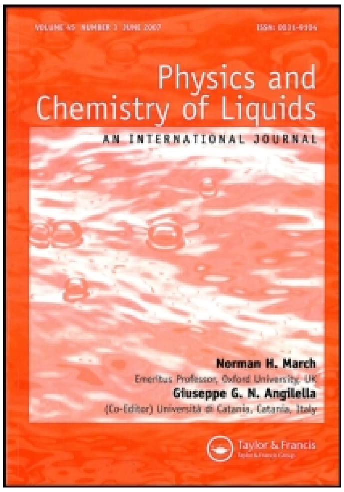

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# A functionalised ionic liquid: 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride

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# A functionalised ionic liquid: 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride

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An ionic liquid (IL) containing an appended 3-chloro-2-hydroxypropyl functionality group 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride was synthesised by the reaction of *N*-methyl imidazole, hydrochloric acid and epichlorohydrin. The ionic liquid showed reasonably high conductivity and heat stability up to 230°C. Its structures were characterised by FT-IR, $^1$H NMR and $^{13}$C NMR spectra. The physical characteristics of the ionic liquid, such as conductivity and solvation abilities have been investigated. Due to its high polarity, the IL is able to dissolve many inorganic salts, and due to hydroxyl-rich microenvironment, it is able to dissolve cellulose go up to 10 (wt%). The ILs can be used for synthesising other ILs or polyelectrolyte.

**Keywords:** 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride; *N*-methyl imidazole; epichlorohydrin; functionalised ionic liquids; synthesis; property

## 1. Introduction

Ionic liquids (ILs) are salts consisting of ions, which exist in the liquid state at ambient temperatures. They have many unique physicochemical properties such as negligible vapour pressure, high thermal and chemical stability, high ionic conductivity, excellent solubility with many substances and so on [1]. ILs have been vigorously studied as reaction solvents [2], separation-extraction solvents [3] and electrolyte materials [4–6].

The properties of ILs can be changed by modification of cation and anion with special functional groups. Functionalised ILs which are incorporated with one or more functional groups or possess special structure, have exhibited enormous potential as a result of particular function and attracted much interest in many fields such as chemical synthesis, separation science, electrochemistry, instrumental analysis and energy sources. So far, people have successfully incorporated ether, hydroxyl, sulfhydryl, carboxylate, carboxyl, Sulphonic groups, chiral groups and so on. The flexible structures provided with two even more same or different functional groups can make the effect enhanced or possess different functionality. For example, Zhu *et al.* [7] has synthesised multi-hydroxyl and sulphonyl dual-functionalised ILs may be used for synthesising other functionalised ILs; Cole *et al.* [8] has synthesised

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sulphonyl functionalised ILs as dual solvent-catalysts in esterification reactions; Li *et al.* [9] has synthesised carboxyl functionalised ILs which were confined to silica gel as catalysts for deoximation under mild conditions; Demberelnyamba *et al.* [10] has synthesised epoxide functionalised ILs, the epoxides in the ILs comprise an extremely versatile group of intermediates and can react with a large range of nucleophiles, electrophiles and others. Branco *et al.* [11] and Holbrey *et al.* [12] have prepared new ILs containing an appended hydroxyl functional group; Chen *et al.* [13] has synthesised chiral ILs derived from nature amino acids.

Task-Specific Ionic Liquids (TSILs) have been regarded by many scholars not only because the designed structure, diversification and the relative simple and mature method in synthesis, but most importantly, because TSILs have exhibited extensive application foreground in many fields [14–17]. Not just as green solvents, their usage has penetrated into functional material, immobilised catalysis, chiral recognisation, absorbance of gas, e.g. $SO_2$, $CO_2$, separation of metal ions and organic compounds, instruments analysis, e.g. GC, HPLC and so on [18–20].

For design of functionalised ILs, we recently investigated a novel ILs with 3-chloro-2-hydroxypropyl group: 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride ILs that can be used as intermediates for designing many other novel ILs or polyelectrolyte. The new 3-chloro-2-hydroxypropyl group ILs is prepared from commercially available cheap starting materials such as *N*-methylimidazole, epichlorohydrin and hydrochloric acid in moderate condition. We report the synthesis and properties of 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride as new functionalised ILs.

