [HMIM][BF ₄] | | 254.08 |
| 4 | 1-Octyl-3-methyl-imidazolium tetrafluoroborate | [OMIM][BF ₄] | | 282.13 |
| 5 | 1-Decyl-3-methyl-imidazolium tetrafluoroborate | [DMIM][BF ₄] | | 310.18 |
| 6 | 1-Butyl-3-methyl-imidazolium nitrate | [BMIM][NO ₃] | | 201.22 |
| 7 | 1-Butyl-3-methyl-imidazolium hexafluorophosphate | [BMIM][PF ₆] | N [PF ₆] ⁻ | 284.18 |
| 8 | 1-Butyl-3-methyl-imidazolium trifluoromethanesulfonate | [BMIM][TFO] | N [CF ₃ SO ₃] ⁻ | 288.3 |
| 9 | 1-Butyl-3-methyl-imidazolium trifluoroacetate | [BMIM][TFA] | | 252.23 |
| | | | | |

(Continued)



Table 1. (Continued)

| No. | Full name | Abbreviated name | Structure | MW $(g mol^{-1})$ |
|-----|---|---------------------------|--|-------------------|
| 10 | 1-Butyl-3-methyl-imidazolium bis(trifluoromethylsulfonyl)imide | [BMIM][Tf ₂ N] | N [N(SO ₂ CF ₃) ₂] ⁻ | 419.36 |
| 11 | 1-Butyl-3-methyl-imidazolium cholate | [BMIM][CHO] | | 546.77 |
| 12 | 1-Butyl-3-methyl-imidazolium chloride | [BMIM][C1] | | 174.67 |
| 13 | 1-Butyl-3-methyl-imidazolium bromide | [BMIM][Br] | | 219.12 |
| 14 | 1-Butyl-3-methyl-imidazolium iodide | [BMIM][I] | | 266.12 |
| 15 | N-Butyl-pyridinium bromide | [BPy][Br] | | 216.12 |
| 16 | 1-Aminoethyl-3methyl-imidazolium bromide | [aEMIM][Br] | | 206.08 |
| 17 | 1-Butyl-2,3-dimethyl-imidazolium tetrafluoroborate | [BMMIM][BF4] | | 240.01 |
| 18 | 1-Butyl-2,3-dimethyl-imidazolium acetate | [BMMIM][Ac] | | 212.29 |
| 19 | 1-Butyl-3-methyl-imidazolium acetate | [BMIM][Ac] | | 198.26 |
| 20 | Tetrabutylammonium acetate | [N ₄₄₄₄][Ac] | C_4H_9 $V_{C_4H_9}$ C_4H_9 $O_{\bar{O}}$ | 301.51 |
| 21 | 1-Allyl-3-butyl-imidazolium bromide | [ABIM][Br] | | 245.16 |
| 22 | Tetradecyltrihexylphosphonium bromide | [P ₆₆₆₁₄][Br] | C ₆ H ₁₃ - C ₆ H ₁₃ (CH ₂) ₁₃ CH ₃ C ₆ H ₁₃ [Br] ⁻ | 563.76 |
| 23 | N-Butyl-N-methylpyrrolidinium bromide | [BMPyrr][Br] | | 222.17 |

Table 2. Maximum absorption wavelength (λ_{max}), absorbance (A) of 23 ILs at different concentration (C), the fitted linear equation, and absorption coefficient (ε)

