Triethylammonium hydrogen sulfate ionic liquid as a low-cost solvent: A short review of synthesis, analysis and applications

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Abstract. This review does not attempt to be comprehensive, but it briefly introduces triethylammonium hydrogen sulfate ionic liquid ([N₂₂₂₀][HSO₄] IL), which has been regarded as a low-cost solvent. It provides guidance regarding the synthesis procedures of the IL and several routine assessments for gaining insight into the properties of the IL. The review also selects examples of applications wherein the IL has been applied. It is hoped that the review will stimulate more research utilising the [N₂₂₂₀][HSO₄] IL across various disciplines of science and engineering.

1 Introduction

Solvents are important either for domestic or commercial uses due to their various functions. In chemical production, solvents serve as media for chemical reactions and reagents for purification/separation of chemicals [2]. However, the majority of solvents employed, such as dichloromethane (CH₂Cl₂) and trichloromethane (CH₃Cl), are volatile organic solvents (VOS), and they carry negative effects to human health and the environment. Ionic liquids (ILs), often regarded as so-called ‘green solvents’, have been proposed as alternatives to VOS. They are liquids at room temperature (or just above up to 100 °C) and entirely composed of ions [3]. Unlike common organic solvents, ILs possess remarkable physical properties, including vanishing vapour pressure, large liquidous range, high thermal stability, good ionic conductivity, and favourable solvation behaviour [3]. This has resulted in ILs being widely employed in various areas of research at laboratory, such as biomass deconstruction [1,4,5], metal extraction [6,7], and catalysis [8]. Despite promising advantages, most ionic liquids are inherently expensive; a major obstacle for many commercial applications. As an example, at the time of writing, the intensively studied 1-butyl-3-methylimidazolium acetate ionic liquid ([C₄C₁im][CH₃COO]) is sold at \$881kg⁻¹ (CAS Number 284049-75-8, Sigma-Aldrich). One must note that prices for small

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quantities should not be treated as the primary guide for commercial utility, but, it is estimated that ILs are 5-20 times more expensive than molecular solvents [9].

In order to ensure commercial utilisation of ILs a practical reality, the purchasing price of ILs needs to be reduced. A way to achieve this is by formulating ILs where their synthesis must be simple and straightforward (at manufacturing scale) consuming inexpensive reagents with minimising environmental impact. Triethylammonium hydrogen sulfate, ($[N_{2220}][HSO_4]$) is one of the ILs that meets the aforementioned criteria. Chen *et al.* conducted the first study on modelling and simulation of the production process of the $[N_{2220}][HSO_4]$ IL using Aspen Plus V7.3 [9]. The simulation estimated the cost price of the IL would be $\$1.24\text{kg}^{-1}$ [4,9].

2 Synthesis of the $[N_{2220}][HSO_4]$ IL

The $[N_{2220}][HSO_4]$ IL can be easily prepared via a simple acid-base neutralisation reaction involving inexpensive reagents: triethylamine (N_{222}), sulfuric acid (H_2SO_4) and water [1,4,9,10]. Based on the Sigma-Aldrich's price check, the first and the second reagents cost not more than $\$100\text{L}^{-1}$. More importantly, the synthesis guarantees 100% yield and produces the IL in double quantity, with only water as the by-product. A report by Shikh Zahari *et al.* can be referred for detailed synthesis procedures of the $[N_{2220}][HSO_4]$ IL (a summary is shown in Fig. 1) [1].

Fig. 1. Synthesis route of the $[N_{2220}][HSO_4]$ IL reported by Shikh Zahari *et al.* [1].

The synthesis has three subsequent steps. In Step 1, N_{222} is mixed with water, forming an immiscible mixture (Fig. 1 (a)). Step 2 involves dropwise addition of aqueous H_2SO_4 to the N_{222} - H_2O mixture at room temperature (Fig. 1 (b)), and the reaction is likely to follow mechanism in Fig. 2.

Fig. 2. Mechanism of the synthesis of the $[N_{2220}][HSO_4]$ IL [1,4].

