

A Facilitate Process to Prepare Hydrophilic Ionic Liquid Monomers Free Of Halide Impurity and Their Electrochemical Properties.

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A facilitate and halide-free process to prepare ionic liquid monomers with various anions was developed with dialkylsulphate as the alkylating agent. The results imply that the process was efficient to prepare ionic liquid monomers for poly ionic liquids which have been proposed as promising alternative polymer electrolyte for various electric devices such as fuel cell, Li ion battery. Furthermore, ionic conductivity of both the ionic liquid monomers was measured as a function of temperature. Electrochemical window was measured with acyclic voltammogram (CV) method. The results show that it is a facilitate and versatile method to prepare imidazolium type ionic liquid monomers without halide impurity.

Keywords: ionic liquid monomer, halide free, electrochemical tests, synthesis

1. INTRODUCTION

Ionic liquids (ILs) are organic salts with melting points below 100°C.[1-3] In recent years, ILs have stirred great interest in various fields such as green synthesis, [1, 4] catalysts[5] as well as olefin/paraffin separation[6, 7] for its unique properties such as low vapor pressure, nonflammable. Especially, for its high ionic conductivity, ILs have been proposed as promising electrolyte for fuel cells,[8-10]Li ion batteries [11], supercapacitors [12, 13]. Albeit the several advantages of ILs mentioned above, the liquid state of ILs may be a problem for applications as electrolyte due to leaking.[14] As a result, poly ionic liquids (PIL) are drawing tremendous interest as most PILs are solid while keeping the advantages of ILs. Additionally, PIL has the potential advantage of defined size, shape and geometry, such as thin films, fibers, coatings. Due to the advantages of the PILs, it is

both important and interesting to develop processes to prepare ionic liquids with polymerizable groups and to analyze electrochemical characteristics of the corresponding polymers. Till now, various methods have been developed to prepare PILs. Direct polymerization is an important and widely adopted strategy to prepare PIL. With this strategy, the haloalkane was usually applied to prepare the IL monomer.[15-19] The monomer was then polymerized to obtain PILs. This strategy is efficient to prepare PILs with anion of X (X=halide). In many cases, PILs with other anions are needed. Thus, to prepare PILs with anions other than X, the anion exchange process is usually needed. Like the traditional two-step method for ionic liquid synthesis, this process is easy to conduct to prepare hydrophobic IL monomer with anions of TFSI⁻ or PF₆⁻ which are hydrophobic since the resulted products can be easily separated from the solution of the by-product in water.

However, if hydrophilic PILs are needed, the anion exchange process with assistance of silver salts for its usually low solubility in water to separate the product from the by-product is needed. Unfortunately, the silver salts are limited for the high price. Additionally, it is difficult to completely remove the by-product (silver halide). [20] As a result, the PILs obtained in this way are usually contaminated with halide impurities. For the well known negative effects of halide impurities such as poisoning of catalysts, corrosion of steel material,[21, 22] great efforts have been devoted to developing halide-free process to prepare ILs. However, only a few works focusing on halide-free process for PILs are reported. Ohno group has reported a process by neutralizing N-vinyl imidazole with a corresponding acid.[23] This process seems efficient only to prepare monoalkylimidazolium PILs. For dialkylimidazolium PILs, more halide-free processes that are quick and easy to conduct are still highly needed. Recently, we reported a green and efficient process to prepare halide-free dialkylimidazolium ILs with dialkylsulphate as the alkyl agent basing on the low solubility of potassium alkylsulphate.[24] However, the previous work focused only on preparing ionic liquids.

This paper continues our previous research focusing on developing a process to prepare halide-free polymerizable ionic liquid monomers. The principle in our previous work was confirmed to be feasible to prepare for halide-free ionic liquid monomers. Two ionic liquid monomers were prepared. The ionic conductivity of the two monomers was measured. Other properties such as viscosity were also characterized with corresponding methods. This work presents a complementary synthetic route to the previous existing strategies to prepare various polymerizable ionic liquids, and some electrochemical properties were characterized.

2. EXPERIMENTAL

2.1 Synthesis of PIL

N-vinylimidazole (97%) was purchased and distilled before used to obtain a clean colorless liquid. Diethylsulphate (99.7%), KOH (85%), and ethanol (99.7%) were used as received.

