

Identification of novel chemical structures of sulfo-imidazolium zwitterionic-type salt basis on 2D NMR analysis

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ARTICLE INFO

Article history:

Received 22 October 2018

Received in revised form

30 November 2018

Accepted 30 November 2018

Available online 3 December 2018

Keywords:

NMR analysis

Sulfo-functionalized liquid salt

Zwitterionic structure

ABSTRACT

The reaction of the equimolar mixture of imidazole and 1,4-butanediol was performed at 90 °C in ethylbenzene for 12 h and the zwitterionic and ionic structures of the product investigated by the NMR analysis. The present work displayed the great importance of 2D NMR analysis on the structure elucidation of this sulfonic acid functionalized liquid salt. The results of NMR analysis demonstrate that 4-imidazole-1-yl-butane-1-sulfonic acid did not exist and really a mixture of zwitterionic and ionic compounds is produced.

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1. Introduction

Ionic liquids (ILs) are widely utilized in the multicomponent reactions as the solvent, catalyst or dual solvent-catalyst due to unique physicochemical and environmentally benign properties [1–9]. The organic products and the ionic liquids can be separated in the different phases and this can decrease the consumption of toxic and volatile organic solvents and avoid tedious and complex separation and purification technologies [10,11].

The imidazolium cations containing covalently-bound anionic sulfonate groups were synthesized through the equimolar reaction of *N*-alkylimidazole and 1,3-propanediol or 1,4-butanediol in acetone, and the NMR spectra data were presented [12,13]. Firstly, Hajra et al. showed a structure of the product of the reaction of imidazole with 1,4-butanediol and named it as 4-(1-imidazolium)butane sulfonate which was used in one-pot synthesis of β -nitroamines [14]. 4-(1-Imidazolium)butane sulfonate was used in a three-component synthesis of 2-amidoalkyl and 2-carbamatoalkyl naphthols [15], and the mechanism reaction was illustrated using a chemical structure of 4-(1-imidazolium)butane sulfonate as previously reported in the literature [14]. Then, this compound was used as an organocatalyst for the synthesis of tetrazoles [16] and the regioselective ring-opening of aziridines [17]; nevertheless, no spectroscopic and physical data for the claimed

structure entitled 4-(1-imidazolium)butane sulfonate was exhibited. Furthermore, this compound is observed in the chemical list of the chemical supplier “Accel Pharmtech” as 1*H*-imidazole-1-butanediol sulfonic acid with CAS No: 1094601-09-8 [18].

To the best of our knowledge, no spectroscopic and physical data were displayed for this zwitterionic-type salt in the literature. We interested in this reaction and its product when we observed the unusual 1D NMR of product, and proposed the equilibrium structures. We repeated the reaction several times, but the results were identical. On the other hand, the proposed equilibrium structures did not convince us; thus we used 2D NMR to describe the unusual 1D NMR and excess peaks. It was approved that the reaction of imidazole and 1,4-butanediol could not produce 4-(1-imidazolium)-butane sulfonate.

2. Experimental

2.1. Materials and methods

Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich, and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and FT-IR, NMR and elemental analysis. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates. The purity determination and MS (EI) data of the products were accomplished by GC-MS on an Agilent 6890N GC system with a 5973N mass selective detector under 70 eV conditions. The FT-IR

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spectra were recorded on a Perkin Elmer 781 Spectrophotometer using KBr pellets for solid and neat for liquid samples in the range of 4000–400 cm^{-1} . In all the cases the ^1H and ^{13}C NMR spectra were recorded with Bruker Avance III 600 MHz and 400 MHz instruments. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. The amount of water in the liquid salt was determined by Karl Fisher (KF) titration, using a Metrohm 831 kF coulometer in conditions of ambient humidity and room temperature. The pH readings were recorded by a pH meter F-71, LAQUA-HORIBA Scientific at 27 ± 1 °C.

2.2. Synthesis of novel liquid salt

Imidazole (0.68 ± 0.01 g, 10 mmol) was added to 1,4-butanediol (1.1 ± 0.1 mL, 10.7 ± 0.1 mmol) and stirred continuously for 12 h at 90 ± 1 °C in ethylbenzene (5.0 ± 0.1 mL) to obtain the liquid salt (I + II) as a clear, viscous and colorless liquid. The solvent was then removed by rotary evaporation and the viscous liquid was washed with EtOAc ($3 \times 5.0 \pm 0.1$ mL) to remove unreacted starting materials. The resulting liquid salt (I + II) was dried to constant weight in vacuum at 60 °C (1.72 ± 0.01 g, yield $84.2 \pm 0.1\%$).

