New Epoxide Molten Salts: Key Intermediates for Designing Novel Ionic Liquids

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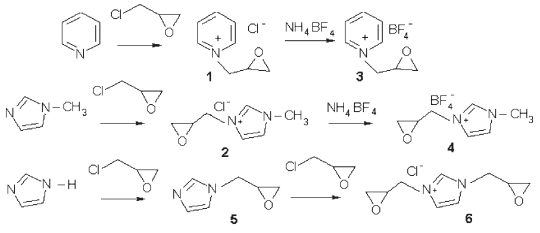
Room temperature ILs, based pyridinium and imidazolium cations containing glycidyl (2,3-epoxypropyl) chains have been synthesized in an attempt to design new functionalized ILs. The epoxides in glycidyl ILs comprise an extremely versatile group of intermediates and can react with a large range of nucleophiles, electrophiles and others, resulting in the production of novel ILs with different functional groups.

Ionic liquids (ILs) have been recognized as a next generation of green solvents and further they are now implicated for use in a lot of applications such as electrolytes,[1] bio-process operations, separation processes, solvents for reactions and catalysis.[2] By a judicious combination of cations and anions it is possible to adjust the solvent properties to the requirement of the reactions, thus creating an almost indefinite set of "designer solvents".[3]

However, several urgent problems regarding the functionalization, coordination properties, solvent characteristics, and further cost reduction of ILs still remain to be solved. For design of functionalized ILs we recently investigated a series of new ILs based on the *N*-vinyl-2-pyrrolidinonium (*N*-alkyl-γ-butylrolactam)[1] and here report a new family of ILs with 2,3-epoxypropyl (glycidyl) chains: glycidyl pyridinium and glycidyl imidazolium ILs that can be used as intermediates for designing many other novel ILs. If alkylation is carried out in flask under atmospheric pressure, then ether might be used in the methatesis reaction, where alkylazole halides are reacted with metal salts of desired anions (Scheme 1). The new epoxide ILs is prepared from commercially available cheap starting materials such as pyridine, *N*-methylimidazole, imidazole, and epichlorohydrin or epibromohydrin in moderate condition. Compared with alkyl halogenides, the epichlorohydrin and epibromohydrin act as highly reactive alkylation reagents in the presence of electroacceptor epoxide group. The direct alkylation in the case of pyridine is highly exothermic; we carried it out in acetonitrile for 24 h at room temperature, and in the case of methylimidazole for 12 h under reflux. For synthesis of the symmetrical diglycidylimidazolium ILs, imidazole was deprotonated by sodium ethanoate to give 1-glycidylimidazole and then followed by alkylation in acetonitrile.[4] After removing the solvent the liquid residue was washed several times by hexane. For further purification the product was recrystallized several times from the dry cold acetone. The overall yields of all three ILs were higher than 85%. Subsequent methatesis reactions with NH_4BF_4 in acetonitrile for 24 h give the ILs with minimum of 72% yield. The ILs was repeatedly washed with small amount of cold water until no precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The resulting ILs was passed through the columns with activated charcoal, silica and neutral alumina. After drying for 12 h in a vacuum oven at 60 °C, the relatively viscous glycidyl ILs formed and further proceeded to ring opening reactions. The products of ring opening reactions are the specifically designed ILs that can be adopted as highly efficient absorbents for separating and recovering CO_2. FAB–MS and NMR were used to verify the structure and composition of new epoxide ILs and their derivatives.[5] The ^1H, ^{13}C NMR, and FAB–MS spectra of ILs were recorded on a Bruker AMX FT 500 MHz NMR spectrometer and a Jeol LTD JMS-HX110 high resolution tandem mass spectrometer. The glass transition temperatures were measured by a Du Pont Instrument Differential Scanning Calorimeter. All the ILs have sufficiently low glass transition temperatures below $T_g = -33.43$ °C of *N*-glycidylpyridinium chloride (**1**).



Scheme 1.

