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Investigation on Solvation of *meso*-Tetrakis(4-aminophenyl)-porphyrin in Imidazolium-Based Ionic Liquids by Spectroscopic Methods

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The solvation and protonation of the meso-tetrakis(4-aminophenyl)porphyrin (TAPP) were investigated by spectroscopic methods in aqueous and organic solutions of imidazolium-based ionic liquids: 1-ethyl-3-methylimidazolium bromide [C_2mim]Br, 1-dodecyl-3-methylimidazolium bromide [C_{12}mim]Br, 1-dodecyl-3-methylimidazolium chloride [C_{12}mim]Cl, 1-tetradecyl-3-methylimidazolium chloride [C_{14}mim]Cl). The Soret band of TAPP exhibited a bathochromic shift in [C_{12}mim]Cl, [C_{12}mim]Br and [C_{14}mim]Cl media with respect to those obtained in conventional aqueous solution. The spectroscopic characteristics of compounds depend on the polarity of the medium. The protonation of TAPP in ionic liquids is dependent not only on the concentration of ionic liquids as proton sources, but also on the characteristic of anion and viscosity of ILs.

Keywords: Porphyrins, optical properties, solutions, solvation, ionic liquids, aggregation.

Исследование сольватации *мезо*-тетракис(4-аминофенил)-порфирина в ионных жидкостях на основе имидазолия спектральными методами

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Сольватацию мезо-тетракис(4-аминофенил)порфирина (TAPP) исследовали спектральными методами в водных и органических растворах ионных жидкостей на основе имидазолия: 1-этил-3-метилимидазолия бромида [C_2mim]Br, 1-додецил-3-метилимидазолия бромида [C_{12}mim]Br, 1-додецил-3-метилимидазолийхлорид [C_{12}mim]Cl, 1-тетрадецил-3-метилимидазолийхлорид [C_{14}mim]Cl). Полоса Соре TAPP демонстрировала батохромный сдвиг соответственно в средах [C_{12}mim]Cl, [C_{12}mim]Br и [C_{14}mim]Cl по сравнению с полосой, полученной в обычном водном растворе. Показано, что спектральные характеристики соединений зависят от полярности среды. Протонирование TAPP в ионных жидкостях зависит не только от концентрации ионных жидкостей как источников протонов, но и от характеристики аниона и вязкости ИЖ.

Ключевые слова: Порфирины, оптические свойства, растворы, сольватация, ионные жидкости, агрегация.

Introduction

Ionic liquids (ILs) have a wide range of promising applications due to their unique properties. With the advent of room temperature ionic liquids (RTIL), it was hoped that their use would help optimize many processes and create fundamentally new technologies that correspond to modern trends in "green chemistry".[1-3] Today, ionic liquids are considered as the latest environmentally friendly solvents that are capable of dissolving a wide range of organic and inorganic compounds and thereby replacing volatile organic compounds in industry.[4-8]

The purposeful choice of cationic and anionic components of an ionic liquid allows creating "designer solvents" based on them for a wide range of applications. An effective strategy for «tuning» the properties of ionic liquids for specific tasks is their combination with salts, organic solvents or water. The addition of a solvent can dramatically change the properties of ionic liquids, while water is the most studied solvent used to "tune" ionic liquids. This ensures the orientation of ionic liquids to specific tasks and opens up wide opportunities for their application in chemistry, biochemistry, biology, medicine and various technologies.[8-13]

In this regard, for the practical use of ILS as solvents, their behavior in contact with water is important, which determines their nature. In particular, imidazolium-based ILs are stable in water, which expands the possibilities of their application. The reaction medium has a decisive influence on the rate of reactions and their direction. In this regard, understanding the fundamental aspects of the interaction of a solute with an ionic liquid, such as solvation dynamics, aggregation, is of key importance for both theoretical chemistry and technological processes.[14,15]

Several studies have shown that solvation dynamics in ionic liquids can be biphasic or a more complex non-exponential form.[16,17] In biphasic dynamics, the faster and slower components are attributed to the diffusional movement of the anion and the collective motion of the anion and cation, respectively.[18-22] Alternative viewpoints, such as the faster component arising from the collective motion of the anion and the cation, also exist.[23] In fact, solvation in ionic liquids compared to dipolar solvents can be attributed to their much larger viscosities.[20,23] In specific cases, it has been found that solvation is cation size-dependent.[24]