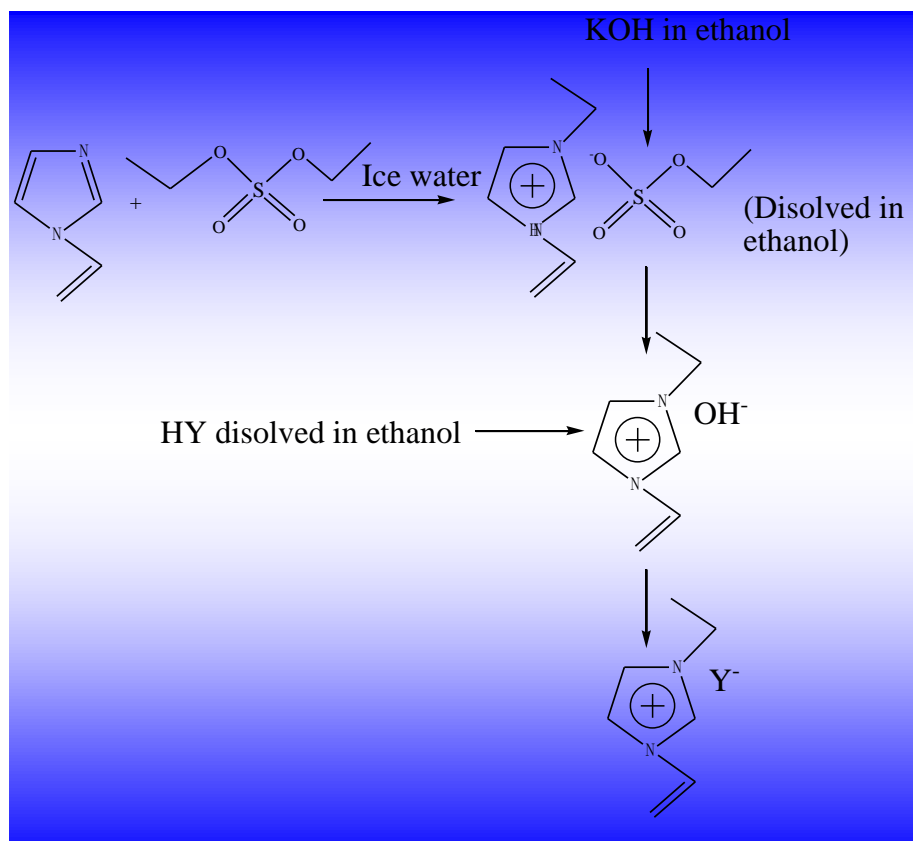


Figure 1. The synthesis process of ionic liquids free of halide (R1 and R2[alkyl; Y[desired anion)

Fig.1 illustrates the full experimental process to prepare the ionic liquid monomers via the acid-base process. N-vinylimidazole was firstly alkalinized with diethylsulphate to obtain ethylvinylimidazolium ethylsulphate ([Veim]EtOSO₃) by adding diethylsulphate in drop wise using a dropping funnel to N-vinylimidazole immersed in an ice bath while keeping stirred for approximately 3 hours, and a viscous clear liquid was obtained as [Veim]EtOSO₃.

The [Veim]EtOSO₃ was dissolved in ethanol and the solution was added slowly to KOH (1.5 times that of [Veim]EtSO₃ in molar) solution in ethanol while stirring vigorously. White precipitate was generated and filtered. The filtrate was harvested as [Veim]OH solution in ethanol.