3. Results and discussion

In continue of our interesting to the synthesis of new IIs [19–23], very recently, we have reported the “plausible” structures of 4-imidazole-1-yl-butane-1-sulfonic acid (ImBu-SO₃H) in an equilibrium state basis on only 1D NMR analysis (Scheme 1) [24,25].

Fortunately, the 2D NMR analysis of ImBu-SO₃H provided additional information on the molecular conformation which helped to accomplish the structural characterization in liquid, herein, we described our results on the structure elucidation of the reaction product of the equimolar mixture of imidazole and 1,4-butanediol in ethylbenzene using the correlation spectroscopy (COSY) and heteronuclear multiple bond correlation (HMBC) experiments. The impact of the ^1H , ^1H -COSY, ^1H , ^{13}C - and ^1H , ^{15}N HMBC correlations were demonstrated for the preservation or elimination of some structures.

Interestingly, when the equimolar reaction of imidazole and 1,4-butanediol were heated and stirred in dry ethylbenzene at 90 °C for 12 h, a colorless liquid salt containing 4-[3-(4-sulfo-butyl)-imidazole-1-yl]-butane-1-sulfonate (I) and 4-imidazole-1-yl-butane-1-sulfonate imidazolium (II) was isolated in $84.2 \pm 0.1\%$ yield as a zwitterionic and ionic structure, respectively (Scheme 2). The same results were obtained in all experiments.

3.1. FTIR characterization

In the FTIR of the liquid salt (I + II), a broad band centered at 3423 cm^{-1} along with a weak absorption as shoulder at 1643 cm^{-1} can be arisen from the bonding vibration of water molecules due to moisture absorption by liquid salt and N-H stretching vibrations of imidazolium ring (See Supplementary Fig. 1) [26].

Three aromatic C-H stretching vibrations in the imidazolium ring viz. $\nu\text{C-H5}$, $\nu\text{C-H4}$ and $\nu\text{C-H2}$ are observed in region $3140\text{--}3100 \text{ cm}^{-1}$ [27,28]. The absorptions at 2962 and 2858 cm^{-1} are

mainly characteristic of C–H symmetric and asymmetric stretching vibrations of methylene groups in the alkyl chain part [28]. The vibration bands with wavenumbers in the range of $1587\text{--}1457 \text{ cm}^{-1}$ represent mainly the C–C and C–N bond stretching within the imidazole ring and ring deformation modes. Among these vibrations, the bands at 1567 cm^{-1} and 1457 cm^{-1} may be assigned to the C=N functions and the strong band at 1587 cm^{-1} should correspond to the C=C stretching vibrations of the imidazolium cation [29,30]. The asymmetric and symmetric stretching and bending for S–O vibrations of the sulfonic acid group were observed as strong absorptions centered at 1159 and 598 cm^{-1} [31]. By comparison with S–OH bending frequencies in sulfuric acid and other sulfonic acids, the band at 1033 cm^{-1} was assigned to S–OH bend [22].

3.2. NMR characterization

The ^1H NMR spectra of the liquid salt (I + II) gave sharp signals in CD₃OD (See Supplementary Fig. 2). The novel liquid salt contained a total of three aromatic protons attached to imidazole ring and eight aliphatic protons. The constitution of a new chemical is frequently considered elucidated as soon as an assigned structure is in accordance with connectivity information derived from 2D NMR experiments such as ^1H , ^1H -COSY, ^1H , ^{13}C - and ^1H , ^{15}N HMBC.

