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## Preparation of colorless ionic liquids “on water” for spectroscopy

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### ARTICLE INFO

#### Article history:

Received 4 August 2008

Received in revised form 19 December 2008

Accepted 21 December 2008

Available online 15 January 2009

#### Keywords:

Ionic liquids

Colorless

On water

Green chemistry

Spectroscopy

### ABSTRACT

Although colorless ionic liquids (ILs) are most desirable, as synthesized they frequently bear color, despite appearing pure by most analytical techniques. It leads to some uncertainties and limits for the fundamental research and applications of ILs, such as spectroscopy. Using 1-butyl-3-methylimidazolium bromide (BMIMBr), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>) and 1-hexyl-3-methylimidazolium bromide (HMIMBr) as models, we demonstrated that following classic preparing method except that the water was added as solvent, colorless ILs could be facilely prepared. Neither critical pre-treatment of starting materials and pre-cautions during the reaction nor time-consuming and costly post-decolor-purification was needed. The effects of “on water” reaction conditions on preparing colorless IL and the reason why using water as solvent could produce colorless ILs were also preliminary investigated. It was found that the reactant solubility played an important role in the preparation of colorless ILs. Not only as a method to evaluate the quality of as-synthesized ILs, but also as a spectroscopic analytical applications, UV–vis spectra showed that the ILs by this “on water” method was spectral pure and sufficient for future fundamental spectroscopic research and applications.

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### 1. Introduction

Recently room temperature ionic liquids (RTILs) have attracted considerable interest in many fields of chemistry and chemical industry. Their unique physicochemical properties such as negligible vapor pressure, nonflammability, and thermal stability make them as “green” alternatives to conventional organic solvents in a range of synthesis, catalysis, electrochemistry and liquid–liquid extraction [1–4]. Although common ILs should be colorless, they frequently bear color as synthesized [1,5]. After much investigation over the last two decades, the source(s) of color have not been definitely identified [6]. For example, 1,3-dialkylimidazolium halides, typically used as starting ILs to synthesize other ILs bearing other counteranions, are often yellow or even brown, despite appearing pure by most analytical techniques (e.g. NMR, mass spectrometry, HPLC and ion chromatography) other than UV–vis spectroscopy [1,6]. Hence, to date, the chemical structure of the colored impurities is still difficult to be determined. Although until now there is no direct evidence that the colored impurities will affect the chemical or physical properties of ionic liquids, they have a major influence upon measurements containing light absorption or emission. This will lead to many uncertainties and even limitations in various ILs applications such as analytical chemistry [12], photochemistry

[7–11], and *in situ* UV–vis spectroscopy [13–17], thus colorless ILs are most desirable.

There are two general approaches for the preparation of less colored ILs. The first method mainly includes some special purification of starting materials before the synthesis besides simple distillation and controlling the reaction in low temperature (e.g. in ice bath). The special purification of starting materials usually contains extracting the alkyl halide with concentrated sulfuric acid, followed by neutralizing with a concentrated NaHCO<sub>3</sub>-solution and drying with MgSO<sub>4</sub> [17]. The second method is post-treatment of the as-prepared colored ILs, i.e. discolor-purification by charcoal or alumina columns [1,6,18].

In this paper we present a new facile method to prepare colorless ILs by using water as solvent (i.e. in an “on water” reaction system [19–24]) without any special pretreatment of the starting materials. The colored species did not appear during the whole reaction, thus further time-consuming and costly discolor-purification was also excluded. The approach described here would offer a convenient model system to obtain colorless ILs for spectroscopic analytic researches and applications.

### 2. Experimental

#### 2.1. Materials

1-Bromobutane (98%), 1-bromohexane (98%) and NaBF<sub>4</sub> (98%) were purchased from Sinopharm Chemical Reagent Co. Ltd., China

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**Table 1**  
Preparation conditions and yields of BMIMBr under N<sub>2</sub> protection.

Rxn	Molar ratio <sup>a</sup>	Solvent	v/v <sup>b</sup>	Time (h)	Temp. (°C)	Yield (%)
1	2:1	Water	0.85:1	24	60	61
2	2:1	Water	0.85:1	24	70	96
3	2:1	Water	0.85:1	24	80	98
4	2:1	Water	0.85:1	12	70	72
5	2:1	Water	0.85:1	48	70	97
6	2:1	Water	0.42:1	24	70	94
7	2:1	Water	1.70:1	24	70	87
8	1.2:1	Water	0.85:1	24	70	91
9	2.5:1	Water	0.85:1	24	70	98
10	2	No solvent	–	24	70	99
11	1.2	No solvent	–	24	70	97

<sup>a</sup> Molar ratio of 1-bromobutane to 1-methylimidazole.