Tetrapyrrole macroheterocyclic compounds attract the attention of researchers as a key link in the creation of functional materials for various applications.[24,25] Their high chemical stability, the ability to coordinate almost any metal, the excellent chromophoric properties of the π-conjugated macrocycle system, biocompatibility, and high sensitivity to the external environment of the molecule allow this class of compounds to be effectively used to form catalytically, photo- and biologically active materials. Among them, the group of synthetic tetraarylporphyrins occupies a special place. The active use of *meso*-aryl-substituted porphyrins is due to their availability, high stability, reactivity, and well-developed methodologies for their preparation.[26]

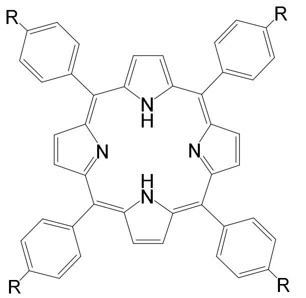
Amino groups in the phenyl rings of tetraaryl-porphyrin ensure its high reactivity and functional activity in various chemical processes. They are of particular interest as active structural units that make it possible to form porphyrin polymers on their basis,[27] immobilizates in bulk and on the surface of a polymer material.[28,29] To date, tetraaminophenylporphyrins and their metal complexes have proven themselves in the creation of electroactive film materials to create high-speed optoelectronic devices and highly active catalysts[24,30-33] and as effective photo-sensitizers for the destruction of cancer cells and inhibition of tumor growth.[34-36]

In this regard, the expansion of possible areas of application of the unique properties of porphyrins and their metal complexes requires the solution of the issue of proposing effective methods for transferring poorly soluble tetrapyrrole macroheterocyclic compounds into a dissolved state and obtaining stable aqueous solutions compatible with biological media.

One way to increase the solubility of tetrapyrroles is to use ionic liquids as alternative solvents.

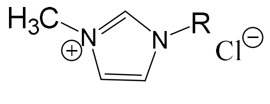
Studies of the interaction of tetrapyrrole macrohetero-cyclic compounds with ionic liquids attract special attention of researchers due to the unique properties of both components. Although at present there are only a few works devoted to individual studies of porphyrin–IL systems, it is possible to single out the outlined directions of these studies. The mutual influence of porphyrin and IL in the resulting system contributes to an increase in electro-catalytic activity in the process of oxygen reduction,[37] in the creation of organic photovoltaic cells,[38] in efficient aldehyde olefination reactions,[39] bifunctional catalysts for cyclo addition of carbon dioxide to epoxides,[40] styrene epoxidation,[41] catalysis of the Heck reaction.[42] Ionic liquids can be used as "green solvents" for the synthesis of porphyrins and their metal complexes,[43-45] stabilizers of porphyrin solutions in water and on the electrode surface.[46] Ionic porphyrins can be a constituent part of a porphyrin-containing ionic liquid.[47,48]

Our study is focused on how the spectroscopic characteristics of TAPP are affected by: 1) the transition from an organic solution with IL to an aqueous solution; 2) the ratio of TAPP:IL in solution; 3) specific structure of IL.



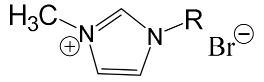
R=H – *meso*-tetraphenylporphine

R=NH_2 – *meso*-tetrakis(4-amino-phenyl)porphyrin



R = $C_{12}H_{25}$ – 1-dodecyl-3-methylimidazolium chloride [C_{12}mim]Cl

R = $C_{14}H_{29}$ – 1-tetradecyl-3-methylimidazolium chloride [C_{14}mim]Cl



R=C_2H_5 – 1-ethyl-3-methylimidazolium bromide [C_2mim]Br

R=$C_{12}H_{25}$ – 1-dodecyl-3-methylimidazolium bromide [C_{12}mim]Br

Table 1. Specification of the chemicals.[a]

Name	Source	Mass Fraction Purity	CAS number	ω_{H2O}, %
1-Ethyl-3-methylimidazolium bromide $[C_2mim]Br$	J&K Scientific	≥ 0.98	65039-08-9	0.78
1-Tetradecyl-3-methylimidazolium chloride $[C_{14}mim]Cl$	GmbH & Co, Germany	≥ 0.98	171058-21-2	0.94
1-Dodecyl-3-methylimidazolium bromide $[C_{12}mim]Br$	GmbH & Co, Germany	≥ 0.98	61546-00-7	0.52
1-Dodecyl-3-methylimidazolium chloride $[C_{12}mim]Cl$	GmbH & Co, Germany	≥ 0.98	114569-84-5	0.61
Trichloromethane	Vekton, Russia	≥ 0.998	67-66-3	0.05
Ethyl alcohol	Konstanta-farm, Russia	≥ 0.95	64-17-5	5

[a] All the chemicals were used without further purification.