Fig. 2 demonstrates that the reaction progresses via complete proton transfer. This is based on the fact that the pK_a difference between N_{222} ($pK_a = 18$) and H_2SO_4 ($pK_a = -3$) is greater than 10, which is in good agreement with the prediction of Angell *et al.* [11]. Complete proton transfer (as shown mechanism in Fig. 2) leads to the formation of a salt, consisting of $[N_{2220}]^+$ cation and $[HSO_4]^-$ anion, that is soluble in water (Fig. 1 (c)). This can also be an indicator of the reaction completion, as evidenced by the formation of a single phase and clear solution (Fig. 1 (c)). Step 3, removal of excess water from the IL, is

optional depending on targeted applications. If the presence of water is undesired, the removal of excess water must be conducted to yield a dried IL (Fig. 1 (c)), otherwise, the drying step can be omitted.

3 Analysis of the [N₂₂₂₀][HSO₄] IL

3.1 Composition

Nucleus magnetic resonance (NMR) analysis is a routine assessment conducted on newly synthesised ILs. It is to confirm molecular structures of ILs. A previous study compared the [N₂₂₂₀][HSO₄] IL and fresh N₂₂₂; the obtained spectra are shown in Fig. 3 [1].

Fig. 3. ¹H-NMR spectra of (a) fresh N₂₂₂, and (b) the [N₂₂₂₀][HSO₄] IL reported by Shikh Zahari *et al.* [1].

Compared to the fresh N₂₂₂ (Fig. 3 (a)), all δ values in the IL's spectrum (Fig. 3 (b)) shifted downfield. This was deemed to be a strong indicative of the presence of a positive charge on the N in N₂₂₂ (N⁺) owing to protonation by H_2O in H_2SO_4 . The presence of N⁺ affords an inductive effect that pulls electron density from the proton nuclei on C α and C β . As a result, the proton nuclei experiences greater effective magnetic field, as reflected by higher frequency absorbed (Fig. 3 (b)) [1]. The outcomes of this analysis further support the proposed mechanism in Fig. 2.

3.2 Thermal Stability

Thermogravimetric analysis (TGA) provides information on the decomposition pattern of ILs. Fig. 4 displays the decomposition profile of the [N₂₂₂₀][HSO₄] IL as reported by Shikh Zahari *et al.* [1]. It describes that the IL remains thermally stable but begins to decompose when heated above ca. 260 °C. This characteristic is advantageous to many applications, such biomass deconstruction where most effective process utilising ILs occur at 150 - 170°C.

Fig. 4. TGA-Decomposition profile of the $[N_{2220}][HSO_4]$ IL as a function of temperature ($10\text{ }^{\circ}\text{Cmin}^{-1}$ with N_2 flow rate of 10 mLmin^{-1}) reported by Shikh Zahari *et al.* [1].

3.3 Stoichiometry (Acid:Base Ratio)

The proposed mechanism in Fig. 2 shows that the $[N_{2220}][HSO_4]$ IL is formed by a stoichiometric reaction between N_{222} and H_2SO_4 (mole ratio of $N_{222}:H_2SO_4$ is 1:1). However, common experimental errors often lead to non-stoichiometric reaction, yielding the IL with a slight excess of N_{222} or H_2SO_4 . For some applications, this requires close monitoring as a small change in acid: base ratio may bring positive or negative outcomes on chemical processes.

A method developed by M. S.Y. Jennings can be referred to determine the mole ratio of $H_2SO_4:N_{222}$ of the IL [12]. The procedure is as follows: (1) dissolve dried IL (Fig. 1 (d)) in deionised water (IL: H_2O ratio of 80:20 wt:wt); (2) measure the density of the resultant IL- H_2O solution; (3) insert the obtained density value, y , into Equation 1:

$$y = 0.0772x + 1.1135 \quad (1)$$

where y is the density of the IL- H_2O solution, and x is the $H_2SO_4:N_{222}$ ratio. The following conclusion can then be drawn from the measurement: if $x > 1$, the IL contains an excess amount of unreacted H_2SO_4 ; if $x < 1$, the IL contains an excess amount of untreated N_{222} . This conclusion can be further confirmed by measuring the pH of the IL- H_2O solution, as performed by Weigand *et al.*[10]. In short, the greater the density, the higher the $H_2SO_4:N_{222}$ ratio, but the lower the pH value.