| | | | | A | (mg L ⁻ | ¹) | | | | | | 5 |
|-----|---------------------------|-----------------------|-------|-------|--------------------|----------------|-------|------------------------|---------|--------------------------------|-----------------|---|
| No. | IL | λ_{\max} (nm) | 0.625 | 1.25 | 2.5 | 5 | 10 | equation ^{a)} | R^2 | $(Lmg^{\epsilon_{mg}}cm^{-1})$ | $(g mol^{-1})$ | $10^{-5} \varepsilon_{\rm mol}$ (L mol ⁻¹ m ⁻¹) |
| 1 | [EMIM][BF ₄] | 209.9 | 0.238 | 0.386 | 0.654 | 1.221 | 2.201 | y = 0.2094x + 0.1286 | 0.99843 | 0.2094 | 197.97 | 0.4145 |
| 2 | [BMIM][BF ₄] | 211.1 | 0.211 | 0.308 | 0.504 | 0.896 | 1.651 | y = 0.1537x + 0.1185 | 0.99988 | 0.1537 | 226.02 | 0.3474 |
| 3 | [HMIM][BF ₄] | 211.5 | 0.235 | 0.319 | 0.517 | 0.914 | 1.735 | y = 0.1607x + 0.1211 | 0.99966 | 0.1607 | 254.08 | 0.4084 |
| 4 | [OMIM][BF ₄] | 212.0 | 0.154 | 0.235 | 0.390 | 0.703 | 1.328 | y = 0.1251x + 0.0773 | 0.99999 | 0.1251 | 282.13 | 0.3529 |
| 5 | [DMIM][BF ₄] | 211.3 | 0.152 | 0.233 | 0.394 | 0.716 | 1.344 | y = 0.1271x + 0.1271 | 0.99994 | 0.1271 | 310.18 | 0.3944 |
| 6 | [BMIM][NO ₃] | 203.6 | 0.513 | 0.906 | 1.697 | 2.737 | - | y = 0.5042x + 0.2815 | 0.98166 | 0.5042 | 201.22 | 1.0146 |
| 7 | [BMIM][PF ₆] | 209.9 | 0.147 | 0.233 | 0.42 | 0.788 | 1.51 | y = 0.1457x + 0.0550 | 0.99995 | 0.1457 | 284.18 | 0.4140 |
| 8 | [BMIM][TFO] | 211.0 | 0.202 | 0.295 | 0.484 | 0.86 | 1.623 | y = 0.1517x + 0.1057 | 1.00000 | 0.1517 | 288.30 | 0.4372 |
| 9 | [BMIM][TFA] | 211.2 | 0.207 | 0.310 | 0.520 | 0.923 | 1.690 | y = 0.1581x + 0.1175 | 0.99958 | 0.1581 | 252.23 | 0.3987 |
| 10 | [BMIM][Tf ₂ N] | 209.7 | - | 0.232 | 0.366 | 0.570 | 0.965 | y = 0.0825x + 0.1465 | 0.99682 | 0.0825 | 419.36 | 0.3460 |
| 11 | [BMIM][CHO] | 209.3 | - | - | 0.298 | 0.475 | 0.805 | y = 0.0674x + 0.1330 | 0.99938 | 0.0674 | 546.77 | 0.3684 |
| 12 | [BMIM][C1] | 211.4 | 0.286 | 0.458 | 0.747 | 1.32 | 2.296 | y = 0.2132x + 0.1955 | 0.99668 | 0.2132 | 174.67 | 0.3723 |
| 13 | [BMIM][Br] | 191.0 | 0.871 | 1.269 | 1.966 | 2.639 | - | y = 0.3946x + 0.7613 | 0.93781 | 0.3946 | 219.12 | 0.8647 |
| 14 | [BMIM][I] | 223.0 | 0.553 | 0.971 | 1.729 | 3.032 | - | y = 0.5620x + 0.2541 | 0.99626 | 0.5620 | 266.12 | 1.4956 |
| 15 | [BPy][Br] | 258.9 | 0.273 | 0.439 | 0.789 | 1.441 | - | y = 0.2673x + 0.1091 | 0.99965 | 0.2673 | 216.12 | 0.5776 |
| 16 | [aEMIM][Br] | 190.3 | 1.482 | 2.034 | 2.701 | - | - | y = 0.6335x + 1.1485 | 0.96339 | 0.6335 | 206.08 | 1.3055 |
| 17 | [BMMIM][BF4] | 211.6 | 0.344 | 0.549 | 0.906 | 1.603 | 2.596 | y = 0.2391x + 0.2730 | 0.98782 | 0.2391 | 240.01 | 0.5739 |
| 18 | [BMMIM][Ac] | 209.0 | 0.441 | 0.686 | 1.163 | 1.808 | 2.602 | y = 0.2260x + 0.4641 | 0.95268 | 0.2260 | 212.29 | 0.4798 |

"-" indicates not discernible UV maximum absorption peak.

 $^{a)}y$ and x indicate the absorbance (A) and concentration (C) of ILs, respectively.

 $[N_{4444}]$ [Ac], [ABIM][Br], [P_{666,14}][Br], and [BMPyrr][Br]) do not (Table 2 and Fig. 1). [BPy][Br] has the greatest λ_{max} , whereas [aEMMIM][Br] has the lowest. In terms of the ε_{mol} and ε_{mg} , both [BMIM][I] and [aEMMIM][Br] have the greatest values, respectively.

The type of ILs can be deduced by their λ_{max} . Then, the concentrations of ILs can be obtained by the ε_{mol} . The difference in λ_{max} of ILs varying in the concentration is negligible because the concentration of ILs is less than 80 mg/L. The ILs investigated were selected by varying alkyl chain length (Fig. 2), anion (Fig. 3), cation (Fig. 4), and C2 methylation of ILs (Fig. 5).

