

Journal of Chemical, Biological and Physical Sciences



An International Peer Review E-3 Journal of Sciences

Available online at www.jcbps.org

Section A: Chemical Sciences

CODEN (USA): JCBPAT

Research Article

Design, Synthesis and Characterization of new Task-specific Brönsted acidic hydrogensulfate Ionic liquid

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Received: 09 June 2016; Revised: 01 July 2016; Accepted: 03 July 2016

Abstract: We report the synthesis and characterization of a new imidazolium based halogen free ionic liquid (IL) 1-Methyl-3-propane sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate (MIM-PS-LS). By reacting 1-methyl imidazole with 1,3-propane sultone and by exchanging chloride ion with lauryl sulphate anion, IL 1-Methyl-3-propane sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate (MIM-PS-LS). The superior purity of this IL was confirmed with ¹H-NMR, ¹³C-NMR, FT-IR and Mass indicating the helpfulness of this synthetic approach. The Hammett acidity (H₀) shows the [MIM-PS-LS] HSO₄ (0.93) has better acidity than [MIM-PS] Cl.

Keywords: Ionic liquid, NMR, FT-IR, Hammett Acidity

INTRODUCTION

Most of our understanding of chemistry has been based upon the behavior of molecules in the solution phase in molecular solvents. Recently, a new class of solvent has emerged-ionic liquids.¹ Ionic Liquids

(ILs) are generally salts based on a substituted heterocyclic cation with an organic or inorganic anion and exist in liquid state at room temperature. ILs have been called designer solvents due to their ability to vary the ions, thereby modifying and optimizing the ionic liquid physical properties for a specific task.² These ILs can be synthesized in an endless number of ways according to the proper combination of ions. Accordingly, their physical and thermal properties strongly depend on the species of cation and anion as well as the length of the alkyl groups on the cation.³

In recent years, room temperature ionic liquids (RTILs) have received a lot of attention as potential “green” and “designable” solvents.⁴ Although ILs have been studied since the 1950s⁵, these were not part of our studies until water-stable and air-stable ILs such as 1-Methyl-3-propane sulfonic acid imidazolium chloride (MIM-PS). These liquids need not be handled under an inert atmosphere because of the beneficial properties such as negligible vapor pressure, extremely low volatilities or non-volatility, non-flammability, high ionic density, high thermal conductivity, chemical and electrochemical stability, high heat capacity, etc. and a wide temperature range.⁶

Owing to these advantages, ILs have currently been applied as novel solvents in organic synthesis,⁷⁻⁹ catalysis,^{10, 11} electrochemistry,¹² chemical separation,¹³ solid support,¹⁴ and metal extraction. In addition, RTILs have intrinsic ionic conductivity at room temperature and a wide electrochemical window, exhibiting good electrochemical stability in the range of 4.0–5.7 V.^{15,16} ILs have also been used as electrolytes in conducting polymer-based electrochemical devices,¹⁷ in the electrochemical synthesis of conducting polymers,¹⁸ and in the synthesis of conducting polymer organic dispersions,^{19,20} and conducting polymer nanostructures.²¹ More recently, the use of proton-conducting ionic liquids (PCILs) was proposed in order to ensure high anhydrous proton conductivities while maintaining sufficient thermal stability. This domain has since aroused a great deal of interest with a view for application in Proton Exchange Membrane Fuel Cells (PEMFCs).²²⁻²⁵

To design any process involving ILs on an industrial scale, their physical properties and electrochemical characteristics must be primarily provided before any further steps are taken. Therefore, experimental measurements and molecular simulations for physical properties of ILs play key parts in their application to many processes.²⁶ The present work is demonstrated the synthesized and characterization of 1-Methyl-3-propane sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate (MIM-PS-LS). The purity of synthesized IL was confirmed by ¹H-NMR, ¹³C-NMR, FT-IR methods and the Hammett acidity was determined by UV-vis. Method.