The basic solution of [Veim]OH was then neutralized with corresponding acid of HY equaling to the KOH in molar. In this work, H₂SO₄ and HNO₃ were used. To obtain the monomer with NO₃⁻, the HNO₃ was added in slightly excess amount for the reason that the neutralized imidazolium salts can not exist stably and a slightly acid environmental was needed.[24] Crude ionic liquid monomer of [Veim]Y can be obtained after the ethanol was removed by rotary evaporation. The process takes approximately 6 hours. The crude product was then washed with 3×10 ml diethyl to remove some unidentified organic impurities remains in the product and then dried in vacuum at 120°C for 24 hours to obtain the final product. The product obtained above is deep in color. Since this kind of salts are believed to be colorless, the color implies that there are chromophoric impurities in the obtained samples. But it is believed that the chromophoric impurities affect either the chemical or the physical

properties of ILs.[25] The obtained sample of ionic liquid monomer were subsequently submitted for $^1\text{HNMR}$

2.2 Electrochemical tests

The ionic conductivity of both ionic liquid monomer was measured with a conductivity monitor CM-230 (purchased from Shijiazhuang Shengqi Technology Co.,Ltd) with the cell constant of 1.055 cm^{-1} . The temperature was controlled with a water bath. At each temperature, the sample was stabilized for 5 minutes. The temperature range was from 20 to 85°C at 5°C interval.

Electrochemical window was measured with the reported method with some adjustment.[26] On electrochemical station (CHI 650D), cyclic voltammetry (CV) measurement was carried out at a scan rate of $10\text{ mV}\cdot\text{s}^{-1}$ to measure the electrochemical window in the potential range of $-4\sim 4\text{V}$ with the stainless foils as both working and counter electrodes. In the present work, the decomposition voltages were arbitrarily defined as the potential at which the current density changed 5% from the baseline. Before the tests, nitrogen gas was introduced at $100\text{ ml}\cdot\text{min}^{-1}$ to the sample for 20 minutes to drive off the oxygen that may exist in the sample.

2.3 Viscosity measurement

The obtained samples was characterized for viscosity with rotary viscosity meter (NDS-53, Shanghai Yoke Instrument Co.,LTD) in the temperature range of 20 to 95°C with 5°C interval. The temperature was controlled in the same way for ionic conductivity measurement.

3. RESULTS AND DISCUSSION

3.1 Synthesis

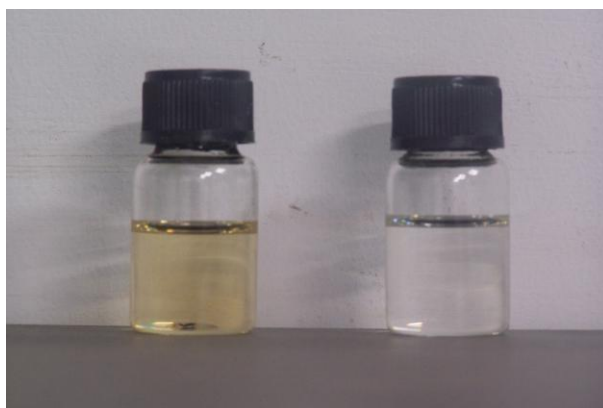


Figure 2. Pictures of N-vinylimidazole(*left* before distilled, *right* after distilled)

The received N-vinylimidazole was yellow as shown in Fig. 2. Thus, the starting material was distilled to get a colorless liquid as shown in Fig 2. It was founded that the colorless liquid shall become yellow again after stored for a long time.

The process mainly takes the advantage of the fast ion exchange between the OH^- and EtOSO_3^- as a result of the large solubility difference of $[\text{Veim}]\text{EtOSO}_3$ and KEtOSO_3 in ethanol. According to our previous experiments, the solubility of KEtOSO_3 in ethanol is pretty low.[24] If the solubility of $[\text{Veim}]\text{EtOSO}_3$ is high enough, we think that the principle of preparing ionic liquid in reference [24] can be utilized to prepare PILs by introducing polymerizable group into the cation. The experiment shows that the $[\text{Veim}]\text{EtOSO}_3$ is nearly miscible with ethanol. As a result, the above process was proposed and checked to prepare polymerizable ionic liquids. Although the solubility difference of the starting material have been utilized in the existing reports, the solubility difference is much higher and a much swifter process was resulted.[27] In the present study, only ionic liquid monomer with HSO_4^- and NO_3^- was prepared, it is reasonable to speculate that the process can provide monomers with other anions as implied in our previous work. It should be mentioned that the diethylsulphate should be added with the n-vinylimidazole immersed in ice bath, otherwise the cation shall be destroyed by the heated released strongly from the reaction between the n-vinylimidazole and diethylsulphate. Additionally, the KOH and $[\text{Veim}]\text{EtOSO}_3$ should be dissolved in ethanol separately before mixed, or the cation shall be destroyed by the strong basic KOH and the synthesis shall result in failure. The $[\text{Veim}]\text{OH}$ solution should be neutralized with corresponding acids before the ethanol was evaporated as the $[\text{Veim}]\text{OH}$ can not exist in pure state. The $^1\text{HNMR}$ implies that the ionic liquid monomer was obtained as desired. Since the polymerization of the monomer with AIBN added has been reported by several reports, the polymerization is a well known process and was not further checked.[28, 29]