<sup>b</sup> v/v (volume ratio) of water to reactant.

and used as-received. 1-methylimidazole (99+%) was obtained from Kaile Chemical Factory (China) and newly distilled before use. All the water used in experiments was purified using a Millipore-Q system.

## 2.2. Preparation of BMIMBr, HMIMBr and BMIMBF<sub>4</sub>

The general procedure for the synthesis of 1-butyl-3-methylimidazolium bromide (BMIMBr) “on water” was similar with previously published procedures [1,25], excepting using water as the solvent. Typically, a mixture of 1-methylimidazole and 1-bromobutane with different ratios was heated under N<sub>2</sub> protection with water as the solvent (Table 1). When the reaction time was completed, the excessive phase-separated 1-bromobutane was first decanted. Then, the residual 1-bromobutane and water were removed under reduced pressure at 70 °C. The preparation of 1-hexyl-3-methylimidazolium bromide (HMIMBr) “on water” was similar to that of BMIMBr.

The general procedure for the synthesis of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF<sub>4</sub>) was according to the references [1]. BMIMBr (21.9 g, 0.1 mol) was dissolved in 100 mL of acetone, to which an equimolar amount of NaBF<sub>4</sub> was added. The mixture was then stirred for about 1 h upon which the white precipitate was formed at the bottom of the beaker. The acetone layer was filtered, and the solvent was evaporated under reduced pressure at 50 °C.

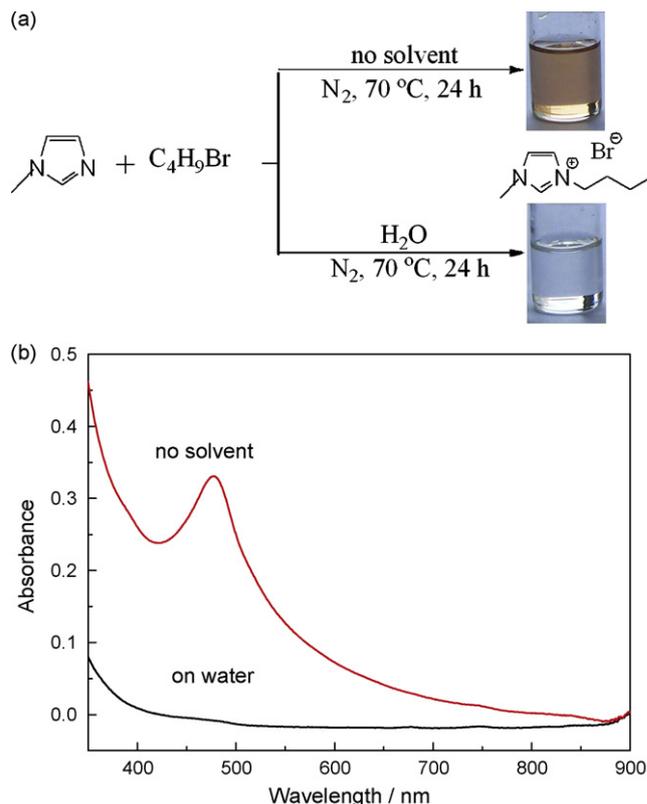
## 2.3. Instruments

UV–vis–NIR spectra and photographs of 1,3-dialkylimidazolium halides in liquid were recorded on a CARY 500 UV–vis–NIR spectrometer and a Kodak DX6340 digital camera, respectively. <sup>1</sup>H NMR spectra were obtained on a Varian Unity-400 (400 MHz) NMR spectrometer with tetramethylsilane (TMS) as an internal standard in per-deuterated dimethyl sulfoxide (DMSO-*d*<sub>6</sub>), where chemical shifts were reported with the indicated solvent as an internal reference. Coupling constants were reported in Hz. The full names of splitting abbreviations were listed as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet.

## 2.4. NMR results

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) for BMIMBr prepared without solvents and from “on water” reaction were the same: δ 9.16 (s, 1H), 7.78 (s, 1H), 7.71 (s, 1H), 4.16 (t, *J* = 7.15 Hz, 2H), 3.85 (s, 3H), 1.76 (m, 2H), 1.25 (m, 2H), 0.90 (t, *J* = 7.35 Hz, 3H).

<sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) for HMIMBr prepared without solvents and from “on water” reaction were also the same: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) for HMIMBr prepared without solvents: δ 9.14



**Fig. 1.** Photographs (a) and UV–vis absorption spectra (b) of BMIMBr in liquid prepared on water (lower) and without any solvent (upper).