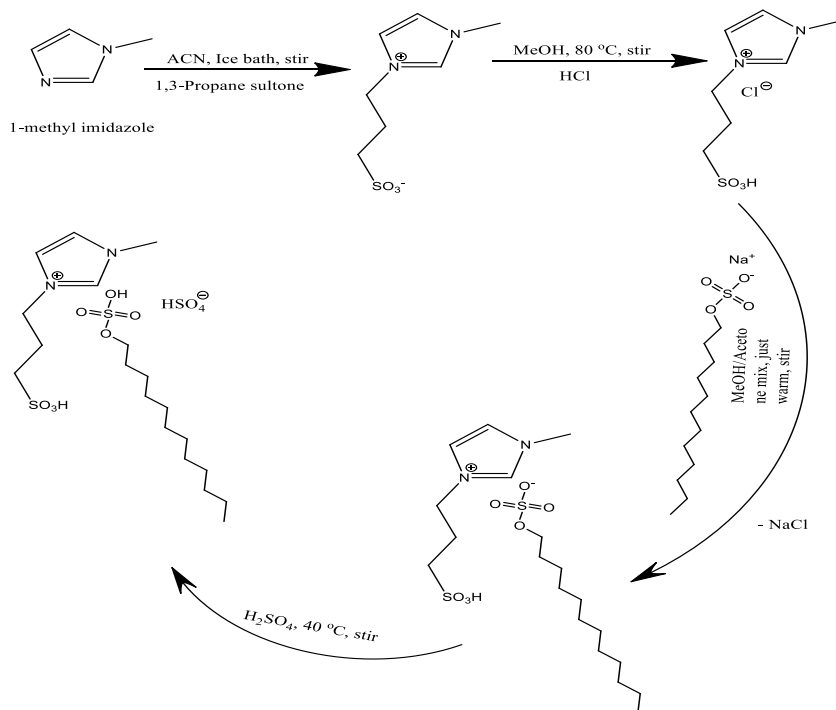
MATERIAL AND METHODS

Reagent grade 1-methyl imidazole (99.9%), sodium dodecyl sulphate (99.8%), ethyl acetate (99.8%) were purchased from Sigma-Aldrich and used without further purification. Acetone, ethanol, acetonitrile, methanol, H₂SO₄ and HCl were purchased from Himedia with > 99% purity. ¹H-NMR and ¹³C-NMR spectra in *d*-acetone were measured using Advance 400MHz NMR (Bruker Scientific Corporation Ltd. Switzerland) NMR spectrometer operating at proton frequency of 400 MHz; proton chemical shifts were recorded relative to an internal TMS standard. FT-IR spectra were recorded using ABB FTIR, Canada, in the range 400 – 3500 cm⁻¹. UV-vis. spectra were recorded on a Shimadzu, Japan (UV-160A) (Toshbro Pvt. Ltd. Mumbai) was used to record the absorption spectra. UV-Vis. measurements were performed on

Agilent B453 spectrophotometer for acidity evaluation. Solutions of the ILs were prepared from deionized water and the ILs (dried under vacuum at 80 °C for 2 h).

