



Synthesis and Spectroscopic Characterization of Protic Tris(2-Hydroxyethyl)-Ammonium Ionic Liquids

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Abstract: Protic ionic liquids (PILs) having tris(2-hydroxyethyl)ammonium (or triethanolammonium) as cations and methacrylate, dihydrogenborate, formate, and acetate as anions have been synthesized through stoichiometric neutralization reaction. PILs have been characterized by elemental analyses, FTIR, ¹H and ¹³C NMR spectroscopic methods. The viscosity of **PIL4** was measured using a cone-and-plate viscometer at ambient temperature. The viscosity value indicates that the fluidity of **PIL4** is 829 cP (the viscosity of water is 0.7977 cP at 30 °C).

Keywords: Protic ionic liquids, Spectroscopy, Synthesis, Triethanolammonium salts, Viscosity.

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INTRODUCTION

In general, ionic liquids (ILs) are liquid at temperatures below 100 °C and those liquids can remain fluid in a wide temperature range (1). ILs have attracted intense interest in both academia and industry in recent years due to their impressive properties such as low volatility, high dissolution capacity, large electrochemical window, and high thermal and electrical conductivity (2-4). One of the most important properties of ILs is their environmentally friendly and non-hazardous nature due to negligible vapor pressures. Thus, ILs have recently been of great interest as green chemicals rather than conventional solvents (5).

PILs are obtained by proton transfer between a Brønsted acid and a Brønsted base (6). An equimolar amount of acid and base react together in a uniform or aqueous solution. In general, the rest of ILs can be classified as aprotic ILs (AILs), but there are some subclasses similar to PILs such as Brønsted acidic ILs, which are typically functionalized to have a proton

present on the anion. PILs have many applications as lubricants (7, 8), biologically active materials (9, 10), electrolytes (11-13), catalysts (14 15), etc.

Hydroxylammonium-based PILs have hydrogen bond donor properties that significantly increase their applications. Hydroxylammonium IL has been used to dissolve many insoluble polymers such as zein (an industrially important natural polymer), polyaniline and polypyrrole (16). The effect of the hydroxyl group on the dissolution with polar solvents in this type of IL was disclosed by determining the solvatochromic parameter (17). Nowadays, aqueous monoethanolamine has been used for the removal of CO₂ from natural gas in industrial processes due to serious environmental concerns about volatility, recovery and abrasiveness (18). Yuan et al. synthesized a series of hydroxylammonium ILs and determined the solubility of SO₂ at atmospheric pressure (19). Garaev et al. found that hydroxylammonium-based ILs with carboxylate anion are highly biodegradable and practically non-toxic (20).

Ahfad-Hosseini et al. developed a new method for the synthesis of celecoxib (a selective COX-2 inhibitor) with high yield and least environmental hazard using tris-(2-hydroxyethyl)ammonium acetate (II) as IL and evaluated the effect of IL concentration and reaction temperatures on the yield of celecoxib production (21). Furthermore, the physicochemical properties of hydroxylammonium-based ILs such as glass transition temperature, density, conductivity, sound velocity, viscosity and decomposition temperature at different temperatures have been studied intensively (22-25).