There are several advantages and reasons to synthesize the ILs with a glycidyl group. By modification of the glycidyl ILs' cation and anion, their properties can be turned in many ways. Epoxides (oxiranes) in a glycidyl group comprise an extremely versatile group of intermediates and possess several advantages such as their ready availability and exceptional reactivity. The oxirane ring can be opened under almost all nucleophilic, electrophilic, neutral, thermal and free radical conditions. Therefore, the epoxides in the cation of glycidyl ILs can react with a large range of nucleophiles, electrophiles and others, resulting in the production of new ILs with different groups. Nucleophiles attack on the ring electrophilic carbon causing it to break, resulting in ring opening, which relieves the ring strain and finally produces the 2-substituted alcohol derivatives. The weak nucleophiles such as water, alcohols, and amines[6] react with epoxides in the presence of acid catalysts.[7]

Other types of oxirane cleavage reactions include a nucleophilic attack on oxirane ring hydrogen, an electrophilic attack on oxirane ring oxygen, homolytic cleavages (free radical, photolytic and thermal), and cycloaddition[8] reations. Also, the extended oxirane in the glycidyl group present in cations might lead to specific interactions with guest/host molecules to form clathrate inclusion compounds.[9]

Davis and co-workers[10] have investigated an interesting primary amino substitued new IL in its pure state in order to capture CO_2. Epoxides in glycidyl ILs readily is opened on treatment with ammonia and amines to give different new ILs with alcohol amino group in cation which can be used for separating and re-

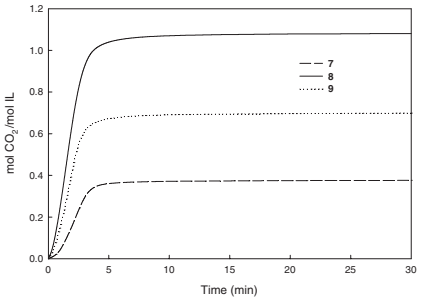
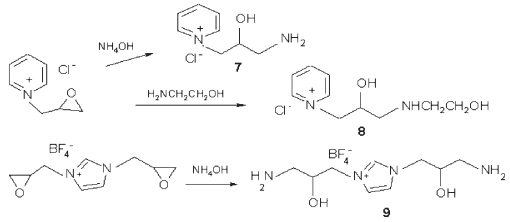


Figure 1. Solubility of carbon dioxide in aqueous solutions of 10 wt % **7**, **8**, and **9** at 298 K, 10 bar.

covering acid gases. For ring opening reaction the equimoles of *N*-glycidylpyridinium IL and ammonium or primary amines (Scheme 2) were added to an equal volume of methanol and refluxed until the IL with alcohol and amino groups formed. The crude product was purified by extraction and distillation in vacuum. The small yield of *N*-glycidylpyridinium IL could be avoided by using an excess of ammonia and ammonium carbonate. The mixture was allowed to stir at 60 °C for 24 h in a tightly closed screw-cap flask under 2 atm. After cooling the reaction mixture the excess ammonia and water were removed by distillation at reduced pressure. Yields of pyridinium and imidazolium salts are 96 and 89%, respectively.



Scheme 2.

Figure 1 indicates that the solubilities of CO_2 in 10 wt % aqueous solutions of **7**, **8**, and **9**, were all comparable to that in alkanolamines. Therefore, only a relatively small amount of the specifically designed alcohol amino ILs can be used as potential CO_2 absorbents in aqueous state to replace conventional alkanolamines.

These epoxide molten salts could be applied to the cycloaddition of CO_2 and medicine by introduction of quaternary pyridinium, imidazolium and other ammonium group to different aminosaccharides without any additional catalysts and reaction solvents. Also, one of the possible applications of alcoholamino ILs is a synthesis of nanoparticles, because these ILs are composed of core ions, branching sites, and alcoholamino group that usually form a well defined surface.

The use of different onium compounds such as sulfonium, ammonium, phosphonium etc. with epichlorohydrin and epibromohydrin for design of new epoxide ILs will greatly reduce their production cost and the resulting ILs can be applied to a variety of chemical industries as key intermediates for synthesizing many other novel ILs.