Synthetic procedures

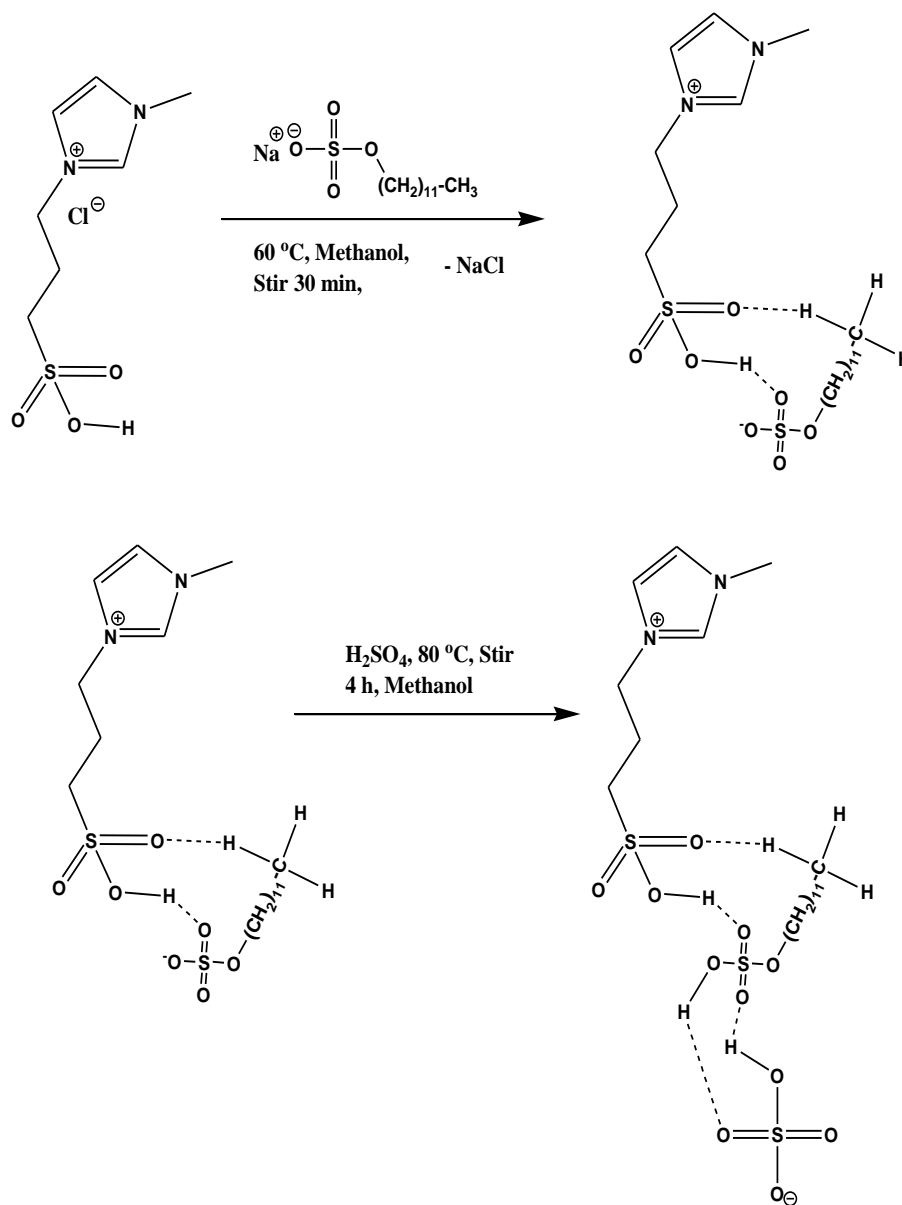
Synthesis of 1-Methyl-3-propane sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate (MIM-PS-LS): 1-Methyl imidazole (5.0 g, 0.037 mol) was dissolved in toluene and to it a solution of 1,3-propane sultone in toluene was added with stirring in a round bottom flask at 0 °C. After addition was finished the reaction was allowed to stir at RT for 24 h. The resultant white colored mass was filtered out, washed with toluene and then with diethyl ether and vacuum dried at 100 °C. To zwitterion mass a stoichiometric amount of conc. HCl was added drop wise and the mixture stirred for 6 h at 40 °C. The IL formed was washed with ether to remove any non-ionic residues and vacuum dried at 80 °C for 24 h. Finally, the ILs viscous oil ([MIM-PS]Cl) was kept in sealed tube under argon atmosphere. The MIM-PS-LS was synthesized from the metathesis reaction between sodium lauryl sulphate and MIM-PS-LS in acetone/methanol mixture under mild heating. The IL-solvent mixture was filtered to remove sodium chloride (NaCl) and the filtrate was put into a round-bottomed flask to be in oven at 75 ± 0.1 °C under a vacuum in order to remove any residual acetone. The resultant product is semi solid light yellow to brown colored waxy type material which is partially soluble in water ($\sim 0.01 - 0.05$ %w/v). Then, a stoichiometric amount of conc. H_2SO_4 was added drop wise and the mixture stirred for 3 h at 40 °C. The IL formed was washed with ether to remove any non-ionic residues and vacuum dried at 70 °C for 12 h. Finally, the ILs viscous oil ([MIM-PS-LS]) was kept in sealed tube under argon atmosphere. The MIM-PS-LS was characterized by ^1H - and ^{13}C -NMR, Mass and by FTIR. The reaction scheme for synthesis of ILs is given in **Scheme 1**.