Experimental

Materials

Table 1 includes the information on the source and the purity of chemical reagents used in this work. All these chemicals were used in the experiments without any additional purification. The purity analysis method for chemicals is ^1H and ^{13}C NMR spectroscopy. Bi-distilled water was used to create aqueous solutions.

meso-Tetrakis(*4*-aminophenyl)porphyrin and *meso*-tetraphenylporphin were synthesized by the known techniques.[49,50]

Apparatus

The UV–vis absorption spectra were taken on SHIMADZU UV-3600 plus spectrophotometer (Kyoto, Japan) and the fluorescence on Solar CM-2203 spectrofluorimeter (Minsk, Republic of Belarus). Fluorescence spectra were obtained at 568 nm excitation. All the experiments were performed at room temperature.

Procedures

Initially, a certain amount of TAPP was directly dissolved in chloroform, and ILs – in ethanol. Different concentrations of ILs were obtained by diluting the stock solution. TAPP concentration was controlled by electronic absorption spectra. After mixing TAPP solutions and ILs, several solutions were prepared with different molar ratios of TAPP:ILs. The concentration of porphyrin in all experiments was constant $4.2\cdot10^{-5}$ mol/L, and the concentration of ionic liquid in the working solution varied from $4.5\cdot10^{-5}$ to $4.8\cdot10^{-2}$ mol/L. To study the properties of these systems in an aqueous medium, they were isolated in solid form by evaporation of volatile organic solvents of chloroform and ethanol, and the resulting solid residue was dissolved in bidistilled water.

Results and Discussion

Absorption spectra of TAPP in binary organic solutions ILs

The absorption spectra of TPP and TAPP have been measured with four different ILs, namely, $[C_2mim]Br$, $[C_{12}mim]Cl$, $[C_{12}mim]Br$ and $[C_{14}mim]Cl$. The absorption spectra of TAPP with ionic liquids display obvious differences in organic and aqueous solutions, as summarized in Table 2. TAPP as free base (H_2TAPP^{4-}) with D_{2h} symmetry exists usually in neutral aqueous solution of ILs, two nitrogen atoms of the macrocyclic core of H_2TAPP^{4-} remaining unprotonated form.

When analyzing the electronic spectra of organic solutions of various porphyrin-ionic liquid systems and comparing them with the spectra of pure porphyrin in chloroform, the following results were obtained.

For all solutions of *meso*-tetraphenylporphin in any ionic liquid, a hypsochromic shift of 0.5–3.5 nm is observed which does not depend on the molar ratio of porphyrin to ionic liquid, as well as the hypochromic effect.

For the tetra(4-aminophenyl)-porphyrin system with $[C_2mim]Br$, a hypsochromic shift of 1–2.5 nm, similar to that for TPP, is observed, independent on the molar ratio of porphyrin to IL. Also, the system, in comparison with a blank sample of porphyrin, has a change in the absorption intensity of the bands: it decreases for the Soret band, and increases for the bands in the visible region.

The TAPP - $[C_{12}mim]Br$ system has a bathochromic shift by 1–2 nm, which does not depend on the molar ratio of porphyrin to IL. The intensity of the Soret and III bands in the visible region decreases, while the intensity of the I and II bands' increases, compared to TPP in chloroform.

Table 2. Electronic absorption spectra at the molar ratio porphyrin : ionic liquid 1:100.

