



Ionic liquids derived from esters of Glycine Betaine: Synthesis and characterization



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ABSTRACT

A series of new “green” ionic liquids was prepared in two or three steps from natural and low expense Glycine Betaine (GB). Esterification of GB was carried out with methanesulfonic acid and primary alcohols with alkyl chains containing 6, 12, 14, 16 and 22 atoms of carbon. Anionic metathesis from these cationic esters with inorganic (ClO_4^- , BF_4^-) or biobased ($(S)\text{-CH}_3\text{-CHOH-COO}^-$ (Lac^-)) anions was then achieved to afford a range of fully characterized ionic liquids. The influence of the alkyl chain length and the chemical nature of the counter anion on physicochemical properties such as melting point, glass transition, decomposition temperatures and viscosity has been investigated.

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1. Introduction

Ionic liquids (ILs) are commonly defined as salts with a melting point below 100 °C. Most of traditional ILs are constituted by the association of alkylphosphonium, alkylammonium, dialkylimidazolium, dialkylpyrrolidinium or alkylpyridinium cations with a bulky anion such as Cl^- , AlCl_4^- , PF_6^- , BF_4^- , $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, CF_3CO_2^- or CF_3SO_3^- . Due to their specific physicochemical properties including a low vapor pressure, high thermal and chemical stability, non-flammability, large electrochemical window, and outstanding ability to dissolve a wide range of compounds [1–3], ILs have found a range of applications in various areas including for instance chemical synthesis, catalysis [4–9], electrochemistry [10–12] or analytical chemistry [13,14].

ILs today are considered as “greener” alternatives to volatile organic solvents, mainly due to their negligible vapor pressure. Their non-volatility is a common property to all ILs that enable them to generate only little atmospheric pollution as compared to conventional solvents. For this reason, ILs are considered as “green solvents” but taking into account the twelve principles of green chemistry, the terminology “green” is still open for debate. The most commonly used ILs, based on imidazolium cations and fluorinated anions are synthetic chemicals, and therefore are not as green as desired. Chloroaluminate-based ILs are air and water sensitive. Hexafluorophosphate and tetrafluoroborate-based ILs are unstable towards hydrolysis, potentially releasing HF in contact with moisture [15]. Although ILs cannot enter the environment by

evaporation, most of them are water soluble and could easily enter the biosphere by this way [16].

Even the no-volatility of ILs has been questioned especially by the work of Earle et al. [17] which has shown that some ILs can be evaporated and recondensed under relatively mild conditions. Recently Marlair et al. [18] have highlighted that ILs are flammable and have physicochemical properties such as the heat of combustion that is close to conventional combustible materials such as wood or plastic. Regarding safety towards human health and environment, it was shown that certain conventional ILs are toxic towards a panel of micro-organisms representative of different ecosystems and could generate environmental damages in particular in the event of accidental release [19].

In order to obtain “green” ionic liquids, the starting materials must be at least non-toxic, while for a perfect solution, they should be renewable. Moreover, the development of new “green” ILs still requires relatively low cost synthetic route and easy preparation. Bio-renewable natural compounds are ideal materials from the viewpoints of both environmental and economical concerns [20]. Some syntheses of ILs have been reported, using lactates [21,22], acesulfamates [23,24], levulinate [25], carbohydrate derivatives [26,27] or amino acids [28] for the anionic part, and choline [29,30] carbohydrates [31] or amino acids [32–34] for the cationic species.

In this work, Glycine Betaine (GB) was used for the IL synthesis. Glycine Betaine (GB) is a natural and cost-effective substance possessing a quaternary trimethylalkylammonium moiety and a carboxylate function, useful to conceive new ILs. GB constitutes an abundant raw material representing 27% of molasses of sugar beet in weight. It is obtained after extraction of saccharose and currently remains few developed as

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a by-product of the sugar industry. GB is very well known as one of the most powerful osmoprotectant identified so far, and has been widely studied for this specific property [35–38]. More recently scientists have also focused on its capacity to form deep eutectic solvents with urea, citric acid or malonic acid [39,40]. One example of protonated betaine bis(trifluoromethylsulfonyl)imide [41,42] IL has been described and used for the extraction of neodymium(III) and the selective solubilization of metal oxides.