3.1.1 Effect of alkyl chain length

Figure 2 presents ε_{mol} , ε_{mg} , and λ_{max} of UV spectra of ILs varying in alkyl chain length (i.e., [EMIM][BF₄], [BMIM][BF₄], [HMIM][BF₄],

Table 3. Absorbance (*A*) of [EMIM][BF₄] at different concentration (*C*) by UV spectroscopy with the length of cuvette d = 1 mm and 1 cm^a)

| | d = 1 | d = 1 mm | | | | |
|---------------------------|-------|-------------------|-------|--|--|--|
| $C (\mathrm{mg L^{-1}})$ | A | 10A ^{b)} | A | | | |
| 0.625 | - | - | 0.238 | | | |
| 1.25 | - | - | 0.386 | | | |
| 2.5 | 0.067 | 0.67 | 0.654 | | | |
| 5 | 0.128 | 1.28 | 1.221 | | | |
| 10 | 0.248 | 2.48 | 2.201 | | | |
| 20 | 0.475 | 4.75 | - | | | |
| 40 | 0.929 | 9.29 | - | | | |
| 80 | 1.739 | 17.39 | - | | | |

"-" indicates that the UV maximum absorption peak is not discernible.

^{a)}The maximum absorption wavelength (λ_{max}) for the path length of cuvette d = 1 cm and 1 mm is almost identical, i.e., $\lambda_{max} = 209.9$ nm. ^{b)}The absorbance *A* with the path length d = 1 mm multiplied by 10 for a good comparison with the path length d = 1 cm, and then was depicted in Fig. 6. [OMIM][BF₄], and [DMIM][BF₄]). Fitting the concentrations of ILs with their corresponding absorbance according to the Lambert-Beer law:

Soil Air Water

$$A = \varepsilon c d \tag{1}$$

gave a linear tendency (Fig. 2a). A, ε , c, d indicate the absorbance, absorption coefficient, concentration of ILs, and the path length of cuvette, respectively. Then, ε_{mg} and ε_{mol} can be calculated. For simplicity, ε_{mol} was divided by 10⁵ (Table 2 and Fig. 2). The data process is also conducted for other presentation in this paper.

The tendency of absorption coefficient is interesting. The value of ε_{mg} decreases with a longer chain length (Fig. 2b). However, the value of ε_{mol} shows a complicated tendency. Two minimum points, ([BMIM][BF₄]) and [OMIM][BF₄]), and three maximum points ([EMIM][BF₄], [HMIM][BF₄], and [DMIM][BF₄]) exist among the ILs investigated varying in chain length (Fig. 2b). The structure change of ILs varying in alkyl chain length is complicated.

The detection limits of IL concentrations varying in the alkyl chain length measured by UV spectroscopy with the path length



Figure 1. Overview of the molar absorption coefficient ε_{mol} , the mass absorption coefficient ε_{mg} , and the maximum absorption wavelength λ_{max} of ILs.





Figure 2. Relationship between the absorbance A and the concentration C of ILs varying in alkyl chain length (a), and on absorption coefficient ε and maximum absorption wavelength λ_{max} of ILs (b).



Figure 3. Relationship between the absorbance and the concentration of ILs varying in anion (a), and on absorption coefficient ε and maximum absorption wavelength λ_{max} of ILs (b).

of 1 cm are from 0.625 to 10 mg/L (Fig. 2). The effect of cuvette with a shorter path length d = 1 mm is also investigated. Results show that it could determine a more concentrated ILs as much as 80 mg/L (Fig. 6 and Table 3). The absorption coefficient, i.e., the slope of the linear fitted line, is almost identical (Fig. 6), indicating a favorable consistency to measure the concentrations of ILs by a different path length. It is expected that more concentrated or

more dilute ILs could be quantified by changing the path length of cuvette.

3.1.2 Effect of anion

Figure 3 shows the effect of anion on the ε_{mol} , ε_{mg} , and λ_{max} . There was a linear relationship between the concentration of ILs with



Figure 4. Relationship between the absorbance and the concentration of ILs varying in cation (a), and on absorption coefficient ε and maximum absorption wavelength λ_{max} of ILs (b).