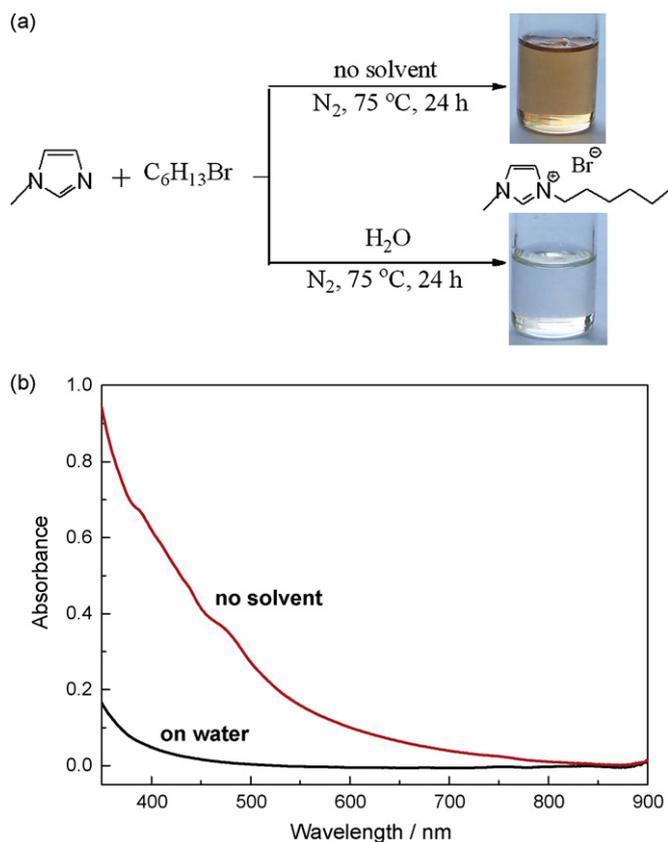
(s, 1H), 7.77 (s, 1H), 7.70 (s, 1H), 4.15 (t, *J* = 7.20 Hz, 2H), 3.85 (s, 3H), 1.77 (m, 2H), 1.26 (m, 6H), 0.86 (t, *J* = 6.88 Hz, 3H).

## 3. Results and discussion

In a typical experiment of preparing colorless BMIMBr on water, a conventional oil bath with magnetic stirring bar was used. The biphasic liquid mixture was stirred vigorously under N<sub>2</sub> at 70 °C for 24 h. Because the product BMIMBr was soluble in water, the progress of the reaction could be visually monitored. It was observed that the volume of the 1-bromobutane phase gradually decreased and the mixture became more clarified with time. Excess un-reacted 1-bromobutane phase was colorless and could be easily removed and recycled by the phase split. At last, water and residual 1-bromobutane were removed under reduced pressure at 70 °C. Unlike the conventional synthesis with organic solvents (e.g. toluene) or without solvents (only with excessive alkyl halide), in which the IL is insoluble, our reaction system did not form a viscous product-rich layer, which was favorable to stirring and heat transfer [1].

Both BMIMBr prepared “on water” and that without solvents (the control experiment) were found to be pure by <sup>1</sup>H NMR (see Section 2). However, they appeared distinct in color by naked eye. BMIMBr prepared “on water” was clear and transparent (Fig. 1a, lower), with no appreciable absorption in the visible range (Fig. 1b, lower). The control reaction under similar conditions but without water yielded an orange/yellow product (Fig. 1a, upper) with strong absorption in the range 400–600 nm (Fig. 1b, upper).

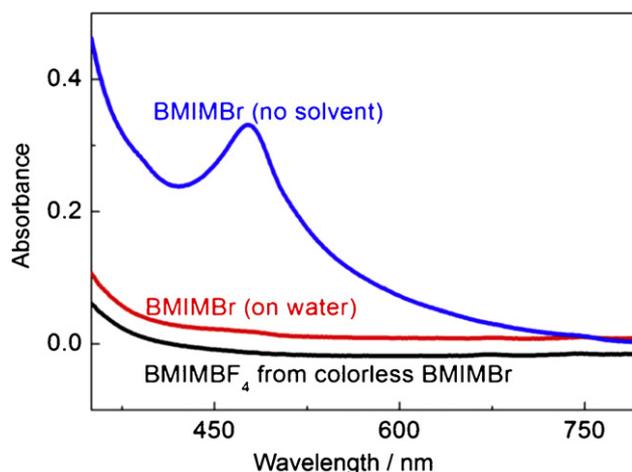
To investigate applicability of “on water” reaction to prepare other similar ILs, HMIMBr was also synthesized using water as solvent in a similar way as described above. As shown in Fig. 2, colorless product with no appreciable absorption in the visible range was