Within this context, the aim of this study was to produce novel “green” ILs with GB esters as cationic moiety. Some of GB esters associated with various counter ions such as chloride, hydroxide and laurate were previously synthesized and used successfully as cationic surfactant in formulation of new emulsions with improved biodegradability properties [43]. To our knowledge, their use as building block to generate ionic liquids has never been described. This paper, deals with the synthesis and the characterization of 20 salts incorporating cationic esters of trimethyl(2-alkoxy-2-oxoethyl) ammonium (GBOC_n^+) associated with inorganic (ClO_4^- , BF_4^- , and Dca^-) or biobased ($(S)\text{-CH}_3\text{-CHOH-COO}^-$ (Lac^-)) anions. The influence of the alkyl chain length (C_6 , C_{12} , C_{14} , C_{16} , C_{22}), grafted by esterification reactions on GB, and the nature of the anions on the physicochemical and thermal properties of the ILs (Scheme 1) were investigated to elucidate structure–properties relationships.

2. Experimental section

2.1. Materials

Glycine Betaine, methanesulfonic acid, the primary alcohols (*n*-hexanol, *n*-dodecanol, *n*-tetradecanol, *n*-hexadecanol, *n*-docosanol) and the sodium salts (dicyanamide, perchlorate and tetrafluoroborate) were purchased from Sigma Aldrich and used as received. Potassium lactate was prepared by the reaction of potassium hydroxide and (*S*)-lactic acid. All aqueous solutions were prepared with distilled water.

2.2. Physicochemical analysis

Elemental analyses (C, H, N and S) were carried out on a Perkin-Elmer 2400 C, H, N and S element analyzer in our University.

IR spectrum of liquid IL ($\text{GBOC}_6\text{-Dca}$) was recorded on a Bruker Alpha-T FTIR spectrometer using NaCl plates, whereas those of solid compounds were obtained in KBr pellets with a Nicolet Avatar 320 apparatus.

^1H and ^{13}C NMR spectra were recorded at room temperature with a Bruker AC 250 spectrometer (250 MHz for ^1H , 62.5 MHz for ^{13}C). Chemical shifts (in ppm) for ^1H and ^{13}C NMR spectra were referenced to residual protic solvent peaks.

The decomposition temperatures of the ILs were measured using a Netzsch TG 209 F3 Tarsus thermogravimetric analyzer under argon atmosphere, with the mass of TGA samples varying between 10 and 20 mg. Samples were heated from 30 °C to 400 °C with a heating rate of 10 °C/min. The decomposition temperatures are reported in terms of T_{onset} (the intersection of the zero mass loss baseline and the tangent line through T_{peak} , where T_{peak} is the peak temperature of the time derivative of the mass loss curve $d(\text{mass})/dt$).

Differential scanning calorimetry (DSC) experiments were carried out on a TA Instruments Q100 under a nitrogen atmosphere with a heating rate of 10 °C min^{-1} .

The viscosity was measured with a Brookfield Viscosimeter DV-II + Pro. The temperature of the sample was maintained to 80 or 90 °C \pm 0.1 °C by an external temperature control CPE 51.

Optical rotations were determined on a Perkin Elmer Model 341 polarimeter at 589 nm.