The structures were established from the extensive 1D- (^1H and ^{13}C) and 2D- (^1H - ^1H COSY, ^1H - ^{13}C - and ^1H , ^{15}N -HMBC) NMR spectroscopy analysis of the liquid salt (I + II). In the ^1H NMR spectrum of the liquid salt (I + II) in CD₃OD (See Supplementary Fig. 2), the CH of the imidazole structures appeared the following order:

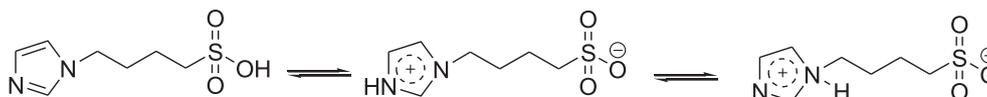
Imidazole ring (A): CH-2 was characterized as a singlet at δ_{H} 9.09 ppm and a doublet at δ_{H} 7.70 ppm with coupling constant 1.6 Hz was attributed to CH-4 and CH-5. The ratio of the peak areas (CH-2:CH-4 and CH-5 = 0.67: 1.40) was close to the expected stoichiometric value (1:2) for the imidazolium ring (A).

Imidazole ring (B): a singlet at δ_{H} 8.76 ppm and two triplets at δ_{H} 7.61 ppm and δ_{H} 7.48 ppm with coupling constant 1.6 and 1.5 Hz were assigned to CH-2, CH-4, and CH-5, respectively. The ratio of the peak areas (CH-2:CH-4:CH-5 = 0.99:1.00:1.00) was close to the expected stoichiometric value (1:1:1) for this imidazolium ring.

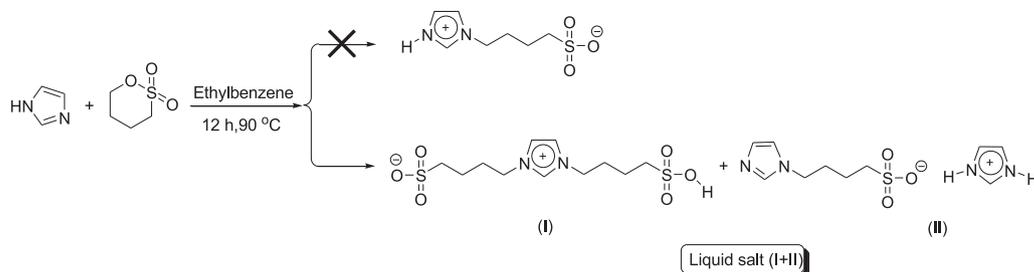
Imidazole ring (C): CH-2 was observed as a singlet at δ_{H} 8.72 ppm and CH-4 and CH-5 were displayed as a doublet at δ_{H} 7.52 ppm with a coupling constant of 1.1 Hz. The ratio of the peak areas (CH-2:CH-4 and CH-5 = 1.09:2.21) was close to the expected stoichiometric value (1:2) for the imidazolium ring (C).

Based on the peak areas of three imidazole rings A, B, and C, the methylene hydrogens in the butyl moiety as carbon spacer were calculated as $(1.40 \times 2) + (2.21 \times 1) = 5.01$ which were approximately average peak areas viz. CH₂-6 (5.02), CH₂-7 (5.14), CH₂-8 (5.06), and CH₂-9 (5.62) in the ^1H NMR spectrum. The three imidazole rings determined from ^1H NMR spectroscopic studies was further confirmed by a ^1H , ^1H -COSY study of the liquid salt (I + II) in CD₃OD (Scheme 3) (See Supplementary Fig. 2).

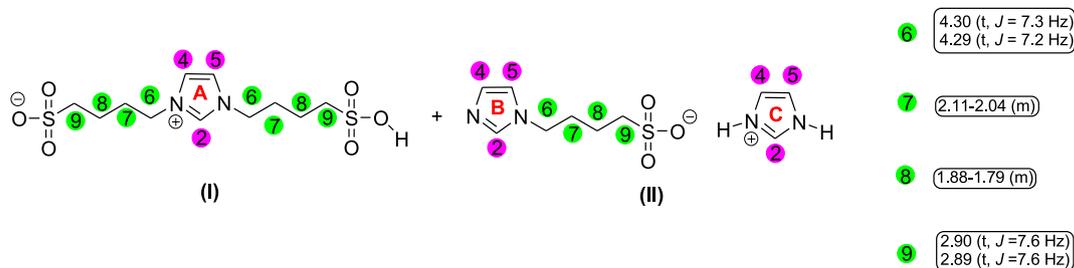
In the ^1H NMR spectrum, the CH₂ of the C-6 gives two triplets at δ_{H} 4.30 and δ_{H} 4.29 ppm with coupling constant 7.3 Hz and 7.2 Hz, respectively, which shows a ^1H , ^1H -COSY correlation with a multiplet hydrogen signal at δ_{H} 2.11–2.04 ppm, assigning it to C-7. The methylene hydrogens of the C-9 appear as two triplets at δ_{H} 2.90 and 2.89 ppm with coupling constant 7.5 Hz and 7.4 Hz,



Scheme 1. The equilibrium between the “plausible” alternative structures of 4-imidazole-1-yl-butane-1-sulfonic acid (ImBu-SO₃H).