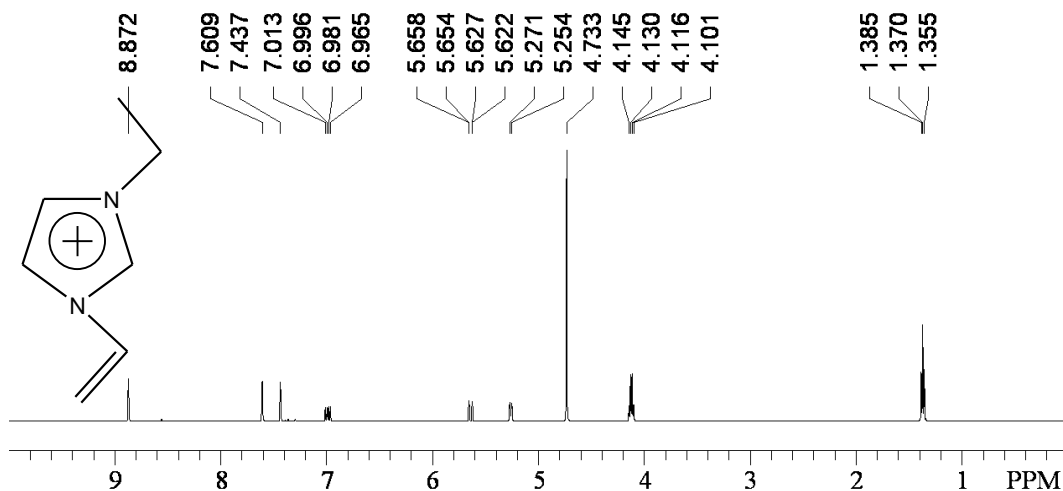


Figure 3. Pictures for the samples, from left to right: $[\text{Veim}]\text{HSO}_4$, $[\text{Veim}]\text{NO}_3$

Fig. 3 shows the picture of the ionic liquid monomers. It can be observed the samples are brown although this kind of IL is believed to be colorless. However, usually the chromophoric impurities are accepted since no evidence has been found that the impurity affect either the chemical or the physical properties of these salts.

Fig. 4 shows the $^1\text{HNMR}$ result for the sample of $[\text{Veim}]\text{HSO}_4$. Since the two samples are of the common cation, only one $^1\text{HNMR}$ result was given. The detailed attribution of each peak was

presented at the bottom of Fig. 4. One point to be mentioned is that the peak at 4.73 ppm is that of D of the solvent D₂O. It can be seen that the result is well inconsistent with the actual structure of the cation.



δ H (500 MHz, D₂O) 8.87 (s, 1H; imidazole H), 7.60(s, 1H; imidazole H) , 7.43 (s, 1H; imidazole H) , 7.01-6.96 (m, 1H; -CH=CH₂), 5.65-5.62 (m, 1H; -CH=CH₂), 5.37-5.25 (m, 1H; -CH=CH₂), 4.14-4.10 (m, 2H; -CH₂CH₃), 1.38-1.35 (t, 3H; -CH₂CH₃).

