Journal of Molecular Liquids 225 (2017) 217–223

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Synthesis and physicochemical properties of new tropine-based chiral dication ionic liquids

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ARTICLE INFO

Article history:
Received 21 July 2016
Accepted 26 September 2016
Available online 17 November 2016

Keywords:
Ionic liquids
Synthesis
Density
Viscosity
Conductivity

ABSTRACT

A new series of chiral dicationic ionic liquids (DILs) were successfully synthesized and characterized by IR and NMR. The density of the whole family of ILs was measured and related physical properties including thermal expansion coefficient, molecular volume, standard molar entropy, and crystal energy were estimated by theoretical methods. Moreover, the viscosity, conductivity of DILs and the binary mixtures of ionic liquid + water were determined. The data were correlated with Arrhenius equation and VogeL-Fulcher-Tamman (VFT) equation and the results were discussed subsequently. Furthermore, the molar conductivity, dissociation equilibrium constant and critical micelle concentration of DIL solution were deduced by experimental or theoretical methods. At last, the influences of the carbon chain of ILs and temperature on density, viscosity and conductivity were discussed.

1. Introduction

In the past decades, ionic liquids (ILs) have always been associated with the idea of "green chemistry" [1,2]. Due to the excellent properties, ILs have been applied in many fields such as catalytic, electrolytes, adsorption, extraction, chromatographic applications, aqueous two-phase system and have achieved good effect [3–17].

Recently, the interest in dicationic ionic liquids (DILs) is increasing because of their unique characteristics such as higher thermal stability and wider liquid range compared to monocationic ILs (MILs). Although more and more DILs have been continuously developed including imidazolium [18–21], pyridinium [22,23], ammonium [24–26], it is obvious that the current DILs are mostly the first or second generation of ILs. However, tropine-based ILs with better biocompatibility are more conform to the conception of the third generation of ILs. A family of novel tropine-based MILs, derived from hydrolyzate of tropane alkaloids, have been creatively developed in our previous work [27,28]. Among the MILs, a few of chiral tropine-based monocationic ILs (CMILs) have been applied in resolution with good results [28]. But further study of synthesis and physicochemical properties of tropine-based chiral DILs has not been reported.

In this work, four new chiral DILs based on tropine-cations and L-proline anion were synthesized with quaternarization and metathesis reactions and were fully characterized by FT-IR, ^{1}H and ^{13}C NMR. The thermal behaviors of these chiral ILs were investigated using thermogravimetric/differential thermal gravity (TG/DTG). In order to provide reliable basic data for future applications, the specific rotation, density, viscosity, conductivity and more important properties were studied with experimental or theoretical methods.

2. Experimental

2.1. Reagents and materials

Tropine and L-proline were purchased from Huawen Chemical Co. Ltd. (Zhengzhou, China). 1.3-Dibromopropane, 1.4-dibromobutane, strong-base anion exchange resin and other solvents were purchased from Kelong Chemical Co. Ltd. (Chengdu, China). Pentamethylene dibromide and hexamethylene dibromide were purchased from Aladdin Industrial Co. Ltd. (Shanghai, China). All reagents and solvents were of pure analytical grade and were used without further purification. Deionized water was obtained by the UPR-I-5T water purification system from Ultrapure Technology Co. Ltd. (Chengdu, China).

2.2. Synthesis and characterization

Synthesis of [BuDTr]Br_2: Tropine (14.83 g, 0.105 mol) was added to a 50 mL one-neck round-bottom flask containing dry toluene as solvent, then 1.4-dibromobutane (10.80 g, 0.5 mol) was added dropwise. After the mixture was heated to reflux with constant stirring for 24 h, the resulting white solid was collected by filtration and washed 3 times with excess of acetone. The white solid was then dried under vacuum at 323 K. The mass of dry solid was 11.09 g with yield of 94%.

Synthesis of [BuDTr][OH]$_2$: 0.01 mol [BuDTr]Br_2 was dissolved in 100 mL deionized water then loaded on a column of strongly basic styrene 201*7 type anion exchange resin (0.315–1.25 mm, Kelong Chemical Co., Ltd., Chengdu, China) and eluted. The reaction progress was

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http://dx.doi.org/10.1016/j.molliq.2016.09.098
0167-7322/

monitored by concentrated $AgNO_3$ aqueous solution. After the ion exchange between Br^- and OH^-, no precipitation of AgBr was found with an addition of a few drops of $AgNO_3$ solution and the yield was 91%.