Scheme 1. Reaction mechanism for synthesis of IL.

RESULTS AND DISCUSSION

Characterization of IL: The synthesis of 1-Methyl-3-propane sulfonic acid imidazolium chloride (MIM-PS) IL with chloride ions and the modified (desired) IL with lauryl sulphate anion follows the general reaction scheme presented in **Scheme 1**. The modified imidazolium based halogen-free IL is semi solid or waxy material having high purity and good yields. The purity of the products was identified based on several techniques. The results of ^1H -NMR, ^{13}C -NMR spectra indicated the high purity of IL (all step including used reagents) without unexpected signals from unreacted starting materials are shown in spectra's from component A to G. Careful examination of the FT-IR results **Fig. 1** showed all functional groups expected for IL. The molecular self-assembly of the IL by hydrogen bonds is given in **Scheme 2**.



Scheme 2. Proposed molecular self-assembly of the IL by hydrogen bonds.

FT-IR studies

FT-IR (KBr, cm^{-1}) ν_{max} : **MIM-PS-LS**: 3096, 2915-2831, 1722-1579, 1398, 1150-1028, 873, 654. **MIM-PS**: 2981, 2516-2298, 1770-1435, 1169-1030, 764-589. The corresponding FT-IR spectral data of ILs are presented in **Fig. 1**.

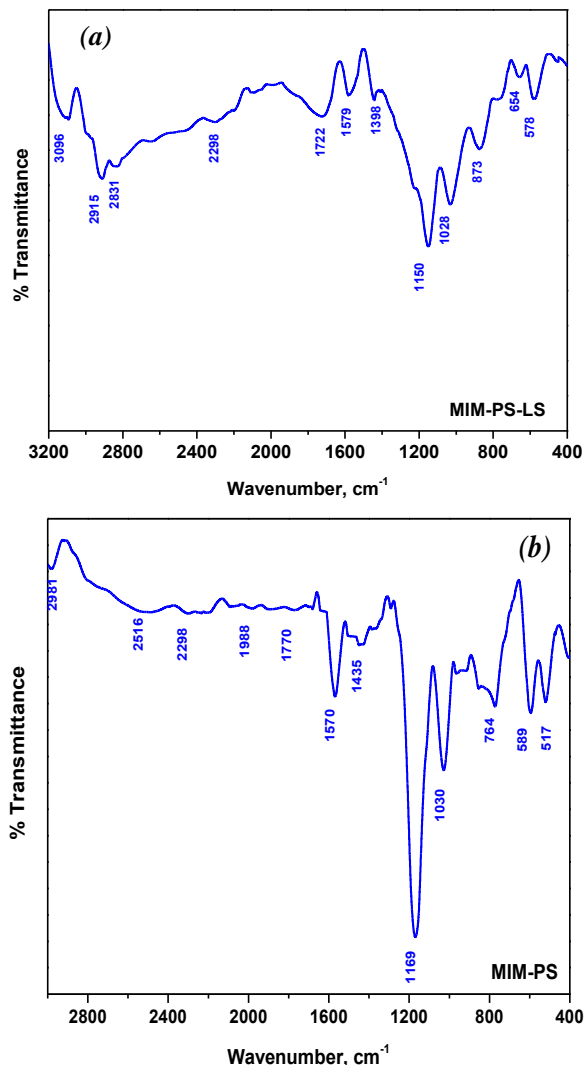


Fig. 1: FT-IR spectra of synthesized ILs (a) MIM-PS-LS (component: G) and (b) MIM-PS (component: D).