Scheme 2. The synthesis of liquid salt (I + II).



Scheme 3. The atom numbering of the zwitterion and ionic structures in the liquid salt (I + II).

respectively, which showed a $^1\text{H}, ^1\text{H}$ -COSY correlation with methylene hydrogen signal at δ_{H} 1.87–1.79 ppm assigned to C-8. The methylene hydrogens C-8 displayed a signal correlation with a multiplet hydrogen signal at 2.11–2.04 ppm.

Then, the $^1\text{H}, ^1\text{H}$ -COSY correlation of the hydrogens of C-6 with the hydrogens of imidazole rings **A**, **B**, and **C** were investigated (See Supplementary Fig. s. 3 and 4). The methylene hydrogens of C-6 exhibited the $^1\text{H}, ^1\text{H}$ -COSY correlation with hydrogen signal at δ_{H} 9.09 (imidazole ring **A**), 8.76 (imidazole ring **B**), 7.70 (imidazole ring **A**), 7.61 (imidazole ring **B**), and 7.48 (imidazole ring **B**) ppm, however, no correlation was observed between hydrogens of C-6 and imidazole ring **C** at δ_{H} 8.72 and 7.52 ppm.

The $^1\text{H}, ^1\text{H}$ -COSY correlation of hydrogen signals at δ_{H} 7.48 and 7.61 with hydrogen signal 8.76 ppm was observed and hydrogen signals at δ_{H} 7.70 ppm were also correlated to the hydrogen signals at δ_{H} 8.72 and 9.09 ppm, respectively (See Supplementary Fig. 4). In addition, no the $^1\text{H}, ^1\text{H}$ -COSY correlation was observed between the CH-2, CH-4, and CH-5 of imidazole ring **C** at δ_{H} 8.72 and 7.52 ppm with the hydrogens CH₂-6 at δ_{H} 4.30 and 4.29 ppm, which proved the imidazole ring **C** is not connected across the carbon spacer.

The presence of various structures was also illustrated by the ^{13}C NMR experiment (See Supplementary Fig. 5), which displayed the signals for each of the 7 carbon atoms in the plausible structures of the reaction product with chemical shifts at δ_{C} 136.03, 135.42, and 134.15 ppm assigned to CH-2 and at δ_{C} 122.48, 121.47, 121.24, and 119.50 ppm attributed to CH-4 and CH-5 in three imidazole rings. The carbon chemical shifts of carbon spacer were observed at δ_{C} 49.03 and 48.27 ppm for C-6 (N–CH₂), δ_{C} 21.52 and 21.46 ppm for C-7 (N–CH₂–CH₂), δ_{C} 28.81 and 28.53 ppm for C-8 (CH₂–CH₂–SO₃), as well as δ_{C} 50.21 and 50.12 ppm for C-9 (CH₂–SO₃).

The $^1\text{H}, ^{13}\text{C}$ -HMBC in CD₃OD further confirmed the presence of three imidazole rings **A**, **B**, and **C** in the liquid salt (I + II) (See Supplementary Fig. 6 and 7). The hydrogen signals of C-6 shows a HMBCs correlation with C-2, C-4, C-5, C-7, and C-8 at δ_{C} 136.03 (imidazole ring **A**), 135.42 (imidazole ring **B**), 122.48 (imidazole ring **A**), 121.47 (imidazole ring **B**), 121.24 (imidazole ring **B**), 28.81 and 28.53 (C-8), 21.52 and 21.48 ppm (C-7), respectively. The $^1\text{H}, ^{13}\text{C}$ -HMBC correlation was not observed between the hydrogen signals