Synthesis of $[BuDTr][L\text{-}Pro]_2$: 0.021 mol L-proline was dissolved in 100 mL deionized water and then $[BuDTr][OH]_2$ solution obtained from last step was added [29]. The mixture was dried under reduced pressure to remove solvent after stirring in room temperature for 1 h. The result white viscous liquid was dissolved in ethanol and put into refrigerator for 0.5 h and then filtrated under deduced pressure to remove residual L-proline, the filtrate was dried under deduced pressure to remove ethyl alcohol. The product yield was 95%. The residual Br^- was below the detection limit of approximately 1 ppm by an $AgNO_3$ solution test.

IR (KBr, cm^{-1}): 3352, 3046, 2952, 2908, 1623, 1580, 1533, 1428, 1351, 1315, 1268, 1213, 1177, 1101, 1057, 1041, 880, 823, 626. ^1H NMR (400 MHz, D_2O) δ 4.06 (t, $J = 5.4$ Hz, 2H), 3.79 (s, 4H), 3.56 (dd, $J = 8.3$, 6.0 Hz, 2H), 3.32–3.30 (m, 2H), 3.22–3.15 (m, 4H), 3.05 (dt, $J = 11.0$, 6.7 Hz, 2H), 2.95–2.93 (m, 6H), 2.82 (dt, $J = 11.0$, 6.8 Hz, 2H), 2.46 (d, $J = 17.2$ Hz, 4H), 2.39 (d, $J = 8.9$ Hz, 4H), 2.25–2.20 (m, 4H), 2.09–2.04 (m, 4H), 1.88 (d, $J = 16.7$ Hz, 4H), 1.75–1.70 (m, 10H). ^{13}C NMR (100 MHz, D_2O) δ 179.72, 66.86, 66.30, 61.40, 59.96, 57.28, 45.98, 40.23, 33.82, 33.50, 30.15, 24.67, 24.65, 24.43, 19.20.

Synthesis of $[PrDTr][L\text{-}Pro]_2$: Similar procedure as earlier was carried out with tropine and 1.3-dibromopropane as materials, the obtained bromine salt was firstly changed to $[PrDTr][OH]_2$ through metathesis reaction and then to $[PrDTr][L\text{-}Pro]_2$ with neutral reaction with the yield of 85%.

IR (KBr, cm^{-1}): 3401, 3058, 3017, 2961, 2902, 1624, 1577, 1533, 1431, 1351, 1313, 1266, 1221, 1159, 1088, 1055, 869, 809, 625. ^1H NMR (400 MHz, D_2O) δ 4.10 (t, $J = 5.6$ Hz, 2H), 3.87 (s, 4H), 3.65 (dd, $J = 8.4$, 6.2 Hz, 2H), 3.38–3.35 (m, 2H), 3.31–3.25 (m, 4H), 3.12–3.10 (m, 2H,a), 3.04–3.02 (m, 6H), 2.92–2.88 (m, 2H,b), 2.51 (d, $J = 17.2$ Hz, 4H), 2.43 (t, $J = 14.1$ Hz, 4H), 2.25 (d, $J = 17.9$, 4H), 2.13–2.08 (m, 4H), 1.92 (t, $J = 19.0$ Hz, 4H), 1.78–1.73 (m, 8H). ^{13}C NMR (100 MHz, D_2O) δ 179.20, 67.30, 66.80, 61.38, 59.83, 57.26, 45.99, 40.37, 33.83, 33.52, 30.03, 24.63, 24.56, 24.45, 16.16.

Synthesis of $[PnDTr][L\text{-}Pro]_2$: Similar procedure as earlier was carried out with tropine and pentamethylene dibromide as materials, the obtained bromine salt was firstly changed to $[PnDTr][OH]_2$ through metathesis reaction and then to $[PnDTr][L\text{-}Pro]_2$ with neutral reaction with the yield of 87%.

IR (KBr, cm^{-1}): 3339, 3049, 2996, 2951, 2883, 1624, 1580, 1530, 1434, 1352, 1310, 1267, 1214, 1158, 1090, 1055, 1042, 949, 822, 732, 626. ^1H NMR (400 MHz, D_2O) δ 4.06 (t, $J = 5.2$ Hz, 2H), 3.78 (s, 4H), 3.53 (dd, $J = 8.2$, 5.9 Hz, 2H), 3.25–3.22 (m, 2H), 3.7–3.14 (m, 4H), 3.03 (dt, $J = 12.4$, 6.4 Hz, 2H), 2.94–2.92 (m, 6H), 2.79 (dt, $J = 12.4$, 6.4 Hz, 2H), 2.45 (d, $J = 17.0$ Hz, 4H), 2.37 (d, $J = 8.8$ Hz, 4H), 2.25–2.20(m, 4H), 2.05(dd, $J = 8.2$, 5.8 Hz, 4H), 1.86 (dd, $J = 16.5$, 8.9 Hz, 4H), 1.76–1.73 (m, 4H), 1.71–1.67 (m, 6H), 1.36–1.29 (m, 2H). ^{13}C NMR (100 MHz, D_2O) δ 180.07, 66.70, 66.12, 61.42, 60.02, 57.37, 45.98, 40.18, 33.84, 33.51, 30.24, 24.72, 24.45, 22.94, 21.58.