2.3. Synthesis of ionic liquids

2.3.1. Hexylbetainium methanesulfonate ($\text{GBOC}_6\text{-CH}_3\text{SO}_3$)

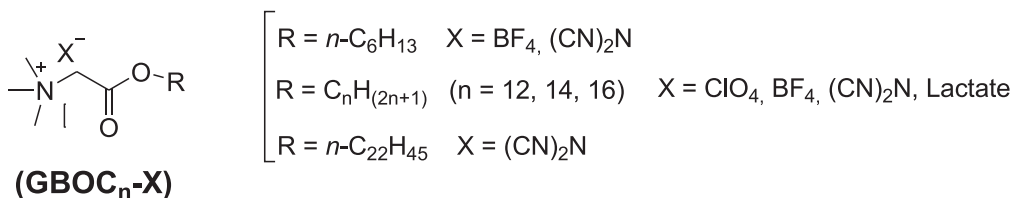
A solution of *n*-hexanol (55 mL, 0.43 mol, 5 equiv.) and methanesulfonic acid (8.4 mL, 128 mmol) was added dropwise to Glycine Betaine (10 g, 85.4 mmol). The reaction mixture was heated to 160 °C with a Dean Stark apparatus to remove the water formed during the esterification. After 1 h, the reaction mixture became homogeneous. The heating was continued for 24 h and the orange solution was cooled down to room temperature. Then, *n*-hexanol was distilled under reduced pressure. The residual excess of alcohol was eliminated with two consecutive washes with Et_2O (2×100 mL). The compound was then extracted with *n*-BuOH/ EtOAc (1/1) (2×100 mL). The combined organic phases were evaporated under reduced pressure. The crude material obtained was purified by recrystallisation from EtOAc/EtOH (1/1) to give a white solid. Yield: (24.1 g, 81.1 mol, 95%). Melting point 103 °C. ^1H NMR: δ_{H} (250 MHz; DMSO-d_6): 0.97 (3H, t, $J = 7.5$ Hz, CH_3), 1.38 (6H, m), 1.73 (2H, q, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{O}$), 2.51 (3H, s, CH_3S), 3.36 (9H, s, $(\text{CH}_3)_3\text{N}$), 4.27 (2H, t, $J = 7.5$ Hz, CH_2O), 4.61 (2H, s, CH_2COO). ^{13}C NMR: δ_{C} (62.5 MHz; DMSO-d_6): 12.1 (CH_3), 20.2, 23.1, 26.0, 29.0 (CH_2), 37.9 (CH_3S), 51.2 ($(\text{CH}_3)_3$), 60.6 (CH_2O), 63.9 (CH_2CO), 163.3 (C=O). IR: $\nu(\text{cm}^{-1})$ 1743 (C=O). Analysis: Calculated for $\text{C}_{12}\text{H}_{27}\text{NO}_5\text{S}$: C 48.46, H 9.15, N 4.70, S 10.78%. Found: C 48.73, H 8.81, N 4.40, S 10.97%.

2.3.2. Alkylbetainium methanesulfonate ($\text{GBOC}_n\text{-CH}_3\text{SO}_3$)

To a suspension of dried Glycine Betaine (8.3 g, 71 mmol, 1.0 equiv.) in methanesulfonic acid (1.5 equiv.), an excess of *n*-alcohol (about 2 equiv.) was added. The reaction mixture was gradually heated to 130–140 °C under reduced pressure (50–100 mbars) to remove the water formed during the reaction. After 1 h, the reaction mixture became homogeneous and after 7 h the brown mixture was cooled down to room temperature and at atmospheric pressure. The crude material was washed with Et_2O (3×200 mL) to remove the excess of fatty alcohol and then purified by recrystallisation from EtOAc/EtOH (1/1). For ($\text{GBOC}_{16}\text{-CH}_3\text{SO}_3$) the purification was done by column chromatography over silica gel using $\text{EtOAc}/i\text{PrOH}/\text{H}_2\text{O}$ (62/30/8) as eluent.

2.3.2.1. Dodecylbetainium methanesulfonate ($\text{GBOC}_{12}\text{-CH}_3\text{SO}_3$)

Yield (23.4 g, 61.3 mmol, 86%). Melting point 104 °C. ^1H NMR: δ_{H} (250 MHz; DMSO-d_6): 0.95 (3H, t, $J = 7.5$ Hz, CH_3), 1.34 (18H, m), 1.70 (2H, q, $J = 7.5$ Hz, $\text{CH}_2\text{CH}_2\text{O}$), 2.52 (3H, s, $\text{CH}_3\text{-S}$), 3.33 (9H, s, $(\text{CH}_3)_3\text{N}$), 4.27 (2H, t, $J = 7.5$ Hz, CH_2O), 4.56 (2H, s, CH_2COO). ^{13}C NMR: δ_{C} (62.5 MHz; DMSO-d_6): 14.2 (CH_3), 22.4, 29.0, 29.2, 29.3, 29.4, 31.6 (CH_2), 40.0 (CH_3S), 53.4 ($(\text{CH}_3)_3$), 62.8 (CH_2O), 66.0 (CH_2CO), 165.3 (C=O). IR: $\nu(\text{cm}^{-1})$ 1750 (C=O). Analysis: Calculated for $\text{C}_{18}\text{H}_{39}\text{NO}_5\text{S}$: C 56.66, H 10.30, N 3.67, S 8.40%. Found: C 56.28, H 10.19, N 3.37, S 8.35%.



Scheme 1. Ionic liquids based on Glycine Betaine esters.

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