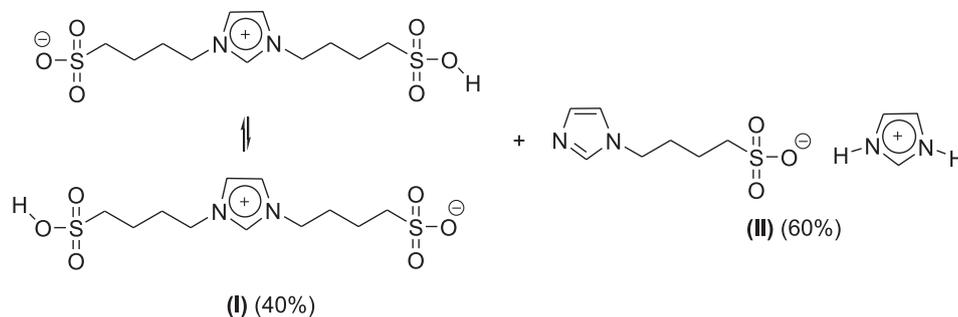
of C-6 and carbon signals of imidazole ring **C** at δ_{C} 134.15 and 119.50 ppm, which verified the imidazole ring **C** is not connected across the carbon spacer as aforementioned by $^1\text{H}, ^1\text{H}$ -COSY.

The hydrogen signal of C-9 displayed the HMBCs correlation with C-7, C-8 at δ_{C} 28.81, 28.53, 21.52 and 21.48 ppm, respectively. The methylene hydrogens of C-8 exhibited the HMBC correlation with C-4, C-3 at δ_{C} 50.21, 50.13, 49.03, 48.27, 28.81, 28.53, respectively, and the HMBC correlation of the hydrogen signal of C-7 was observed with C-6, C-8 at δ_{C} 50.21, 50.13, 49.03, 21.52 and 21.48 ppm, respectively.

The hydrogen signals at δ_{H} 9.09 and 7.70 ppm displayed the HMBCs correlations with δ_{C} 136.03 and 122.48 ppm, which was assigned to imidazole ring **A**. The hydrogen signals at δ_{H} 8.76, 7.61, and 7.48 ppm showed the HMBCs correlations with δ_{C} 135.42, 121.46, 121.24 ppm, which was assigned to imidazole ring **B**. The hydrogens at δ_{H} 8.72 and 7.52 ppm exhibited the HMBCs correlations with δ_{C} 134.15 and 119.50 ppm, which was attributed to imidazole ring **C** (See Supplementary Fig. 7).

The $^1\text{H}, ^{15}\text{N}$ -HMBC spectrum of the liquid salt (I + II) in CD₃OD is shown in Fig. 8 (See Supplementary). The ^1H peaks of imidazole ring **A** and **B** viz. CH-2, CH-4, CH-5, CH₂-6, and CH₂-7 displayed strong correlations with the N-1 and N-3 at δ_{N} 186.20 and 183.1 ppm, while hydrogen signals of imidazole ring **C** showed the correlation with N-1 and N-3 at δ_{N} 178.5 ppm but no correlation was observed between the hydrogen signals of carbon spacer with the nitrogen signals in the imidazole ring **C**.

The liquid salt (I + II) examined here clearly displays the importance of the $^1\text{H}, ^1\text{H}$ -COSY, $^1\text{H}, ^{13}\text{C}$ -HMBC and $^1\text{H}, ^{15}\text{N}$ -HMBC experiment for a comprehensive constitutional analysis. The combination of these NMR experiments allows a systematic investigation of structural proposals based on ^1H and ^{13}C chemical shift. On the basis of our findings, the reaction product of the equimolar mixture of imidazole and 1,4-butanedisulfone is a mixture of 4-[3-(4-sulfo-butyl)-imidazole-1-yl]-butane-1-sulfonate (I) and 4-imidazole-1-yl-butane-1-sulfonate imidazolium (II) which basis on the peak areas, the amount of (I) to (II) in mixture was calculated at $40 \pm 2\%$ (I) to $60 \pm 2\%$ (II) (Scheme 4) (Table 1).



Scheme 4. The elucidated structures of liquid salt (I + II) based on the 2D NMR experiments.

Table 1

The structure data of the liquid salt (I + II) in CD₃OD.