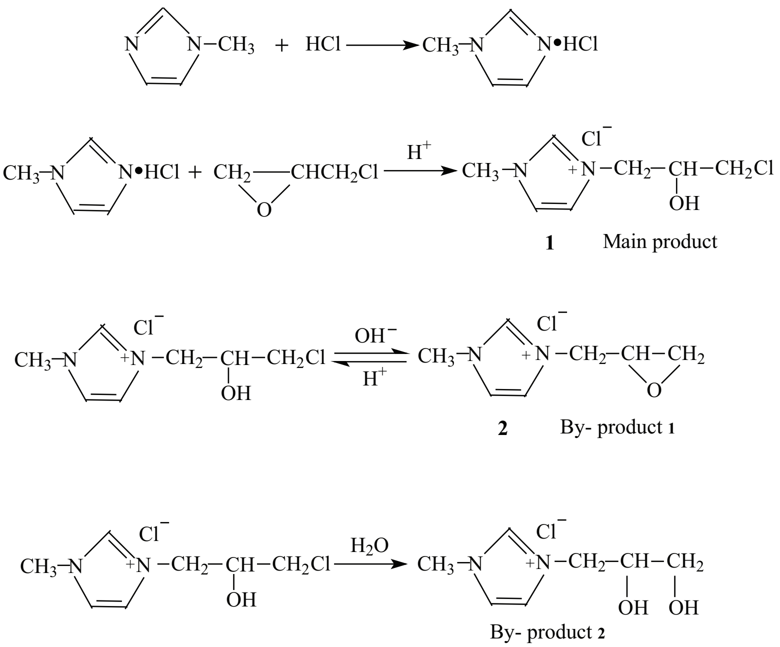
## 2. Experimental

### 2.1. *Materials*

*N*-methyl imidazole (Aldric), epichlorohydrin (Fluka) were distilled before use. Hydrochloric acid, sodium hydroxide, ethanol, aether and silica gel-G60 were analytical grade commercial products.

### 2.2. *Preparation of the ionic liquid (1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride)*

A mixture of 100 mL ethanol and 0.2 mol hydrochloric acid (36% in weight) was placed in a flask equipped with a reflux condenser and a dropping funnel. The flask was mounted in an oil bath. Under vigorous stirring with a magnetic stirring bar, 0.2 mol *N*-methyl imidazole was added dropwise to the flask in about 45 min, then adjusting the solution with the excessive hydrochloric acid to pH $6 \sim 6.5$ in order to avoid producing by-product 1 (Scheme 1). Then, 0.22 mol of epichlorohydrin was dropped slowly into the above aqueous solution at 5°C under agitation. After all epichlorohydrin was dropped, the temperature of the mixed solution was raised to 45°C, the reaction time was maintained for 3 h. The light yellow viscous liquid, 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride, was obtained through removing water, ethanol and small amount of epichlorohydrin by means of the reduced pressure distillation. The ILs was reused four times after treated by ultrasonic extraction with aether, the resulting ILs was passed through the columns



Scheme 1. Formation of the ionic liquid.

with active carbon, silica gel-G60 and neutral alumina. The ILs was dried *in vacuo* at 60°C. The yields of product was approximately 90% and was characterised with IR, $^{1}H$ NMR, $^{13}C$ NMR and TGA.

### 2.3. *Measurements*

$^{1}H$ NMR and $^{13}C$ NMR spectra were measured on a Bruker 250 MHz spectrometer, used DMSO-$d_6$ or $D_2O$ as solvent with TMS as internal standard.

The IR spectra of the sample were recorded with a Fourier transform IR spectrometer (FTIR PE-2000, United States). The test specimen was prepared by the KBr-disk method.

Conductivities were measured by a DDS-11A conductometer.

Cyclic voltammetry (CV) experiments of the ionic liquid were carried out on a CHI 660C electrochemical workstation (CH Instruments, USA).

Thermo-gravimetric analysis (TGA) was performed on NETZSCHSTA 449C. The programmed heating range was from room temperature to 800°C, at a heating rate of 10°C $min^{-1}$ under nitrogen atmosphere.