Figure 4. ¹H NMR for [Veim]⁺

3.2 Ionic conductivity

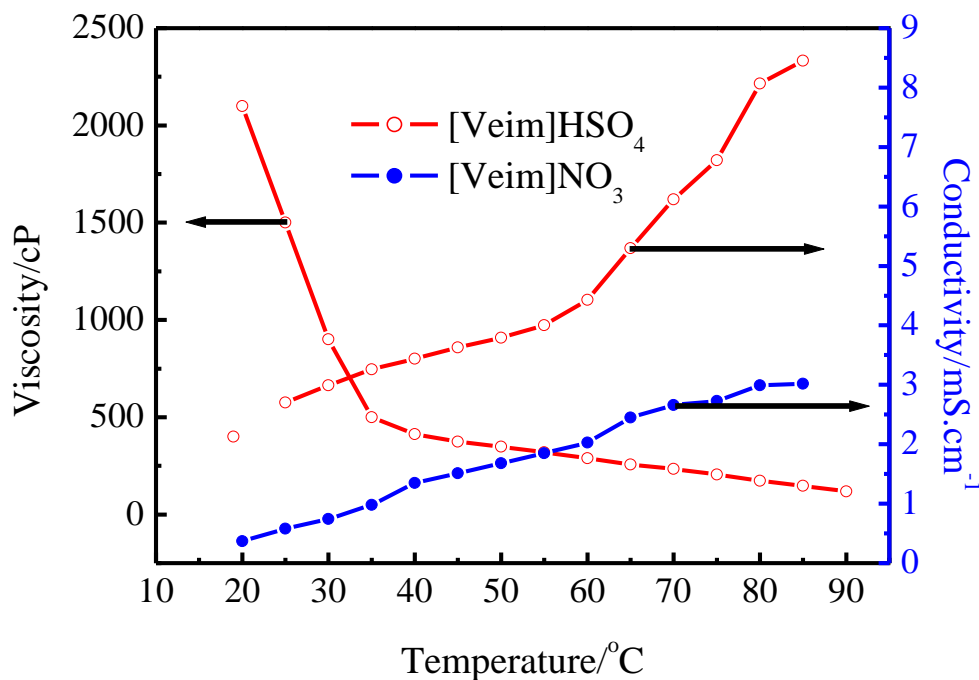


Figure 5. Ionic conductivity and viscosity as a function of temperature

Ionic conductivity is one of the important parameters of ionic liquid or PIL monomers, especially for application as electrolyte of electrochemical devices.[30, 31] It is defined as the reciprocal of proper resistance. The ionic conductivity for the ionic liquid monomer as a function of temperature was measured and is presented in Fig. 5. The conductivity increased with increase in temperature. At 85°C, the conductivity of [Veim]HSO₄ monomer was found to be approximately 8.5 mS.cm⁻¹. The value is slightly lower than that of imidazolium ILs without polymerizable groups.[24] The conductivity of [Veim]NO₃ was even lower and a conductivity of merely 3 mS.cm⁻¹ was found. This means that the anion has severe impact on the IL monomer conductivity. This may be caused by the higher viscosity of the ionic liquid monomer as it is believed that higher viscosity should cause lower ionic conductivity. The viscosity was found to be higher than 5000 cP. This is higher than the upper limit of our viscometer. As a result, the corresponding viscosity was not presented.

3.3 Electrochemical window

The electrochemical window, like the ionic conductivity, is another important property and plays a key role in application of ionic liquids as electrolyte for various electrochemical devices.[32, 33]. The electrochemical window is defined as the difference between the anodic and cathodic decomposition voltages. Usually, electrochemical window was measured with the CV method and the results were given in Fig. 6. It can be seen that the electrochemical window for [Veim]HSO₄ is about 1.74-(-1.88)=3.62 V. The electrochemical window for [Veim]NO₃ is slightly higher and the value is 2.41+1.63=4.04 V. The value is slightly lower than that reported value for dialkylimidazolium ILs.[34] This may be a result of the introducing of vinyl to the cation.