Synthesis of $[HxDTr][L\text{-}Pro]_2$: Similar procedure as earlier was carried out with tropine and hexamethylene dibromide as materials, the obtained bromine salt was firstly changed to $[HxDTr][OH]_2$ through metathesis reaction and then to $[HxDTr][L\text{-}Pro]_2$ with neutral reaction with the yield of 83%.

IR (KBr, cm^{-1}): 3401, 3043, 3008, 2976, 2952, 2913, 2866, 1624, 1580, 1531, 1431, 1349, 1310, 1266, 1234, 1211, 1170, 1096, 1045, 940, 890, 818, 645. ^1H NMR (400 MHz, D_2O) δ 4.05 (t, $J = 5.1$ Hz, 2H), 3.76 (s, 4H), 3.53–3.51 (m, 2H), 3.23–3.19 (m, 2H), 3.14–3.12 (m, 4H), 3.03 (dt, $J = 12.7$, 6.5 Hz, 2H), 2.93–2.91 (m,6H), 2.78 (dt, $J = 12.7$, 6.5 Hz, 2H), 2.44 (d, $J = 16.5$ Hz, 4H), 2.36 (d, $J = 8.9$ Hz, 4H), 2.21 (d, $J = 16.3$ Hz, 4H), 2.07–1.99 (m, 4H), 1.86 (d, $J = 16.5$ Hz, 4H), 1.69–1.68 (m, 6H), 1.32 (s, 4H), 1.08–1.05 (m, 4H). ^{13}C NMR (100 MHz, D_2O) δ 180.98, 66.60, 66.02, 61.45, 60.04, 57.38, 45.96, 40.12, 33.83, 33.51, 30.44, 24.88, 24.70, 24.44, 21.70, 16.79.

An overview of the synthesis of $[CnDTr][L\text{-}Pro]_2$ (d_{1-4}) is depicted in Scheme 1.

2.3. Spectroscopy measurement

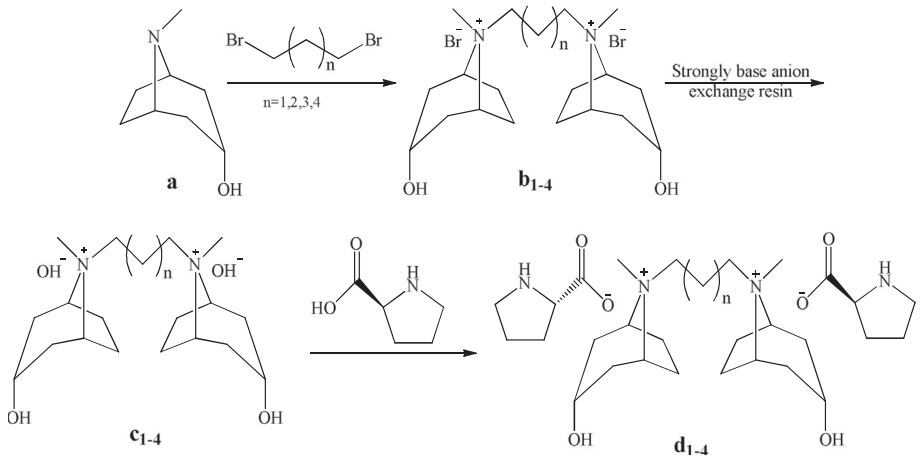
All the spectral measurement was carried out at room temperature. IR spectra were measured with a Perkin Elmer Fourier transform infrared spectrometer (Waltham, USA) in potassium bromide discs, which were scanned from 400 to 4000 cm^{-1} with 4 cm^{-1} resolution. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 MHz nuclear magnetic resonance spectrometer (Fällanden, Switzerland) equipped with a 5 mm probe. Samples (each 15 mg) were dissolved by deuteroxide in the sample tubes

2.4. Measurement of specific rotation

0.2 g $[CnDTr][L\text{-}Pro]_2$ were dissolved in 20 mL deionized water, the measurement of specific rotation of $[CnDTr][L\text{-}Pro]_2$ was carried on an automatic polarimeter at 298.15 K under wavelength of 589 nm with a 100 mm optical tube.

2.5. Measurement of density

The density of degassed water was firstly measured by a Westphal balance. The densities of ILs was then measured in the temperature T = (278.15 to 313.15) K. with intervals of 5 K with the same method.



Scheme 1. Synthesis of novel tropine-based chiral DILs.