## 3. Results and discussion

### 3.1. *FTIR*

Figure 1 illustrates the FTIR spectra of the prepared 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride. The bands at 3383 $cm^{-1}$ corresponds to O–H group because of open-ring of epichlorohydrin in acidic aqueous solution; the bands at

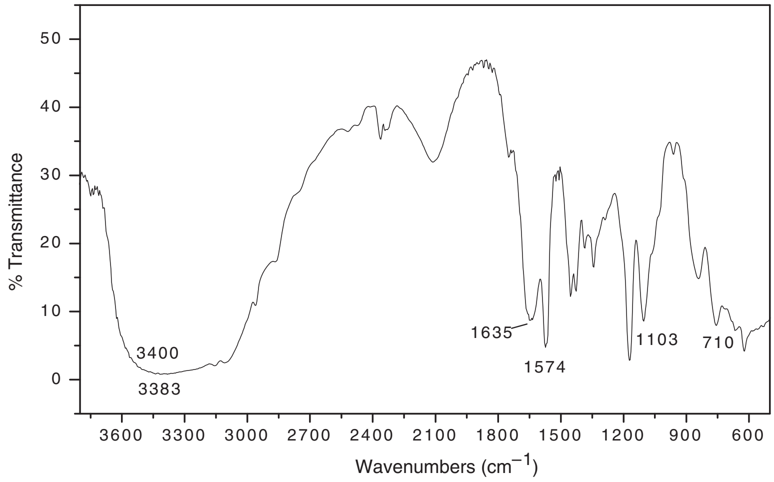


Figure 1. FTIR spectra of the 3-chloro-2-hydroxypropyl-methyl imidazolium chloride ionic liquid.

3400 cm$^{-1}$ corresponds to N–H group, the bands at 1234, 918 and 840 cm$^{-1}$ corresponds to the epoxy group disappeared simultaneously. A strong peak at 1635 and 1574 cm$^{-1}$ corresponds to C=C group and C=N group because of introducing cations of 3-chloro-2-hydroxypropyl-methyl imidazolium. The bands at 1103 cm$^{-1}$ corresponds to C–O group, and 710 cm$^{-1}$corresponds to C–Cl group. The spectra confirmed the structure of 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride ILs.

### 3.2. *$^1$H NMR*

1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride $^1$H NMR (250 MHz, DMSO-d$_6$, $\delta$): 9.09 (s, 1H, ring C(2)H), 7.79–7.54 (dd, 2H, ring C(4,5)H), 5.33 (s, 1H, OH), 4.12 (1H, CH–O), 3.85 (m, 2H, $CH_2$–$N_{ring}$), 3.8 (s, 3H, $CH_3$–$N_{ring}$), 3.7 (2H, $CH_2$–Cl). See constitutional formula 1 in Scheme 1.

1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride $^{13}$C NMR ($D_2O$, $\delta$): 140.4 (ring C(2)), 123.2 (ring C(4,5)), 71.3 (CH–OH), 52.0 ($CH_2$–$N_{ring}$), 47.1 ($CH_2$–Cl) and 35.5 ($CH_3$–$N_{ring}$).

### 3.3. ***Conductivity***

Conductivity of the IL, at room temperature is 2.3 mS cm$^{-1}$ which is reasonably high. The ionic conductivity, $\sigma$, depends largely on temperature and rises exponentially as the temperature increases and reaches 33 mS cm$^{-1}$ at 90°C (Figure 2). This can be ascribed to fast ion mobility at increased temperatures.

The corresponding $\ln \sigma$ *versus* $1/T$ plot is almost linear in a wide temperature range (0 to 90°C). The conductivity relationship can be expressed by Arrhenius equation:

$$\sigma = \mathrm{A}\exp\left(\frac{-E_\mathrm{a}}{\mathrm{RT}}\right),$$

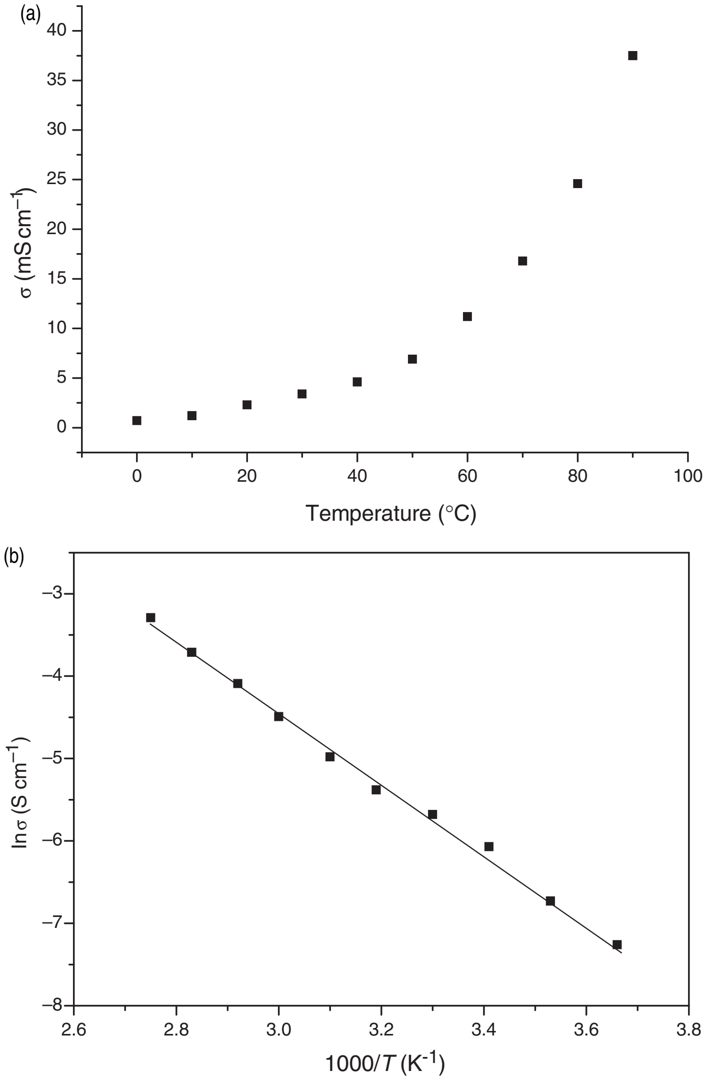


Figure 2. Temperature dependence of conductivity of the ionic liquid, (a) $\sigma$ *vs.* $T$ plot, (b) $\ln \sigma$ *vs.* $1/T$ plot.

where $E_a$ is the activation energy, A is a constant and $T$ is the absolute temperature. From the slope of the curve the activation energy of the ionic conductivity, $E_a$ is estimated as, $E_a = \text{slope} \times \text{R} = 35.87\,\text{kJ}\,\text{mol}^{-1}$, where R is gas constant.

Electrochemical stability of the ionic liquid is important when redox reactions are performed in such a medium. The electrochemical stability was inspected by cyclic voltammetry. Redox stability of the ionic liquid must be imposed by the reduction potential of the 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium cation and oxidation potential of the chlorin anion. The cyclic voltammetry (Figure 3) indicates a useful stability range of about 1.1 V (between −0.1 and +1.0 V). Those limits practically do not change after 20 times of oxidation-reduction cycle.

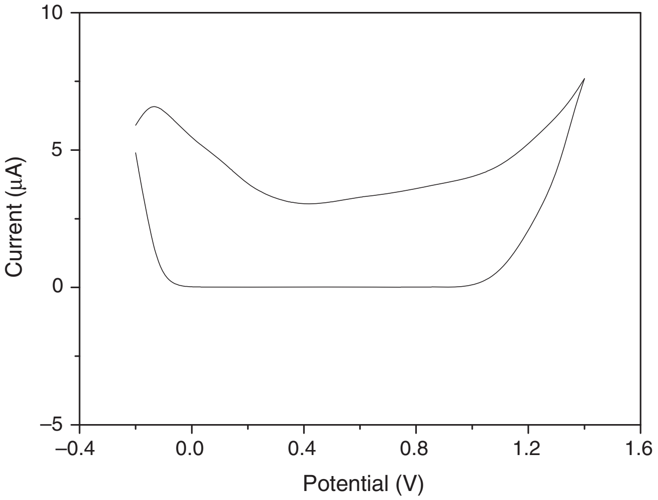


Figure 3. Cyclic voltammetry of the ionic liquid.