The strong absorptions at 1150-1169 cm^{-1} in both the ILs assign to the stretching and bending for S-O bond of sulfonic acid. The N-S stretching vibration also appears at 1028-1013 cm^{-1} . These special IR peaks indicate that the sulfonic group is successfully introduced in the 1-methyl imidazole molecule. On the other hand, the presence of the sulfonic acid group on the nitrogen of 1-methyl imidazole in the ILs liquid increases the number of vibrational modes and brought completely different FT-IR spectra. In addition, C=N and C=C vibrations are observed at 1579 and 1435 cm^{-1} , respectively. The broad and strong bands at 2600-3096 cm^{-1} can be arising from the stretching of the hydroxyl group in the ILs.

¹H NMR and ¹³C NMR studies

¹H and ¹³C NMR spectra of synthesized IL and all reagent used for synthesis of ILs have been presented in following figures. The spectral data confirmed that the synthesized ILs is pure. Component A: Pure 1-Methyl imidazole (**Fig. 2**); Component B: Pure 1,3-Propane sultone (**Fig. 3**); Component C: 1-Methyl-3-Propane Sulfonate imidazolium salt (**Fig. 4**); Component D: 1-Methyl-3-Propane Sulfonic acid imidazolium chloride (**Fig. 5**); Component E: Pure sodium lauryl sulphate (SLS) (**Fig. 6**); Component F: 1-Methyl-3-Propane Sulfonic acid imidazolium lauryl sulphate (**Fig. 7**); Component G: 1-Methyl-3-Propane Sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate (**Fig. 8**).

¹H-NMR (δ_H): (400 MHz; *d*-Acetone; Me₄Si): 3.25 (3H, -CH₃), 6.71 (2H, -CH₂-), 7.23 (1H, -CH-). **¹³C-NMR: δ_C :** 32.5, 122.0, 127.5, 137.5 (**Fig. 2**).