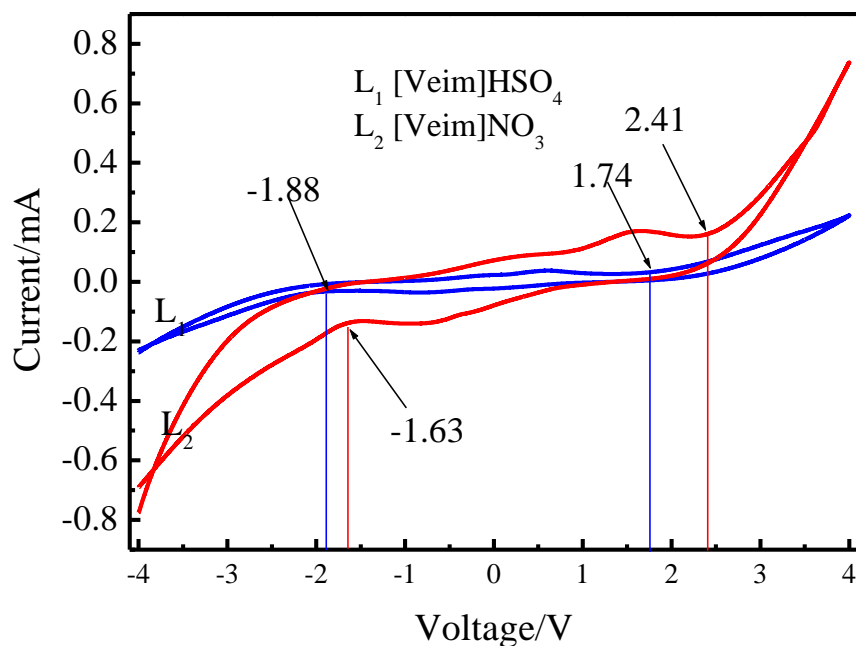


Figure 6. Voltammetric curves recorded for the ionic liquid monomer

However, The value for both [Veim]HSO₄ and [Veim]NO₃ are much higher than that of water, which is about 1.2V. This wide electrochemical window of the ionic liquid monomer endows its potential application as electrolyte in various electrochemical devices working at high voltage. It was reported that the halide impurities such as Br⁻ are responsible for a narrow stability of the order of ca. 2~3V. This narrow of electrochemical window shall not only decrease the working voltage, but also suppresses the stability and life range of the electrochemical device using the ionic liquid as electrolyte. For the PILs obtained from the present method, this negative effect of the halide impurity should be avoided as no halogen was introduced during the synthesis process.

3.4 Viscosity

The viscosity as function of temperature was given in Fig.5 together with the ionic conductivity. The viscosity of [Veim]HSO₄ was found to be around 2000 cP at 20°C, much higher than that of [Emim]HSO₄, which is about 800 cP at the same temperature.[9] The viscosity went down with increase in temperature. This agrees with the reported relationship between viscosity and temperature.[35] The decreasing rate in the temperature range of 20~35°C was found to be much higher than that of 35~90°C. It can also be noticed that the viscosity is higher than that of unpolymerizable ILs at the same temperature. This may be attributed to the introduction of vinyl group to the cation. The viscosity of [Veim]NO₃ was measured at higher temperature range for its higher melting temperature. The viscosity was observed to be much higher than that of [Veim]HSO₄. The higher viscosity may be related to its higher melting points of imidazolium salts with NO₃⁻ as anion.[24, 36] This implies that the anion has obvious influence on the ionic liquid monomer properties such as viscosity. The same phenomenon was also reported by other groups.[26]

3.5 Solubility of the monomers in water and ethanol

An interesting point for the ionic liquid monomer for [Veim]NO₃ was found. In the third step of the monomer synthesis process, the [Veim]NO₃ was found to be dissolved in ethanol, and a solution of [Veim]NO₃ in ethanol can be obtained. Once the ethanol was vaporized, a yellow sticky product was obtained. Interestingly, although the product was obtained from the solution of ethanol, the product was found to be insoluble in ethanol. It was found that the product can be dissolved in water. No similar phenomenon was found for the product of [Veim]HSO₄, which can be dissolved in both water and ethanol. The results mean that the described method is efficient to prepare hydrophilic ionic liquid monomer for PILs free of halide.

4. CONCLUSION

A facilitate method to prepare hydrophilic ionic liquid monomer free of halide impurity was proposed by utilizing the low solubility of KEtOSO₃ and high solubility of imidazolium alkyl sulfate

with polymerizable group. Samples with HSO_4^- and NO_3^- as anion were prepared. The obtained samples of ionic liquid monomer were characterized for ionic conductivity, electrochemical window as well as viscosity with corresponding methods. This study opens a new door to prepare high-quality PILs, which are promising electrolyte for various electrochemical devices requiring film-like electrolyte materials.

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