Name	Wavelength, nm (absorbance)				
	Soret	Q-IV	Q-III	Q-II	Q-I
TPP in chloroform	417 (5.05)	515 (0.36)	549.5 (0.17)	589.5 (0.13)	645.5 (0.11)
TPP+$[C_2mim]Br$	414 (4.30)	512 (0.23)	546 (0.12)	588.5 (0.10)	645 (0.09)
TPP+$[C_{12}mim]Br$	412.5 (4.70)	512 (0.29)	546 (0.14)	588 (0.11)	645 (0.09)
TPP+$[C_{12}mim]Cl$	413 (4.16)	512 (0.22)	546 (0.12)	589 (0.09)	645 (0.07)
TPP+$[C_{14}mim]Cl$	413 (4.28)	512 (0.24)	546 (0.13)	588.5 (0.10)	644.5 (0.09)
TAPP in chloroform	427.5 (2.94)	-	523 (0.15)	562.5 (0.14)	654.5 (0.09)
TAPP+$[C_2mim]Br$	425.5 (2.20)	-	522 (0.14)	564.5 (0.17)	657 (0.11)
TAPP+$[C_{12}mim]Br$	425.5 (2.15)	-	521.5 (0.14)	564.5 (0.16)	657 (0.10)
TAPP+$[C_{12}mim]Cl$	425.5 (2.11)	-	522 (0.13)	564 (0.15)	656.5 (0.10)
TAPP+$[C_{14}mim]Cl$	425.5 (2.09)	-	522 (0.14)	564 (0.16)	657 (0.10)

In a certain range of molar ratios (samples 1-4), the H_2TAPP-[C_{12}mim]Cl system has a hypsochromic shift of the Soret and III bands in the visible region by 1–2 nm and a bathochromic shift of the Ith and IIth bands by 1.5 nm. With increase of the IL amount (sample 5), the peaks are smeared in the visible region. And with even more IL (sample 6), the Soret band bifurcates, the bands in the visible region disappear, and a new one appears at λ=770 nm (Figure 1).

In a certain range of molar ratios (samples 1-5), the TAPP-[C_{14}mim]Cl system has a hypsochromic shift of the Soret band and the IIIth band in the visible region by 1–2 nm and a bathochromic shift of the Ith and IIth bands at 1–1.5 nm. With an increase in the amount of IL (sample 6), the Soret band bifurcates, the bands in the visible region disappear, and a new one appears at λ=767 nm (Figure 2).

The absorption spectra of the sixth sample of TAPP with [C_{12}mim]Cl and [C_{14}mim]Cl are similar in character to the absorption spectra of the protonated TAPP form.

Absorption spectra of TAPP in aqueous solutions of ILs

Due to the low stability of the TPP-[C_2mim]Br, TPP-[C_{12}mim]Br, TAPP-[C_2mim]Br systems, it was not possible to transfer them to an aqueous solution. TPP-[C_{12}mim]Cl and TPP-[C_{14}mim]Cl systems are poorly soluble in water (Figure 3).

Stable aqueous solutions were obtained for the TAPP-[C_{12}mim]Br, TAPP-[C_{12}mim]Cl and TAPP-[C_{14}mim]Cl systems.

When TAPP passes from an organic solvent medium (ethanol-chloroform) to an aqueous medium, a bathochromic shift of several nanometers, from 1 to 15, is observed (what indicates the aggregation of TAPP).

In TAPP systems with ILs in aqueous solutions, the shift of the Soret band is 4–5.5 nm (Figures 4–6). The shift of the bands in the visible region of the spectrum is different and depends on the ratio of TAPP to IL. The highest concentration of TAPP was achieved in systems with a ratio from 1:22 to 1:1118.

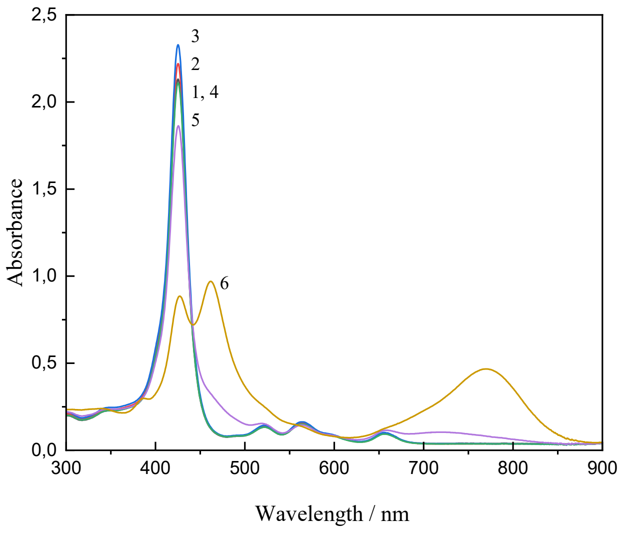


Figure 1. Absorption spectrum of TAPP with [C_{12}mim]Cl in ethanol-chloroform medium. Molar ratio of TAPP to [C_{12}mim]Cl: (1) 1:6, (2) 1:12, (3) 1:22, (4) 1:118, (5) 1:471, (6) 1:1118. TAPP concentration 4.2·10^{-5} mol/L.