Figure 5. Relationship between the absorbance and the concentration of ILs varying in C2 methylation (a), and on absorption coefficient ε and maximum absorption wavelength λ_{max} of ILs (b).

varying anions and their absorbance, which lead to the absorption coefficient (Fig. 3a). The ε_{mol} of ILs varying in anion with the cation [BMIM] was in the ordered of $I > NO_3 > Br > TFO > PF_6 > TFA > CHO > Cl > BF_4 > Tf_2N$ (Fig. 3b). The overall tendency of ε_{mol} was slightly different from that of the ε_{mg} . Particularly, the ε_{mg} of TFO, PF₆ < TFA < CHO, and Cl showed an opposite tendency, i.e., TFO < PF₆ < TFA < CHO < Cl (Fig. 3b).

The range of v_{mol} for ILs varying in anion was more significant than for ILs varying in the alkyl chain length. The range of the former situation (0.34601–1.49557) was about ten times more than that of the latter (0.35294–0.41445; Fig. 3b and Table 2). It indicates that discriminating the content of ILs varying in anion is more accurate that ILs varying in alkyl chain length. However, some ILs (such as [BMIM][Ac]) show no UV λ_{max} , which making the determination of the content of ILs in water is not available.

3.1.3 Effect of cation

The effect of anion on the ε_{mol} , ε_{mg} , and λ_{max} were investigated using six ILs varying in cation with the anion Br (i.e., BPy, BMIM, aEMMIM, ABIM, P_{666,14}, and BMPyrr). The results of three ILs with BPy, BMIM



Figure 6. Relationship between concentration and absorbance of $[EMIM][BF_4]$ by UV spectroscopy with the quartz cuvette length d=1 mm and d=1 cm. Absorbance of $[EMIM][BF_4]$ measured with 1 mm cuvette was multiplied by 10 for a good comparison with that of 1 cm cuvette.

and aEMMIM are presented in Fig. 4, the remaining three ILs with ABIM, $P_{666,14}$, and BMPyrr show no λ_{max} . It gives us a hint that not all the ILs could be determined its content in water by UV spectroscopy because the λ_{max} might not be detected.

From Fig. 4, we can see that both ε_{mol} and ε_{mg} were ordered as aEMMIM > BMIM > BPy. The difference in absorption coefficient and λ_{max} is significant, making a convenient quantification of ILs content in water by UV spectroscopy. Although the λ_{max} of [BMIM][Br] and [aEMIM][Br] are almost identical, their absorption coefficients are easily discernable. In this case, the ILs could also be qualified and quantified by their absorption coefficient, because the value of absorption coefficient of each ILs is unique.

3.1.4 Effect of C2 methylation

The effect of C2 methylation on the ε_{mol} , ε_{mg} , and λ_{max} were investigated using [BMIM][BF₄], [BMIM][BF₄], [BMIM][Ac], and [BMMIM][Ac] (Fig. 5). Results show that for the BF₄-based ILs, non-C2 methylation one [BMIM][BF₄] contributes to a lower absorption coefficient (Fig. 5b). Likewise, non-C2 methylation Ac-based ILs [BMIM] [Ac] even shows no absorption coefficient because there is no λ_{max} . It could thus be concluded that non-C2 methylation ILs have lower absorption coefficient that that of C2 methylation counterpart.

Figure 5 also gives the comparison of anion between Ac and BF₄ (i.e., [BMIM][Ac] and [BMIM][BF₄], [BMMIM][Ac], and [BMMIM][BF₄]). The values of ε_{mol} and ε_{mg} of [BMMIM][Ac] are slightly lower than those of [BMMIM][BF₄].

3.2 Conjugated and inductive effect of ILs

The conjugated and inductive effect of ILs could be qualified by the maximum absorption wavelength λ_{max} . There are three types of conjugated effect (π - π , p- π , and δ - π) and two types of inductive effect (electro-donating and electron-withdrawing). The value of λ_{max} of conjugated effect (π - π > p- π > δ - π) is greater than that of λ_{max} of inductive effect (electro-donating > electron-withdrawing). Conjugated effect (electro-donating > electron-withdrawing). Conjugated effect (electro-donating > electron-withdrawing). Conjugated substitute group tethered to the cation leads to a larger value of λ_{max} , whereas inductive substitute group contributes to a less one.

Figure 7 shows the results of conjugated and inductive effects of ILs in water. In terms of the cation, the maximum absorption wavelengths λ_{max} of pyrrolidium [39] (e.g., [BMPyrr][Br]), tetraammonium (e.g., [N₄₄₄₄][Ac]), and tetraphosphonium salts (e.g., [P_{666,14}][Br])





Figure 7. Conjugated effect and (positive and negative) inductive effect of ILs with the maximum UV absorption wavelength λ_{max} .

salts are not detectable because no conjugated cation exists. The UV spectra of conjugated imidazolium and pyridinium cation are detectable. It could be explained by the existence of π - π conjugated cations ring. Specifically, larger conjugated cation (e.g., [BPy][Br] > [BMIM][Br]) contributes to an easier absorption with a larger value of λ_{max} (Table 2).