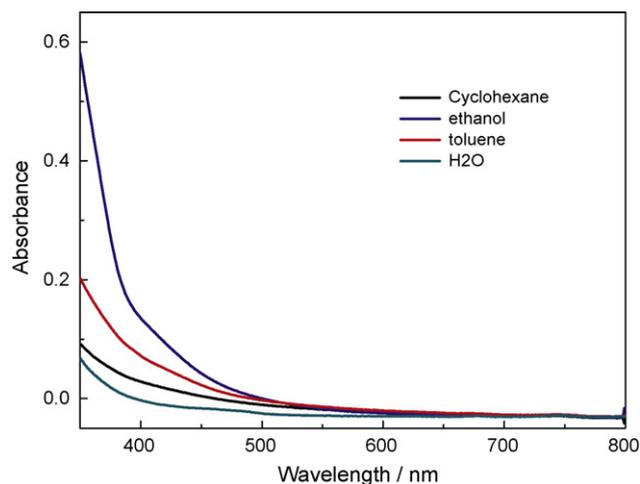
**Fig. 2.** Photographs (a) and UV-vis absorption spectra (b) of BMIMBr in liquid prepared on water (lower) and without any solvent (upper).

again obtained in the “on water” reaction, while the control reaction gave a yellow product.

Because the counteranion-exchange process did not introduce color, via well-developed metathesis method, colorless ILs bearing other counteranions could be facily obtained based on the colorless halide salts as the starting material. For example, colorless BMIMBF<sub>4</sub>, one of most common commercially available ILs, could be obtained from the “on water” colorless BMIMBr via metathesis in NaBF<sub>4</sub>/acetone solution (Fig. 3) [1].



**Fig. 3.** UV-vis absorption of BMIMBr prepared on water (red line) and without any solvent (blue line), and BMIMBF<sub>4</sub> synthesized from BMIMBr (on water) via anion metathesis (black line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 4.** UV-vis absorption of BMIMBr prepared in ethanol, toluene, cyclohexane and water.

It should be noted, for a long time, it has been widely believed that in preparation of ILs, e.g. imidazolium halides, the reaction mixture should be kept dry during the reactions because they are extremely hygroscopic. However, water is usually used in subsequent metathesis or purification of other ILs. It hinted that it was not necessary to absolutely exclude water in the reaction mixture, if the existence of water did not cause unwanted side reactions. Moreover, on the basis of economical and ecological criteria, the use of water as a solvent for organic reactions is highly desirable for organic chemists [19,22–24]. These two facts suggested water might be a suitable solvent to prepare IL. Here <sup>1</sup>H NMR and UV-vis absorption spectra results did surprisingly indicate that water not only could be used as a green solvent (to disperse reactants without causing unwanted side reactions), but also significantly eliminated formation of color impurities. To further understand this surprising result, effects of “on water” reaction conditions on preparing colorless IL, and the reason why using water as solvent could eliminate color were further investigated.

Table 1 lists a series of subsequent reactions, in which parameters were systematically varied to investigate effects on the reaction rate and BMIMBr quality. Twofold dilution of the reactants led to a yield decrease from 96% to 87% (2 and 7, respectively). Concentrating the reactants twofold (6) did not give any increase in yield, and reactions with less than 0.42:1 (v/v) water-to-reactant ratio showed light yellow color. A kinetic study at 70 °C (2, 4, and 5) showed that the reaction was still in progress at 12 h and equilibrates by 24 h. BMIMBr yield improved significantly as temperature increased from 60 °C to 70 °C and further increased only slightly at 80 °C (1, 2, and 3). Below 50 °C, yield was negligible, while above 80 °C, the product again took on light yellow hue. Finally, a concentration study showed that increasing the molar ratio of 1-bromobutane to 1-methylimidazole from 1.2:1 to 2.5:1 led to yield improvement (2, 8, and 9) with most gain realized between 1.2:1 and 2:1. A similar trend was seen in water-free reactions 10 and 11, which, despite having marginally higher yield than the corresponding on-water reactions, gave colored product.