4 Applications of the $[N_{2220}][HSO_4]$ IL

In addition to possessing high thermal stability (Section 2.1.2), the $[N_{2220}][HSO_4]$ IL has been reported to serve other functions. The IL acts as an effective Brønsted acid catalyst and a delignifying agent in biomass deconstruction [1,4,5,10,11], and a protein stabiliser [13].

In biomass deconstruction, the $[HSO_4]^-$ anion of the IL is responsible for catalysing the hydrolysis of major bonds, such as ester bonds, that link cellulose, hemicellulose and lignin polymers in biomass. The $[N_{2220}][HSO_4]$ IL dissolves lignin while cellulose is insoluble in the IL, enabling the separation of lignin from cellulose to be easily done through a simple filtration process [1,5,14,15]. Various types of biomass have been tested, including

switchgrass [4], *Miscanthus* [16], willow [10], oil palm and coconut husk [1]. A regional study showed that deconstruction of oil palm empty fruit bunches (OPEFB) and coconut husk in the $[\text{N}_{2220}][\text{HSO}_4]:\text{H}_2\text{O}$ (80:20 wt:wt) at 120 °C for 2 h successfully recovered 30% cellulose-rich-material (CRM) from both biomass feedstocks [1].

The application of the $[\text{N}_{2220}][\text{HSO}_4]$ IL is not exclusive to the biomass deconstruction. The IL can also be employed in the industry of chemical synthesis. Attri *et al.* utilised the $[\text{N}_{2220}][\text{HSO}_4]$ IL to break carbon-carbon bonds in the cracking process of 2,2-dimethoxypropane [17], a common precursor used in the production of surfactants, polymer formulations and organic syntheses. Relative to the conventional method utilising a mixture of trichlorobenzene and *p*-toluene sulfonic acid, the use of the $[\text{N}_{2220}][\text{HSO}_4]$ IL enhanced both conversion and selectivity by 50% and 20%, respectively. More importantly, such enhancement was obtained at a temperature of 60 °C lower than that of the conventional method. The advantages of the $[\text{N}_{2220}][\text{HSO}_4]$ IL have also been exploited in the Fischer esterification process [18]. The presence of the $[\text{HSO}_4]^-$ anion increases the ester yield, which then resides in the lighter phase away from the heavy IL phase. Thus, this clear separation eases the downstream process. Its recyclability while maintaining the quality and yield as well as its environmentally friendly trait, strengthens its potential in the chemical synthesis industry [17,18]

A study has shown the role of the $[\text{N}_{2220}][\text{HSO}_4]$ IL as a protein stabiliser, which is of interest to the biotechnological and pharmaceutical industries [13]. By using cyclic dipeptides as the protein model compounds, the $[\text{N}_{2220}][\text{HSO}_4]$ IL is able to stabilize the native state of proteins and their functional groups due to the unfavourable interaction between the IL and the protein surface. This finding could catalyse the development of drug delivery applications in both industries.

5 Conclusion

It is hoped that the review has able to provide invaluable insight for scientists seeking to employ an economical IL in their research work. The $[\text{N}_{2220}][\text{HSO}_4]$ IL could be an ideal selection for industrial solvent due to the following reasons: inexpensive (cost price is at \$1.24kg⁻¹), thermally stable at high temperatures, synthesis pathway that is simple and eco-friendly consuming inexpensive reagents, and possess various functions with promising industrial application. It is also hoped that this review can attract enough interest to further expand the application of the $[\text{N}_{2220}][\text{HSO}_4]$ IL to other research areas.

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