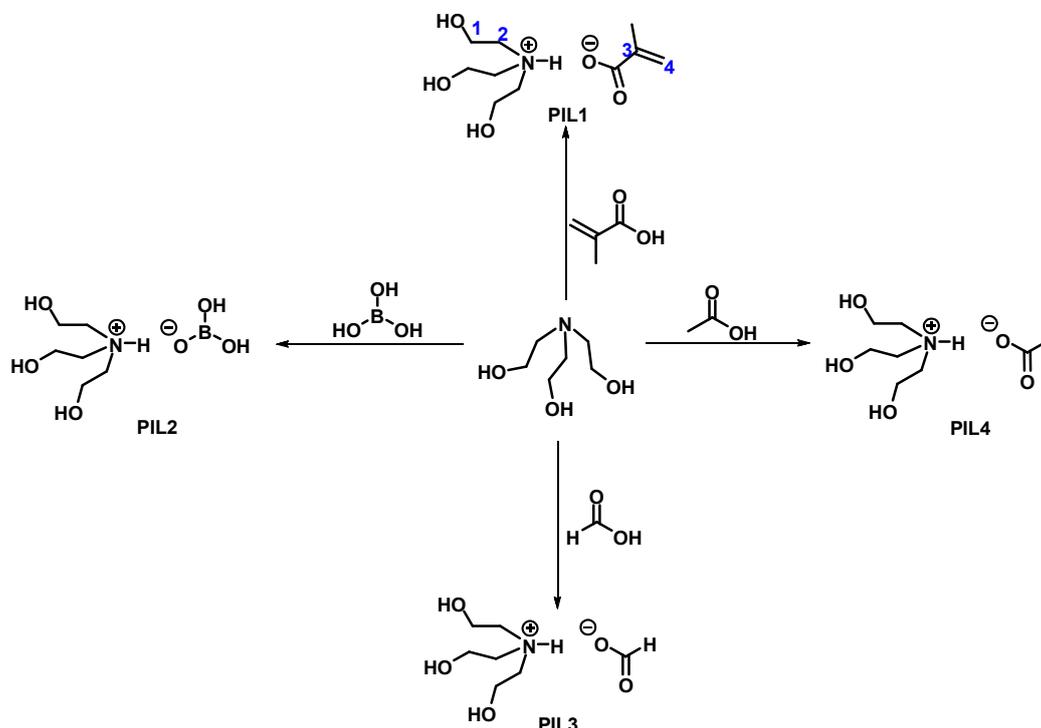
Herein, the PILs consisting of tris(2-hydroxyethyl)ammonium cation and anions of different inorganic or carboxylic acids have been obtained, and these are tris(2-hydroxyethyl)ammonium methacrylate (**PIL1**), tris(2-hydroxyethyl)ammonium dihydrogenborate (**PIL2**), tris(2-hydroxyethyl)ammonium formate (**PIL3**) and tris(2-hydroxyethyl)ammonium acetate (**PIL4**) (Scheme 1). The structure of the synthesized PILs was determined by elemental analysis, FTIR, ^1H and ^{13}C NMR techniques. The

viscosity has been measured at atmospheric pressure with ambient temperature.

EXPERIMENTAL

Material and Methods

Triethanolamine, methacrylic acid, boric acid, formic acid, and acetic acid were purchased from commercial sources and used without further purification. ^1H - and ^{13}C -NMR spectra of the PILs were measured using AC Bruker 400 MHz NMR spectrometer in Methanol- d_4 and D_2O at ambient temperature. FT-IR spectra were recorded on a Jasco FT-IR 4700 spectrometer in the range of 400-4000 cm^{-1} . Elemental analyses were recorded on a Elementar Vario Micro Cube elemental analyzer. The viscosity of **PIL4** was measured using a Brookfield DV2TRVCP Viscometer. The cone and plate method was used where the sample (0.5 mL) was placed between a 2 cm cone and a flat plate. The cone was made to rotate and the viscosity of the sample was measured.



Scheme 1. The scheme represents the PILs.

General procedure for the synthesis of PILs 1-4

The PILs were synthesized according to the previous literature (26). A mixture of triethanolamine (5.00 g, 33.51 mmol) and methacrylic acid (2.89 g, 33.51 mmol), boric acid (2.07 g, 33.51 mmol), formic acid (1.54 g, 33.51

mmol) or acetic acid (2.01 g, 33.51 mmol) is prepared in 1:1 molar ratio. Triethanolamine is placed in a two-necked 100 mL round-bottomed flask, which is fitted with a dropping funnel, and connected to a condenser. Methacrylic acid, boric acid, formic acid or acetic acid is placed in the dropping funnel, and added the acid dropwise to the diethylenetriamine in the flask. The reaction

is vigorous and the rate is controlled by regulating the addition of acid. The reaction should be complete in about 24 h. The PILs thus prepared was kept in a vacuum oven at 80 °C for 48 hours to remove excess moisture formed during the reaction. The dried solvent was sealed with laboratory parafilm to prevent any moisture contamination.