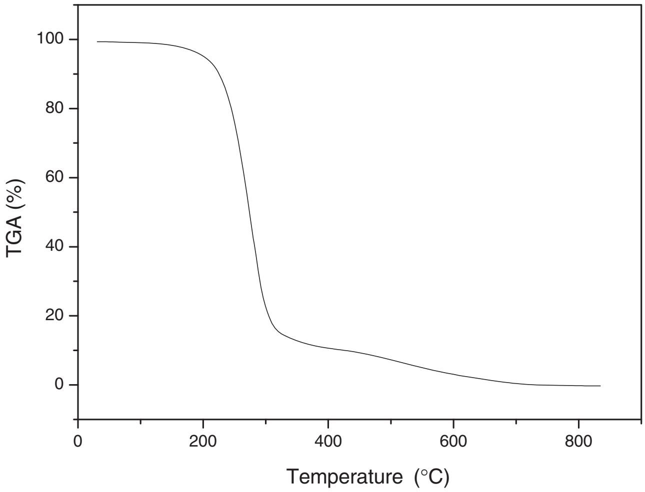


Figure 4. TGA of the ionic liquid.

### 3.4. *Thermo-gravimetric analysis (TGA)*

TGA curve shows a sharp decline around 224°C and an inflection at about 238°C. 90% mass losses occur at 297°C (Figure 4). The IL showed high heat stability up to 220°C under nitrogen atmosphere.

### 3.5. *Solvating properties of the ionic liquid*

The liquid shows high solvating ability for some inorganic salts and polymers. The solubilities were estimated by gradual addition of anhydrous salts. Anhydrous salts were chosen deliberately to avoid disturbing effects of trace water. The alkaline

Table 1. Solubility of various salts in the ionic liquid (at 25°C).

| Substance | Solubility (g/100g) |
|---|---|
| NaCl | 32.6 |
| $Na_2SO_4$ | 21.2 |
| KCl | 31.3 |
| KBr | 31.9 |
| $NH_4Cl$ | 35.2 |

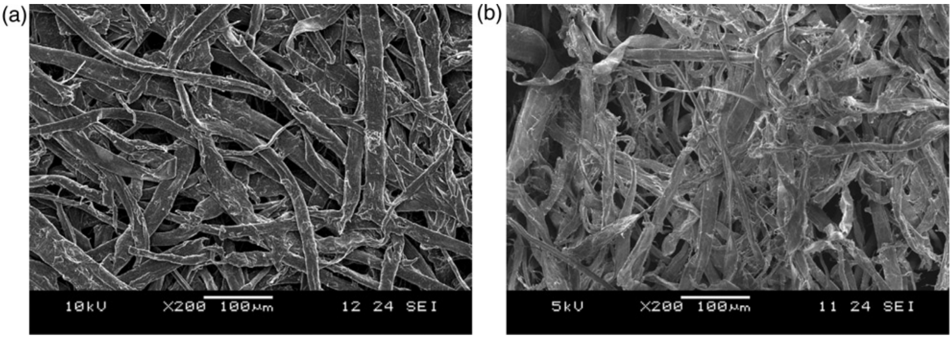


Figure 5. The SEM photographs of initial dissolving pulp (a) and after dissolution in ILs and regenerated into water (b).

metal salts studied (such as NaCl, KBr, KCl and $Na_2SO_4$) are highly soluble in the ionic liquid (Table 1). The high solublility is due to large differences in the electronegativities of anions and cations associated. The solubility increases with the increase of the differences in the electronegativities of anions and cations of inorganic salt.

More important is that celluloses are soluble in the ILs. Solubility of cellulose is 11 g per 100 g of the liquid at 80°C, the advantage being attributed to the hydroxyl-rich microenvironment. The regenerated cellulose was obtained from the cellulose solution by coagulating with deionised water. Scanning Electron Microscopy (SEM) was used to observe the bulk structure; scanning electron micrographs of dissolving pulp and regenerated cellulose are shown in Figure 5. The dissolving pulp shows fibers at 200× magnification in the SEM. After regeneration, the morphology of the material was significantly changed, displaying a rough, but conglomerate texture in which the fibers are fused into a relatively homogeneous macrostructure.