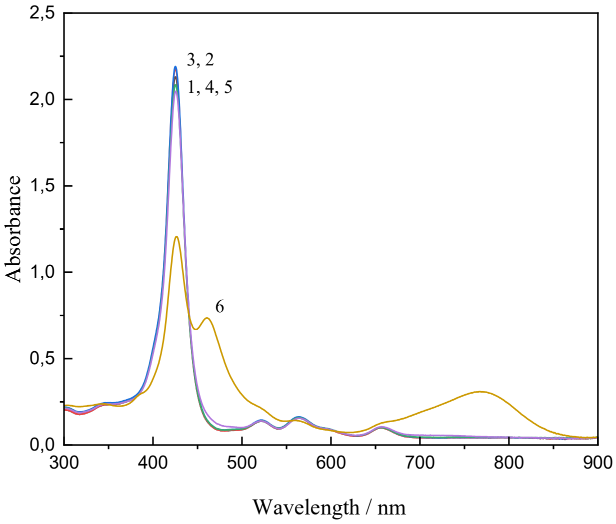


Figure 2. Absorption spectrum of TAPP with [C_{14}mim]Cl in ethanol-chloroform medium. Molar ratio of TAPP to [C_{14}mim]Cl: (1) 1:6, (2) 1:12, (3) 1:23, (4) 1:118, (5) 1:471, (6) 1:1118. TAPP concentration 4.2·10^{-5} mol/L.

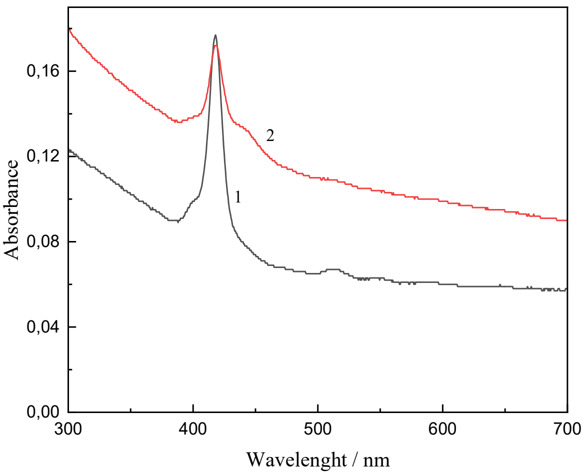


Figure 3. Absorption spectrum of TPP with [C_{12}mim]Cl (1) and [C_{14}mim]Cl (2) in ethanol-chloroform medium. Molar ratio of TPP to IL 1:942. TPP concentration 5.0·10^{-5} mol/L.

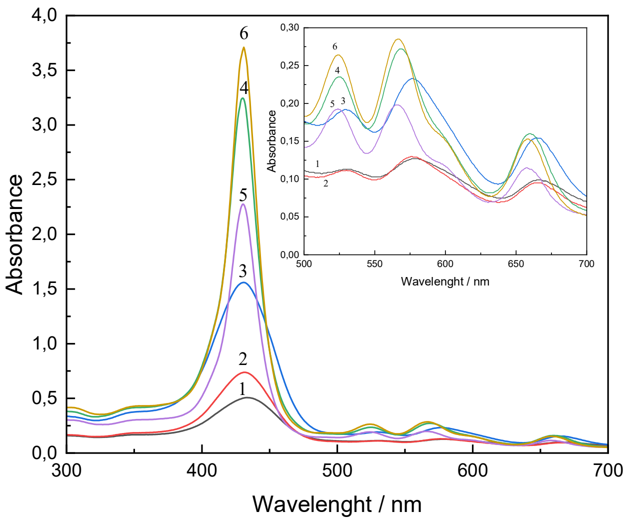


Figure 4. Absorption spectrum of the aqueous solution of the TAPP-[C_{12}mim]Br system. Molar ratio of TAPP to [C_{12}mim]Br: (1) 1:6, (2) 1:12, (3) 1:22, (4) 1:294, (5) 1:530, (6) 1:1118.