Synthesis of PIL1

Anal. Calc. for $C_6H_{16}NO_3^+(C_4H_5O_2^-)$ (%): C, 51.05; H, 9.00; N, 5.95 Found (%): C, 49.96; H, 8.98; N, 5.92. FTIR (cm^{-1}): $\hat{\nu}$ 3232 (O-H), 2922 (C-H aliph.asym.), 2876 (C-H aliph.sym.), 1644 (C=C), 1551, 1445 (COO⁻), 1062 (C-N). ¹H NMR (D₂O, ppm, numberings of protons are given in Scheme 1): 3.91 (t, 6H, ³J_{HH}= 4.7 Hz, **H₁**), 3.38 (t, 6H, ³J_{HH}= 4.7 Hz, **H₂**), 5.62; 5.31 (d, 2H, ²J_{HH}= 1.0 Hz, **H₄**), 1.84 (s, 3H, **CH₃**), 4.69-8.04 (m, 4H, HN⁺, OH). ¹³C NMR (D₂O, ppm, numberings of carbons are given in Scheme 1): 55.55 (**C₁**), 55.36 (**C₂**), 177.38 (C=O), 142.42 (**C₃**), 120.24 (**CH₃**), 18.92 (**C₄**).

Synthesis of PIL2

Anal. Calc. for $C_6H_{16}NO_3^+(BH_2O_3^-)$ (%): C, 34.15; H, 8.60; N, 5.12 Found (%): C, 34.23; H, 8.41; N, 5.18. FTIR (cm^{-1}): $\hat{\nu}$ 3270 (O-H), 2951 (C-H aliph.asym.), 2877 (C-H aliph.sym.), 1369 (B-O), 1065 (C-N). ¹H NMR (methanol-d₄, ppm, numberings of protons are given in Scheme 1): 3.88 (t, 6H, ³J_{HH}= 5.8 Hz, **H₁**), 3.21 (t, 6H, ³J_{HH}= 5.8 Hz, **H₂**), 3.61-8.06 (m, 6H, HN⁺, OH). ¹³C NMR (methanol-d₄, ppm, numberings of carbons are given in Scheme 1): 63.01 (**C₁**), 59.70 (**C₂**).

Synthesis of PIL3

Anal. Calc. for $C_6H_{16}NO_3^+(CHO_2^-)$ (%): C, 43.07; H, 8.78; N, 7.18 Found (%): C, 43.38; H, 8.96; N, 7.22. FTIR (cm^{-1}): $\hat{\nu}$ 3239 (O-H), 2935 (C-H aliph.asym.), 2876 (C-H aliph.sym.), 1588, 1439 (COO⁻), 1060 (C-N). ¹H NMR (methanol-d₄, ppm, numberings of protons are given in Scheme 1): 3.77 (t, 6H, ³J_{HH}= 5.3 Hz, **H₁**), 3.24 (t, 4H, ³J_{HH}= 5.3 Hz, **H₂**), 8.43 (s, 1H, **-H**), 4.77-7.99 (m, 4H, HN⁺, OH). ¹³C NMR (methanol-d₄, ppm, numberings of carbons are given in Scheme 1): 57.35 (**C₁**), 57.16 (**C₂**), 169.95 (C=O).