### 3.6. *Functionality of the ionic liquid*

The 3-chloro-2-hydroxypropyl in ILs can be translated into epoxide under alkaline condition. See constitutional formula 2 in Scheme 1. The approach is as follows: 0.1 mol of 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride was placed in a flask equipped with a reflux condenser and a dropping funnel. The flask was mounted in an oil bath. Under vigorous stirring with a magnetic stirring bar,

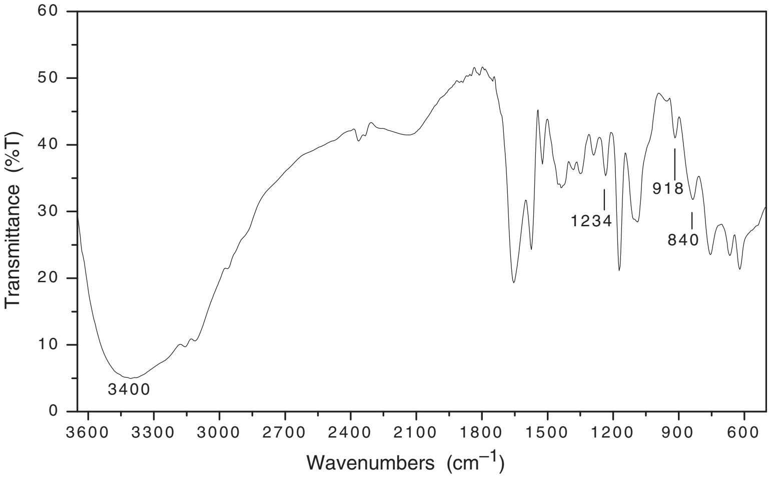


Figure 6. FTIR spectra of the 1-glycidyl-3-methyl imidazolium chloride ionic liquid.

0.11 mol sodium hydroxide (30 wt% alcoholic solution) was added dropwise to the flask at 5°C. After all alcoholic sodium hydroxide solution was dropped, the temperature of the mixed solution was raised to 30°C, and the reaction time was maintained for 4 h. It was filtered while hot, to eliminate sodium chloride solid. The new IL containing an appended 2,3-epoxypropyl (glycidyl) functionality, 1-glycidyl-3-methyl imidazolium chloride, was obtained through removing water and ethanol by means of reduced pressure distillation. The IL was reused four times after treated by ultrasonic extraction with aether, the resulting IL was passed through the columns with active carbon, silica gel-G60 and neutral alumina. The IL was dried *in vacuo* at 40°C. The yield of product was approximately 70% and was characterised with IR, $^1$H NMR and $^{13}$C NMR.

Figure 6 illustrates the FTIR spectra of the prepared 1-glycidyl-3-methyl imidazolium chloride. The bands at 1234, 918 and 840 cm$^{-1}$ correspond to the epoxy group and the spectra confirmed the structure of 1-glycidyl-3-methyl imidazolium chloride IL.

1-Glycidyl-3-methyl imidazolium chloride $^1$H NMR: 250 MHz, DMSO-d$_6$, $\delta$: 8.84 (s, 1H, ring C(2)H), 7.61–7.50 (dd, 2H, ring C(4,5)H), b: 4.58–4.56 (1H, $CHOCH_2$), a: 4.40–4.26 (2H, $CHOCH_2$), 3.95 (s, 2H, $CH_2$–$N_{ring}$), 3.72 (s, 3H, $CH_3$–$N_{ring}$).

1-Glycidyl-3-methyl imidazolium chloride $^{13}$C NMR ($D_2O$, $\delta$): 138.02 (ring C(2)), 124.60 (ring C(4)), 124.30 (ring C(5)), 53.66 ($CH_2$–$N_{ring}$), 35.16 ($CH_3$–$N_{ring}$), 44.21 (CH–O oxirane ring), 37.39 ($OCH_2$ oxirane ring).

The epoxide in ILs comprise an extremely versatile group of intermediates and can react with a large range of nucleophiles, electrophiles and others, resulting in the production of novel ILs with different functional groups. The use of different onium compounds such as sulphonium, ammonium, phosphonium, etc. with epichlorohydrin for design of new epoxide ILs can be applied to a variety of chemical industries. Also, a series of other novel ILs will be produced by anion exchange.

## 4. Conclusions

The new ionic liquid 1-(3-chloro-2-hydroxypropyl)-3-methyl imidazolium chloride is a promising material due to its high conductivity and powerful solvating ability. The functionality of 3-chloro-2-hydroxypropyl resulting ILs can be applied to variety of chemical industries as key intermediates for synthesising many other novel ILs. The functionalised ionic liquid is found to be a novel and an excellent solvent for pulp cellulose with the dissolubility of 10 wt% at 80°C.

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