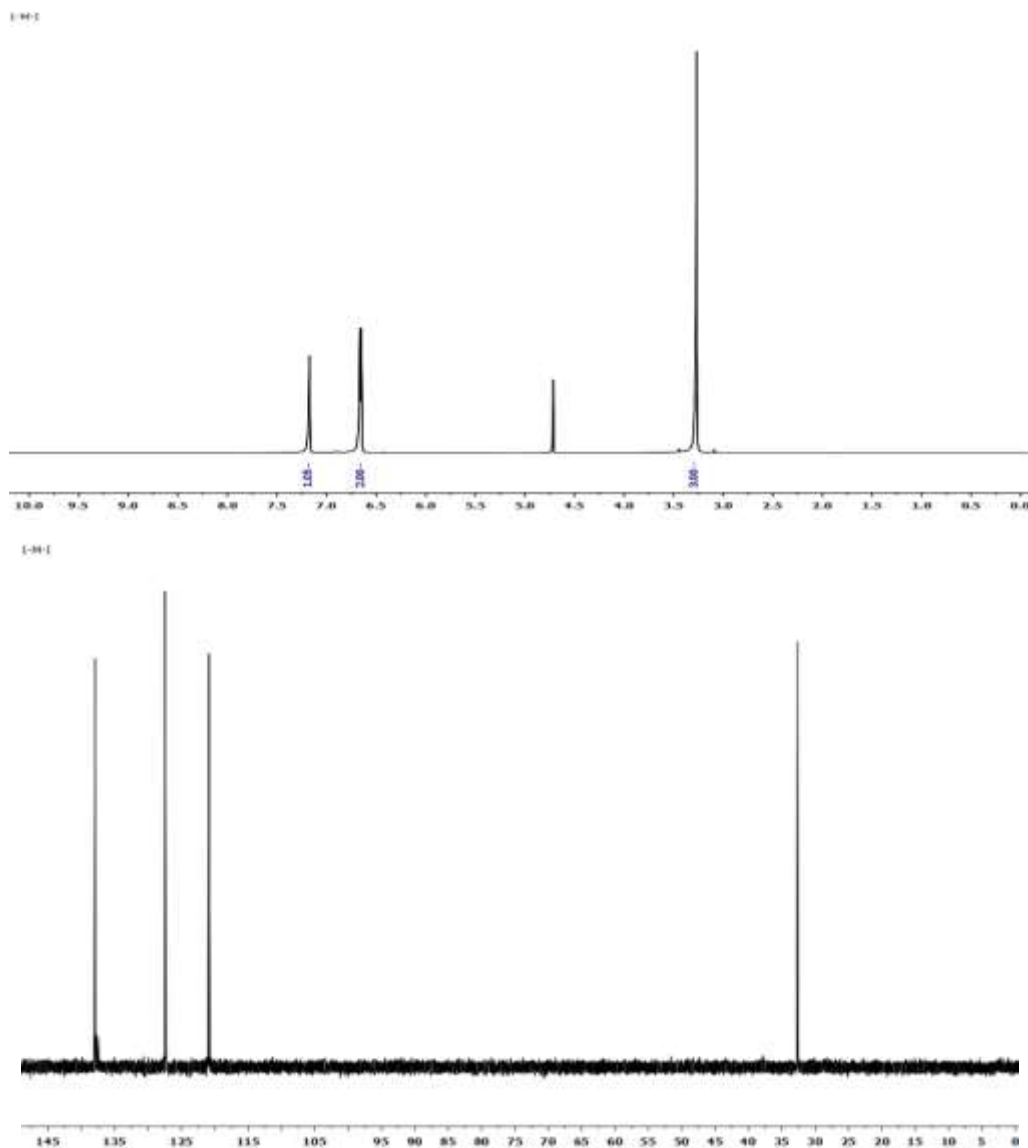


Fig. 2: ¹H and ¹³C spectra of Component [A]: Pure 1-Methyl imidazole

^1H -NMR (δ_{H}): (400 MHz; *d*-Acetone; Me_4Si): 2.5 (2H, $-\text{CH}_2-$), 3.25 (2H, $-\text{CH}_2-$), 4.5 (2H, $-\text{CH}_2-$).
 ^{13}C -NMR: δ_{C} : 27.1, 47.5, 60.0 (**Fig. 3**).