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References and Notes

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5 *N-glycidylpyridinium chloride* [GlPyCl] (**1**). NMR (500 mHz, ^{1}H, D_2O): δ 8.92–8.85 (m, 2H, ring), 8.66–8.59 (m, 1H, ring), 8.16–8.10 (m, 2H, ring), 5.11–4.66 (m, 1H, $CHOCH_2$), 3.80–3.63 (m, 2H, $CHOCH_2$), 1.2–1.17 (d, 2H, CH_2–N_{ring}). FAB–MS (MeOH matrix): m/z 135.9 [100%, $GlPy^+$]. $T_g = -33.43$ °C. *1-Glycidyl-3-methylimidazolium chloride* [GlMICl] (**2**): δ 8.84 (s, 1H, ring C(2)H), 7.61–7.50 (dd, 2H, ring C(4,5)H), 4.58–4.56 (m, 1H, $CHOCH_2$), 4.40–4.26 (m, 2H, $CHOCH_2$), 3.95 (s, 3H, CH_3–N_{ring}), 2.09 (s, 2H, CH_2–N_{ring}). NMR (^{13}C, 125.77 mHz, D_2O): δ 138.02 (ring C(2)), 124.60 (ring C(4)), 121.30 (ring C(5)), 69.66 (CH_2–N_{ring}), 53.16 (CH_3–N_{ring}), 37.39 ($CHOCH_2$ oxirane ring). FAB–MS (MeOH matrix): m/z 139.0 [1-Glycidyl-3-methylimidazolium$^+$] $T_g = -45.28$ °C. *1,3-diglycidylimidazolium chloride* [dGlImCl] (**6**): δ 8.93 (s, 1H, ring C(2)H), 7.83–7.57 (dd, 2H, ring C(4,5)H), 4.62–4.21 (m, 2H, $2CHOCH_2$), 3.72–3.53 (m, 4H, $2CHOCH_2$), 3.42 (s, 2H, CH_2–N_{ring}), 3.39 (s, 2H, CH_2–N_{ring}). NMR (^{13}C, 125.77 mHz, D_2O): δ 137.78 (ring C(2)), 125.12 (ring C(4)), 123.63 (ring C(5)), 69.50 (CH_2–N_{ring}), 53.21 (CH_2–N_{ring}), 37.42 ($CHOCH_2$ oxirane ring). *N-(3-amino-2-hydroxypropyl)-pyridinium chloride* (**7**): δ 8.93–8.86 (m, 2H, ring), 8.65–8.61 (m, 1H, ring), 8.16–8.11 (m, 2H, ring), 4.99–4.88 (m, 1H, CHOH), 4.67–4.54 (m, 2H, CH_2–N), 3.86–3.69 (d, 2H, CH_2–N_{ring}). FAB–MS (MeOH matrix): m/z 153.9 [*N*-(3-amino-2-hydroxypropyl) pyridinium$^+$]. $T_g = -59.66$ °C. *N-(3-aminoethoxyl-2-hydroxypropyl)pyridinium chloride* (**8**): δ 8.91–8.85 (m, 2H, ring), 8.63–8.56 (m, 1H, ring), 8.15–8.07 (m, 2H, ring), 4.75–4.64 (m, 1H, CH–OH), 3.82–3.80 (d, 2H, CH_2–N_{ring}), 3.77–3.57 (m, 4H, CH_2–N), 3.14–3.12 (d, 2H, CH_2–OH), 2.93 (s, 1H, OH), 2.68 (s, 1H, NH), 2.55 (s, 1H, OH). FAB–MS (MeOH matrix): m/z 196.9 [*N*-(3-aminoethoxyl-2-hydroxypropyl) pyridinium$^+$] $T_g = -55.43$ °C. *1.3-di(3-amino-2-hydroxypropyl)imidazolium tetrafluoroborate* (**9**): δ 8.75 (s, 1H, ring C(2)), 7.55–7.45 (dd, 2H, ring C(4.5)), 4.55–4.33 (m, 2H, 2CH), 4.32–4.20 (m, 4H, CH_2–N_{ring}), 3.94 (s, 6H, 2OH, $2NH_2$), 3.66–3.64 (m, 2CH2–N_{amine}). NMR (^{13}C, 125.77 mHz, D_2O): δ 146.03 (ring C(2)), 123.08 (ring C(4)), 120.76 (ring C(5)), 61.25 (CH–OH), 61.21 (CH–OH), 51.63 (CH_2–N_{ring}), 50.21 (CH_2–N_{ring}), 12.28 (CH_2–N_{amine}), 2.44 (CH_2–N_{amine}). $T_g = -71.89$ °C.
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