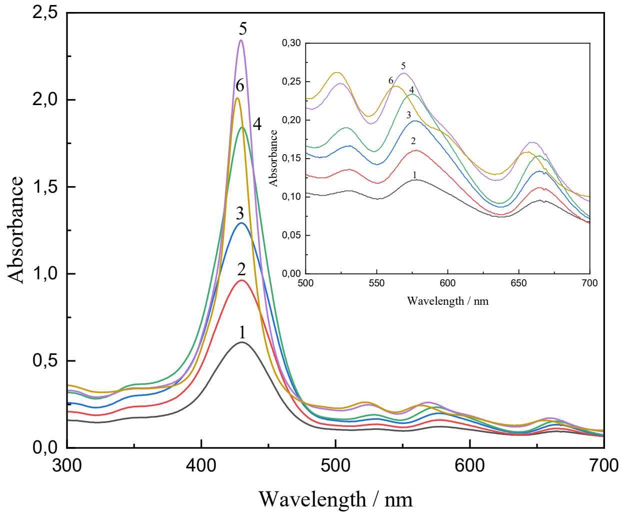


Figure 5. Absorption spectrum of the aqueous solution of the TAPP-[C_{12}mim]Cl system. Molar ratio of TAPP to [C_{12}mim]Cl: (1) 1:6, (2) 1:12, (3) 1:22, (4) 1:118, (5) 1:471, (6) 1:1118.

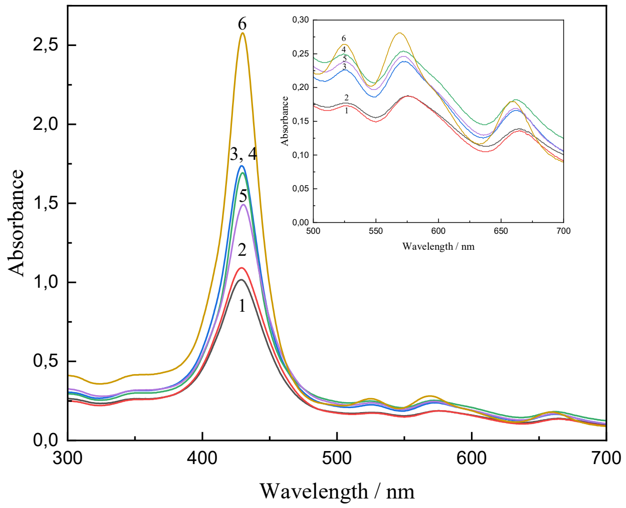


Figure 6. Absorption spectrum of the aqueous solution of the TAPP-[C_{14}mim]Cl system. Molar ratio of TAPP to [C_{14}mim]Cl: (1) 1:6, (2) 1:12, (3) 1:23, (4) 1:118, (5) 1:471, (6) 1:1118.

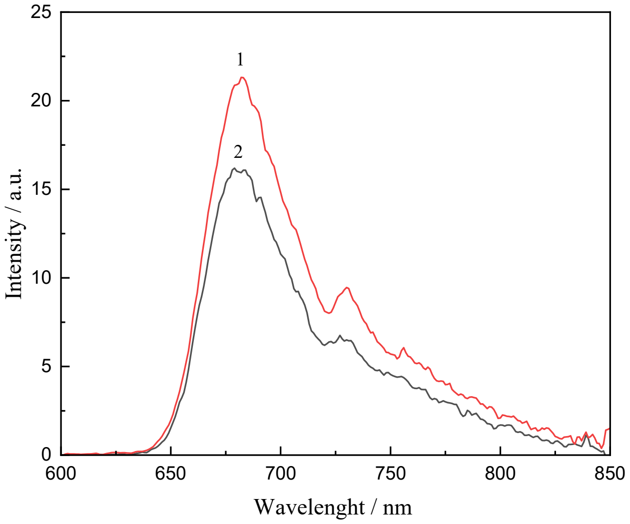


Figure 7. Fluorescence spectra for TAPP with [C_{12}mim]Cl (1) and [C_{12}mim]Br (2) in aqueous solution. Molar ratio of TAPP to IL 1:1118, λ_{ex} was set at 568 nm.