Atoms	4-[3-(4-Sulfo-butyl)-imidazole-1-yl]-butane-1-sulfonate (I)				The 4-imidazole-1-yl-butane-1-sulfonate anion and imidazolium cation (II)							
					4-Imidazole-1-yl-butane-1-sulfonate anion				Imidazolium cation			
	δ_H (ppm)	J (Hz)	δ_C (ppm)	δ_N (ppm)	δ_C (ppm)	J (Hz)	δ_C (ppm)	δ_N (ppm)	δ_H (ppm)	J (Hz)	δ_C (ppm)	δ_N (ppm)
CH-2	9.09	s	136.03	—	8.76	s	135.42	—	8.72	s	134.15	—
CH-4	7.70	d, 1.7	122.48	—	7.61	t, 1.6	121.46	—	7.52	d, 1.1	119.50	—
CH-5	7.70	d, 1.7	122.48	—	7.48	t, 1.5	121.24	—	7.52	d, 1.1	119.50	—
CH ₂ -6	4.30	t, 7.3	49.03	—	4.29	t, 7.2	48.27	—	—	—	—	—
CH ₂ -7	1.87–1.79	m	21.49	—	1.87–1.79	m	21.46	—	—	—	—	—
CH ₂ -8	2.11–2.04	m	28.81	—	2.11–2.04	m	28.53	—	—	—	—	—
CH ₂ -9	2.90	t, 7.5	50.20	—	2.89	t, 7.4	50.12	—	—	—	—	—
N-1	—	—	—	183.1	—	—	—	186.2	—	—	—	178.5
N-3	—	—	—	183.1	—	—	—	183.1	—	—	—	178.5

3.3. Physical properties of liquid salt

The amount of water in the liquid salt (I + II) was determined 0.11 ± 0.03 wt. %. The conditions of temperature, pressure and drying time were 100 ± 2 °C, 80 ± 2 mbar, and 12 h, respectively. A vacuum oven was used to dry the liquid salt (I + II) before evaluation of its water content. The pH of 0.01 ± 0.002 M aqueous solution of liquid salt (I + II) was recorded 2.6 ± 0.1 . The standard deviation was obtained from three replicate determinations on the different three days. The liquid salt (I + II) was soluble in DMSO, DMF, water, methanol, and ethanol and it was immiscible with diethyl ether, ethyl acetate, and CH₂Cl₂.

3.4. Thermal stability of liquid salt

The thermal stability of liquid salt (I + II) was investigated using the thermogravimetric analysis (TGA/DTA) (See [Supplementary Fig. 9](#)). DTA curve of the liquid salt (I + II) obtained by analysis in nitrogen atmosphere showed two peaks below 100 °C. Therefore, it seems that there is the content of inherent air moisture and physically adsorbed water through the hydrogen bonding. The first portion, between 30 ° and 62 °C (DTA ~50 °C) of the curve represents desorption of loosely bound water from the surface of the liquid salt. The second portion from 62 °C to 180 °C (DTA ~80 °C) exhibits the slow desorption of tightly bound water from the liquid salt (I + II). In these portions, the mass losses were 2.11% and 9.97% respectively. The maximum mass loss was 83.98% that is related to the total degradation of imidazole, butane and sulfonic acid fragments of the liquid salt (I + II) at 250–400 °C and the liquid salt (I + II) was practically decomposed. The onset of temperature degradation of the liquid salt (I + II) was observed around 250 °C, and its thermal decomposition ends around 400 °C. Thus, the liquid salt (I + II) is thermally stable even at relatively high temperatures.

4. Conclusion

In summary, the reaction of the equimolar mixture of imidazole and 1,4-butane sultone was performed at 90 °C in ethylbenzene for 12 h, and the structure of the product was elucidated by FTIR, ¹H and ¹³C NMR, ¹H,¹H-COSY, ¹H,¹³C- and ¹H,¹⁵N-HMBC analysis. Based on the NMR analysis, the ionic liquid of 4-(1-imidazolium)butane sulfonate could not be produced through the current procedure as previously reported in the literature. Two novel zwitterionic-type and ionic structures *viz.* 4-[3-(4-sulfo-butyl)-imidazole-1-yl]-butane-1-sulfonate (I) and 4-imidazole-1-yl-butane-1-sulfonate imidazolium (II) were observed in the liquid salt which their structures was confirmed using 2D NMR. Some of the physical properties, pH of the aqueous solution, and thermal stability of the liquid salt were determined. The more experiments for the preparation of the zwitterion 4-[3-(4-sulfo-butyl)-imidazole-1-yl]-butane-1-sulfonate is performing in our laboratory.

Acknowledgments

The author is grateful to staff members in the Analytical and Testing Center of the University of Malaya for partial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molstruc.2018.11.106>.

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