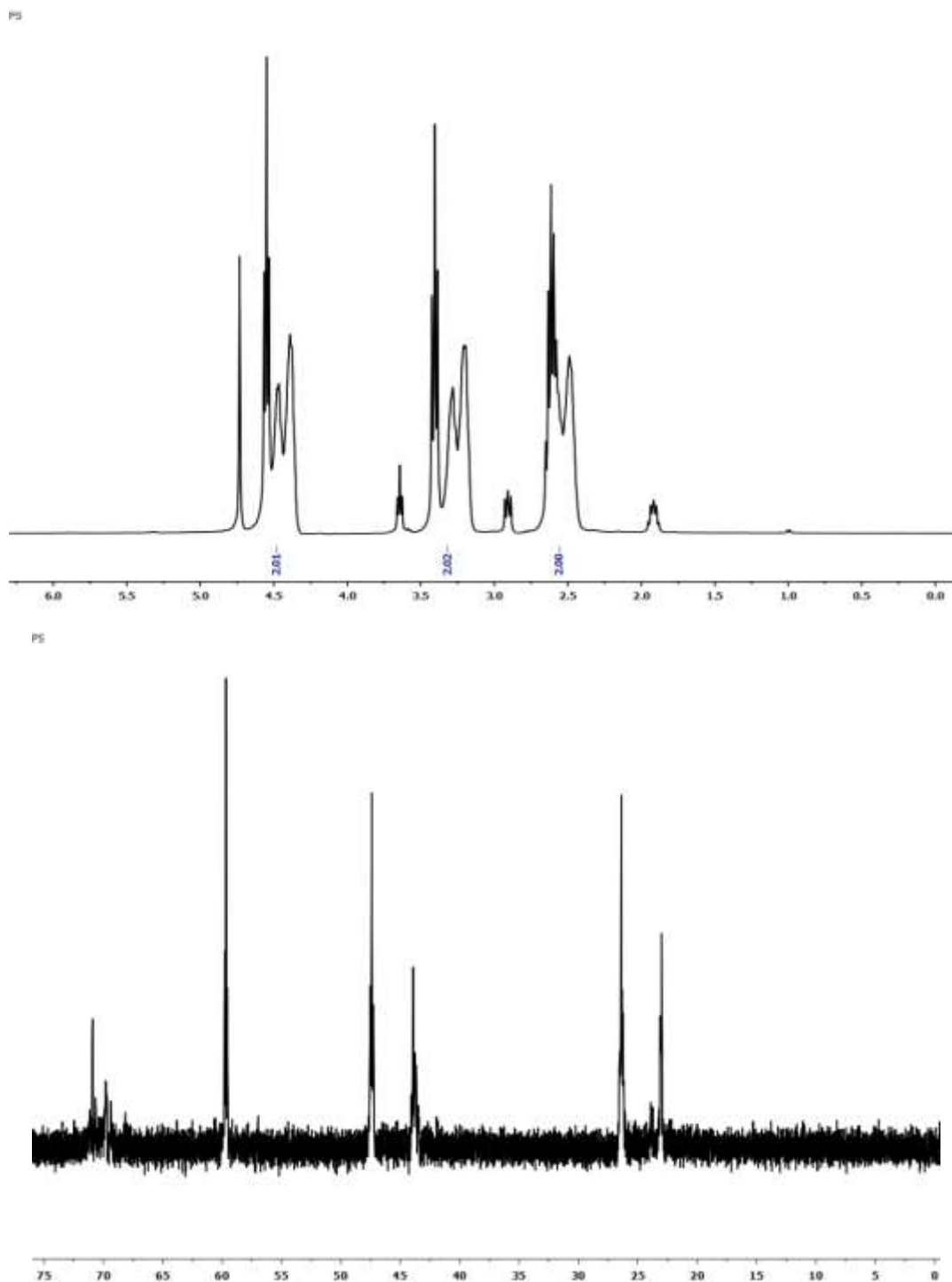


Fig. 3: ^1H and ^{13}C spectra of Component [B]: Pure 1,3-Propane sultone

^1H -NMR (δ_{H}): (400 MHz; *d*-Acetone; Me_4Si): 2.25 (2H, $-\text{CH}_2-$), 2.8 (2H, $-\text{CH}_2-$), 3.9 (3H, $-\text{CH}_3$), 4.4 (2H, $-\text{CH}_2-$), 7.5 (2H, $(-\text{CH}-)_2$), 8.75 (1H, $-\text{CH}-$). **^{13}C -NMR:** δ_{C} : 25.1, 35.0, 47.5, 122.5, 124.0, 137.5 (Fig. 4).