Synthesis of PIL4

Anal. Calc. for $C_6H_{16}NO_3^+(C_2H_3O_2^-)$ (%): C, 45.92; H, 9.15; N, 6.69 Found (%): C, 46.13; H, 8.91; N, 6.82. FTIR (cm^{-1}): $\hat{\nu}$ 3187 (O-H), 2924 (C-H aliph.asym.), 2864 (C-H aliph.sym.), 1563, 1397 (COO⁻), 1062 (C-N). ¹H NMR (methanol-d₄, ppm, numberings of protons are given in Scheme 1): 3.70 (t, 6H, ³J_{HH}= 5.4 Hz, **H₁**), 3.05 (t, 6H, ³J_{HH}=

5.4 Hz, **H₂**), 1.83 (s, 3H, **-CH₃**), 4.77-7.97 (m, 4H, HN⁺, OH). ¹³C NMR (methanol-d₄, ppm, numberings of carbons are given in Scheme 1): 58.31 (**C₁**), 57.49 (**C₂**), 23.14 (**CH₃**), 178.80 (C=O).

RESULTS AND DISCUSSION

Tris(2-hydroxyethyl)ammonium cation based PILs were synthesized by proton transfer between an equimolar amount of triethanolamine, and different acids such as methacrylic acid, boric acid, formic acid or acetic acid (Scheme 1). The triethanolamine and various acids have been selected based on their structural properties and availability. At room temperature, **PIL4** is liquid, while **PIL1-3** are quasi-solid state. All the PILs were soluble in polar protic solvents such as water, methanol, and ethanol. There are publications in which the triethanolamine salt (**PIL3** and **PIL4**) containing formic and acetic acid is indicated (20, 21, 27). However, only ¹H NMR (using DMSO as a solvent) and FT-IR (using a NaCl disk) spectroscopic techniques were used for structural characterization. A structural study based on NMR (¹H- and ¹³C-) spectroscopy of the prepared PILs was subsequently performed in concordance with FT-IR spectra and elemental analysis. Thus, these studies have confirmed the presence of protonated amine.

The chemical shifts, multiplicities and coupling constants of all PILs were determined by interpreting the ¹H and ¹³C NMR signals (Supplementary Material, Figures S1-8), and are presented in the "Experimental Section". The three PILs could easily be dissolved in methanol-d₄, except **PIL1**. For the triethanolammonium cation, the resonance signals of the CH₂ group protons (3.91-3.70 ppm for **H₁** and 3.38-3.05 ppm for **H₂**) in the ¹H NMR spectra of PILs are downfield-shifted compared to the original triethanolamine (3.46 ppm for **H₁** and 2.57 ppm for **H₂**) (28). The chemical shift does not exceed 0.8 ppm. The average coupling constant, ³J_{HH}, is 5.3 Hz. Both the OH and the NH resonances are relatively broad at 3.61-4.77 ppm and 7.97-8.06 ppm, respectively. Further, the carboxylic acid proton (-COOH) at about 8-12 ppm (29) was not observed in the ¹H NMR spectra of the **PIL1**, **PIL3** and **PIL4**. This may be indicative of the formation of PILs. ¹³C NMR chemical shifts of the triethanolammonium cation in the spectra of the studied PILs are in the range of 63.01-55.55 ppm for the neighboring the oxygen atom (**C₁**), while those of the protons adjacent to the nitrogen atom (**C₂**) are in the range of 59.70-55.36 ppm. On the other hand, the carbonyl carbon atoms (C=O) of the **PIL1**, **PIL3** and **PIL4** were

observed at 177.38, 169.95 and 178.80 ppm, respectively.

In tris(2-hydroxyethyl)-ammonium based PILs, the proton of the acid is located on the onium nitrogen atom (N^+H) in the cation and forms trifurcate hydrogen bonds with three hydroxyethyl groups resulting in the formation of the tricyclic protatran cation (30, 31). Therefore, these PILs are known as protatrans (Figure 1).

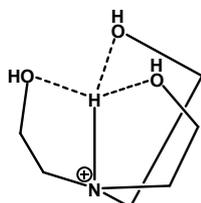


Figure 1. The structure of the tris(2-hydroxyethyl)-ammonium cation (protatran).