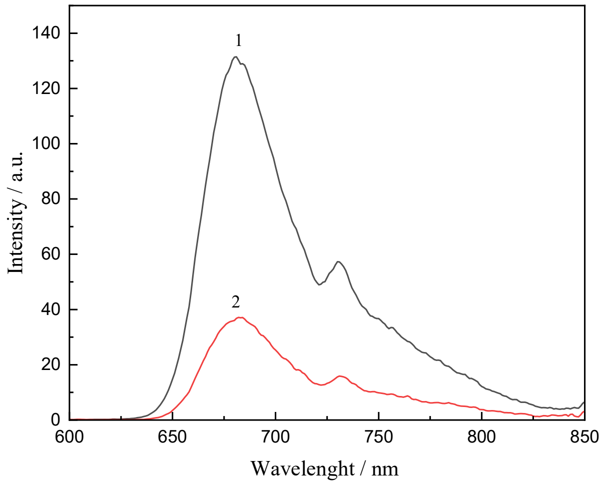


Figure 8. Fluorescence spectra for TAPP with [C12mim]Br in ethanol-chloroform (1) and in aqueous solution (2). Molar ratio of TAPP to IL 1:530, λ_{ex} was set at 568 nm.

The effects of ILs on the fluorescence spectra of TAPP in ILs

The fluorescence spectra of TAPP exhibit one emission band which appears at 681 nm (Figures 7, 8). The fluorescent properties of TAPP are sensitive to the presence of the ILs. The enhancement degree of TAPP emission is greater in the IL containing the Cl^- anion than in systems with [C_{12}mim]Br (Figure 7). Another property is that the fluorescence intensities of TAPP are lower in the water than that observed in conventional solvents in ILs medium (Figure 8).

General solute–solvent interactions between TAPP and ILs. The effect of the solvent polarity

The Soret band of TAPP exhibit a bathochromic shift in [C_{12}mim]Cl, [C_{12}mim]Br and [C_{14}mim]Cl media with respect to those obtained in conventional aqueous solution (Figure 2 and Table 2). It was well-defined that the spectroscopic behavior of compounds depends on the polarity of the medium. Therefore, these ILs should have high polarity comparable to water.[42,43] The polarity of [C_{12}mim]Cl and water is 74.35 and 63.1, respectively, on the ET(30) polarity scale.[44] The polarity of [C_{14}mim]Cl is 48.9 and more polar than acetonitrile (45.6) but less polar than methanol (55.4) on the ET(30) polarity scale.[51] The solvent cage model is frequently used to explain the interaction between solvent and solute.[45,52,53]

A study of the fluorescence spectra of the obtained systems shows that when the system passes from an organic solvent medium to an aqueous medium, fluorescence quenching is observed (Figure 8), which is associated with porphyrin aggregation. It was also noted that in systems with IL containing the Br^- anion, the fluorescence intensity is greater than in systems with Cl^-, which means that in systems with chlorine, aggregation is more pronounced.

The π–π complex of the solute–solvent between TAPP and ILs

The π–π interaction can be taken into account of the absorption profiles of TAPP dissolved in the three ILs medium, respectively (in solutions with ionic liquids). The most significant change in the absorption spectrum of TAPP are happened in [C_{12}mim]Cl and [C_{14}mim]Cl medium, respectively. It indicates a complicated interaction between TAPP and the two ILs besides the general dipolar effect. The imidazolium cation is an aromatic π-system. It is highly possible that the solute–solvent (porphyrin ionic liquid) complex was stabilized by the π–π interaction between the TAPP macrocycle and the aromatic imidazolium cation.[54,55] Moreover, the repulsive force between the positive charges or the negative charges, the π–π interaction between TAPP and imidazolium cation counteract the π–π stacking of the porphyrin itself, which favored the stability and dispersion of TAPP in ILs.[56]

Conclusions

Tetra(4-aminophenyl)porphyrin forms stable systems with imidazolium ionic liquids, which are readily soluble in water. The absorption and fluorescence spectra of TAPP in organic solution of ILs display significant difference compared to aqueous solution. This should be attributed to the complicated interaction including π–π interaction and hydrophobility, electrostatic interaction, dipole-dipole and also proton transfer, *etc*. Both cation and anion should be simultaneously considered in investigation of solute–solvent interaction.[15–19] This might be the largest difference from general dipolar organic solvents. Detail solvation dynamics of TAPP in IL solutions is currently under study in our group.

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