To investigate the reason why using water eliminated color, more control reactions by replacing water with a different protonic solvent (i.e. ethanol) or with one of two nonprotonic solvents (i.e. cyclohexane and toluene) were investigated under similar conditions described above. It was found that IL synthesized in toluene or ethanol was yellow, while that synthesized in cyclohexane was colorless (absorption spectra shown in Fig. 4). This observation indicated that solvents with proton-dissociation equilibria did not prevent the formation of colored product. Moreover, it was noted

that IL was soluble in water or ethanol, but not in cyclohexane or toluene. Thus, it seemed that IL solubility in the solvents had neglected effects on the IL color. Therewith, the effect of reactant solubility in solvents on color formation was further considered. Only one of the reactants was soluble in water (1-methylimidazole) or in cyclohexane (1-bromobutane), and these reaction mixtures contained two liquid phases. However, both reactants were readily soluble in toluene and ethanol, forming a homogenous, single-liquid-phase reaction mixture. Also, in solvent-free reactions, only one liquid phase was present. In single-phase systems, the reactants have higher concentration, i.e. presumably higher reaction rate, than in biphasic systems. This may allow local hot spots (the reaction is mildly exothermic) and formation of trace impurities, which can lead to discoloration of the final product. Therefore, the effect of reactant solubility played an important role in preparation of colorless ILs. As shown, both water and cyclohexane could dissolve only one of the reactants, and they could eliminate the colored impurities. But water was much “greener” than cyclohexane, it was more preferred to be selected as solvent.

Even in the “on water” reaction, it was necessary to exclude oxygen to obtain colorless IL. To investigate whether exposure of reactants to oxygen can cause product coloration, pure 1-methylimidazole or alkyl halide was heated to 70 °C in air for 24 h, respectively. No color developed, indicating that only when both the reactants were present, colored impurities were produced. This result was also in accord with the above-mentioned effect of reactant solubility on color formation, i.e. higher concentration of both reactants in one phase more easily led to colored product.

Characterizations by other methods such as electrochemical method to determine electrochemical window and investigations of physical properties such as melting point and viscosity of ionic liquids from different synthetic methods are very important for their future applications. Our method is similar to classic method to prepare ILs, except that the water was added as solvent, and the purity of as-prepared ionic liquids from our method had been proved by NMR and UV–vis spectroscopy. Thus, if water was removed completely in the final ILs, the electrochemical and physical properties of ILs from this method should not be altered.

In comparison with previous successful examples to prepare colorless ILs, the careful pre-treatment (distill, washing and dry) of starting materials and critical precautions during the reaction [17] or with time-consuming and costly post-decolor-purification [6] were no longer needed by using water as solvent. For example, commercial alkyl-halides (98%) were used as-received and 1-methylimidazole was only fresh distilled, because it was easy to produce color impurities during storing. And the use of organic solvents for reaction and purification was also eliminated. For example, here for preparing imidazolium halides (the starting ILs for other ILs bearing other counteranions), only excessive alkylhalides were used, and moreover, the remainder could be recovered and recycled. Furthermore, the as-produced ionic liquids products in our method were colorless, which did not need further discoloring step, which was somewhat time-consuming and costly. In addition, the reaction steps, time and manpower in our method was similar with the classic method to prepare ILs (without efforts to eliminate colored impurities).

As shown in Figs. 1–3, UV–vis spectra not only prove the quality of the as-prepared ILs, but also shown the examples of applying these colorless ILs in the UV–vis spectroscopic analysis. Moreover, as described aforementioned, colorless ILs from “on water” reaction was more economic. Thus, it would greatly enrich the applications of ILs (especially in large quantity), which were previously hindered by colored impurities.

However, in the current investigation, only the most “popular” colorless imidazolium-based ILs with alkyl group was prepared

without color by “on water” reaction. Investigations of other type of ILs, such as imidazolium-based ILs bearing other halides (e.g. chlorides and iodines) or other cations-based ILs is very important to illustrate whether our method is suitable for all types of ILs. Currently this part of work together with spectroscopic analytic researches and applications of these colorless ILs are ongoing.

#### 4. Conclusion

In conclusion, using 1,3-dialkylimidazolium salts as models, we have demonstrated that water can replace organic solvents for IL preparation and more importantly the “on water” reaction itself did not produce colored impurities, which has been a longstanding challenge in the field. This reaction scheme was relatively green and simple to implement. Besides, the effects of “on water” reaction conditions on preparing colorless IL and the reason why using water as solvent could produce colorless ILs were also preliminary investigated. It was found that the reactant solubility played an important role in the preparation of colorless ILs. It will not only pave the way for economical synthesis of a broad variety of colorless ILs for spectroscopy so as to eliminate the uncertainties and limits, but also motivate theoretical and experimental studies to deepen fundamental understanding of the source(s) of color in ILs and enrich the applications of ILs in spectroscopic analytic researches and applications.

#### Acknowledgments

The authors are most grateful to the National Science Foundation of China (no. 20827004 and no. 20673109), Department of Science and Technology of Jilin Province (no. 20050102) and Ministry of Science and Technology of China (no. 2006BAKB05) for their financial supports.

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