Figure 7 also indicates that electron-withdrawing substitute groups (e.g., amine in [aEMMIM][Br]) show a lower peak than electron-donating substitute groups (e.g., alkyl and C2 methylation), because the former disfavors the p- π or δ - π conjugation effect of the imidazolium cation due to the electron-withdrawing effect, whereas the latter favors the conjugation effect of the imidazolium cation due to the electron-donating effect.

Effect of the anion type on the conjugated and inductive effect of ILs is also shown in Fig. 7. The order of λ_{max} is Ac (no peak) < Br $<\!{\rm NO}_3\!<\!{\rm PF}_6\!<\!{\rm CHO}\!<\!{\rm Tf}_2{\rm N}\!<\!{\rm TFO}\!<\!{\rm BF}_4\!<\!{\rm TFA}\!<\!{\rm Cl}\!<\!{\rm I}.$ [BMIM][Ac] showed no UV spectrum peak, indicating that the anion Ac had the least conjugated interaction with the conjugated imidazolium cation. It might be due to high polarity and hydrogen-donor ability of the anion, forming strong hydrogen-bond with the C2-H of the imidazolium cation thus breaking the conjugated effect of the cation. Previous findings reported that acetate-based ILs were also the most hydrophilic ILs among the ILs varying in anion investigated [16], thus, the conjugated effect of the cation might also be most affected by the polar solvent, i.e., water. Instead, the less polar and hydrogen-donating anion I, which is partially due to its greater atom radius, has a less effect on the conjugated effect of the cation, leading to a maximum λ_{max} among all the ILs varying in anion investigated.

However, the C2-methylaiton counterpart of [BMIIM][Ac], i.e., [BMMIM][Ac], showed a UV spectrum peak (Table 2 and Fig. 7). After C2-methlyation (i.e., [BMMIM][Ac]), the anion Ac might have less potential to interact with the cation (i.e., BMMIM), because the cation of [BMMIM][Ac] provides less hydrogen donor than the cation of [BMIM][Ac] [21, 22, 40]. Without strong hydrogen-bond between the anion and the imidazolium cation (i.e., BMMIM), the cation could possibly be more conjugated, thus a larger value of λ_{max} .

The effect of alkyl chain length (including ethyl, butyl, hexyl, octyl, and decyl) on the UV absorption spectra of ILs with the structure [alkyl-MIM][BF₄] was also investigated (Table 2 and Fig. 7). Results show that longer alkyl chain length (from ethyl to octyl), i.e., more electron-donating effect of the substitute group to the cation, makes

a greater value of λ_{max} . Another interesting finding is that the longest alkyl chain length we investigated here (e.g., decyl) did not show a larger value of λ_{max} (Table 2 and Fig. 7). It might be due to a decreasing effect of electron-donating effect when the alkyl chain length is longer: the value of λ_{max} is increasing less with a longer alkyl chain then reaches a maximum value until octyl, and then the value of λ_{max} is decreasing. This discrepancy is also possibly caused by the aggregation of ILs (i.e., [DMIM][BF₄]) with the longest alkyl chain length [41].

4 Concluding remarks

UV spectroscopy was used to determine the concentrations of ILs in water. The concentration detection limit ranges from 0.625 to 80 mg/L. More importantly, this limit can be tuned by altering the path length of cuvette, i.e., the narrower of the path length, the better of quantifying the concentration of ILs in water. The maximum absorption wavelength λ_{max} of the UV spectra can be used to qualitatively analysis the conjugated and inductive effect of ILs in water. For the cation, the content of ILs with conjugated cation (e.g., pyridinium, imidazolium) could be quantified easier than that without conjugated cation (e.g., pyrrolidium, tetraammonium, tetraphosphonium). As for the anion, the easiest and most difficult UV absorption is the ILs with the anion I and Ac, respectively. Also, the electron-donating group (e.g., alkyl, C2 methylation) in the cation could improve the UV absorption with a larger value of λ_{max} . ILs with a longer chain length show a large value of λ_{max} but with a decreasing effect, i.e., increasing less from ethyl to octyl, then reach a maximum value of λ_{max} for octyl, then decreasing.

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