The results of the FT-IR analyses were very similar for all of the PILs. In the absorption IR spectra of the obtained PILs, a broad characteristic ammonium band of $\nu(N^+H)$ was observed in the range of 2400–3000 cm^{-1} (Figure S9). In the FT-IR spectrum of triethanolamine, the strong band at 3303 cm^{-1} corresponds to the stretching vibrations of the OH groups involved in intramolecular hydrogen bonds. The wide band of $\nu(OH)$ resulting from the high symmetry of the molecules of the PILs was found at about 3232 cm^{-1} . This band is due to the vibrations of the three hydroxy groups of the triethanolammonium cation in which oxygen atoms form intramolecular hydrogen bonds with the N^+H hydrogen atom (Figure 1). A higher strength hydrogen bond formed by the OH groups of the protatran cation with the carboxylic group of the

acid anion results in $\nu(OH)$ bands at low frequencies ($\sim 3153\text{ }cm^{-1}$) (32). This explanation disagrees with the FT-IR results of the PILs, the spectrum of which does not have this band. Protatran methylene CH_2 vibrations correspond to the bands at 2951–2864 cm^{-1} . The PILs show two strong absorption bands between 1563–1551 and 1445–1397 cm^{-1} , which are assigned to the asymmetric and symmetric stretching vibrations of the carboxylate ion, $\nu(COO^-)$, respectively, indicating clearly the PIL formation. At the same time, it was known that the degree and nature of interaction between the cation and anion in protatran is reflected in the frequencies of symmetric and asymmetric vibrations $\nu(COO^-)$ (33, 34). The difference between these values ($\Delta\nu$) is used as a criterion of the structure of the molecule. The value of $\Delta\nu > 200\text{ }cm^{-1}$ points to a significant asymmetry of the carboxylic group, while the value of $\Delta\nu < 200\text{ }cm^{-1}$ is indicative of its approximate symmetry (35). The molecule of **PIL1** is characterized by the vibration bands of the carboxylate anion at 1551 [$\nu_{as}(COO^-)$] and 1445 cm^{-1} [$\nu_s(COO^-)$]. The value of $\Delta\nu$ equal to 106 cm^{-1} points to a significant symmetry of the carboxylic group. It can be assumed that other **PIL3** (149 cm^{-1}) and **PIL4** (166 cm^{-1}) with $\Delta\nu < 200\text{ }cm^{-1}$ have the structure close to that of **PIL1**.

The viscosity of the **PIL4** which was liquid at ambient temperature was measured. Considering the fluidity of **PIL4**, CP52 type spindle was used to measure the viscosity of this PIL, and viscosity value was given in Table 1. Most PILs are viscous liquids, the viscosities being comparable to and greater than the viscosity of water (water's viscosity is 0.7977 cP at 30 °C) (36). Also, the viscosity of the **PIL4** is higher compared to the initial triethanolamine (404 cP at 30 °C) (37).

Table 1. Viscosity data of **PIL4**.

Code	Viscosity (cP)	Temperature (°C)	Speed (RPM)	Torque (%)	Spindle
PIL4	829	29	60	50.1	CP-52

CONCLUSION

Four triethanolammonium-based PILs which belongs to the class of protic alkanolammonium ionic liquids, have been synthesized by proton transfer reaction from carboxylic and inorganic acids to triethanolamine. These PILs show good solubility in polar solvents (water, alcohols, etc.). The PILs have been established by elemental analysis and 1H , ^{13}C NMR, FT-IR spectroscopic methods. It is shown that the obtained spectral characteristics confirm salt formation for all the studied compounds. The structure of PILs depends on the type and strength of hydrogen bonds between the triethanolammonium cation

(protatran) and carboxylate anion, which affects the frequencies of stretching vibrations of OH⁻ and COO⁻ groups.

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