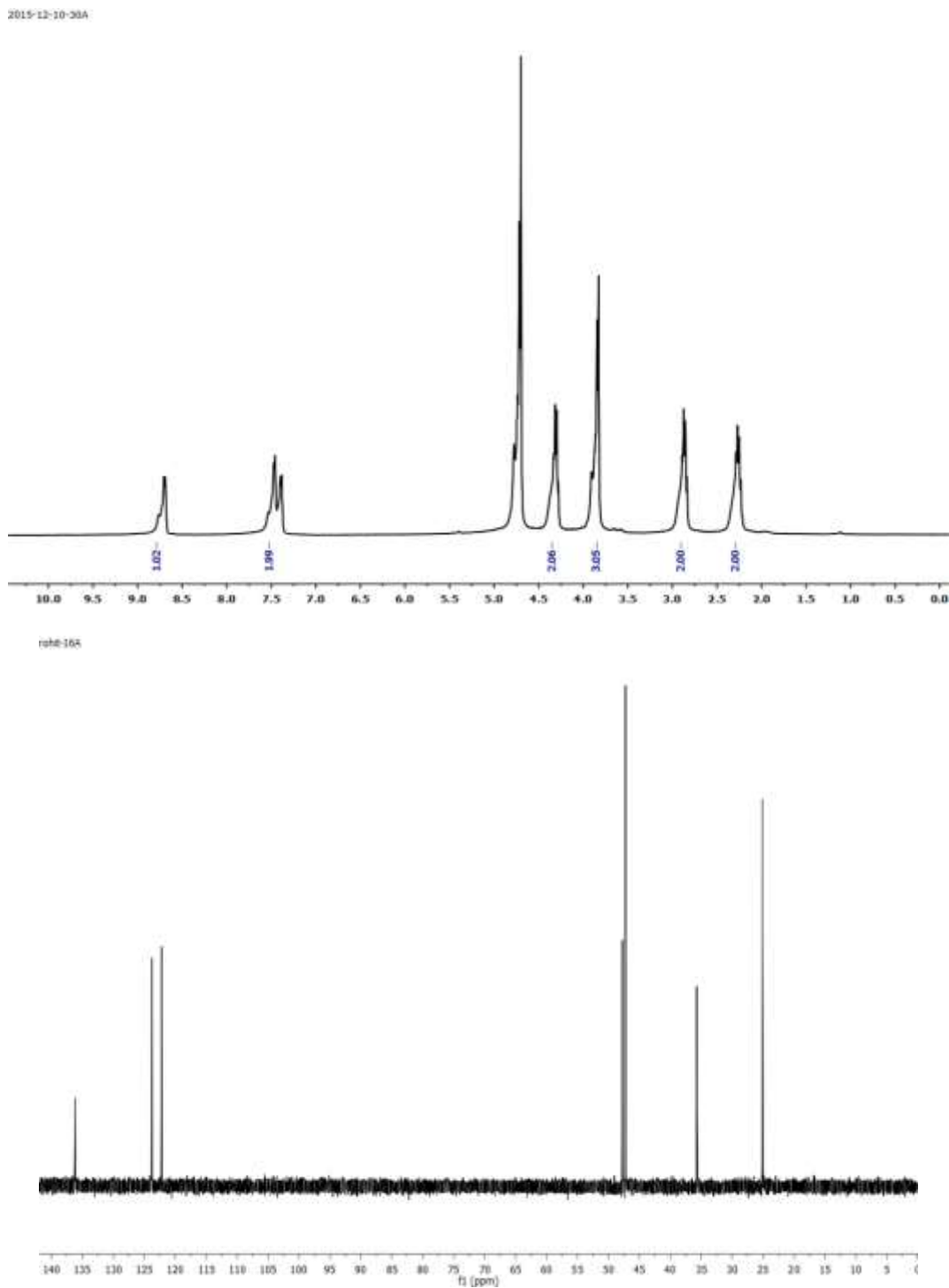


Fig. 4: ^1H and ^{13}C spectra of Component [C]: 1-Methyl-3-Propane Sulfonate imidazolium salt

^1H -NMR (δ_{H}): (400 MHz; *d*-Acetone; Me_4Si): 2.25 (2H, $-\text{CH}_2-$), 2.4 (1H, $-\text{SO}_3\text{H}$), 2.5 (2H, $-\text{CH}_2-$), 3.9 (3H, $-\text{CH}_3$), 4.4 (2H, $-\text{CH}_2-$), 7.75 (2H, $(-\text{CH}-)_2$), 9.25 (1H, $-\text{CH}-$). **^{13}C -NMR:** δ_{C} : 25.1, 35.0, 47.5, 122.0, 124.5, 136.8 (**Fig. 5**).

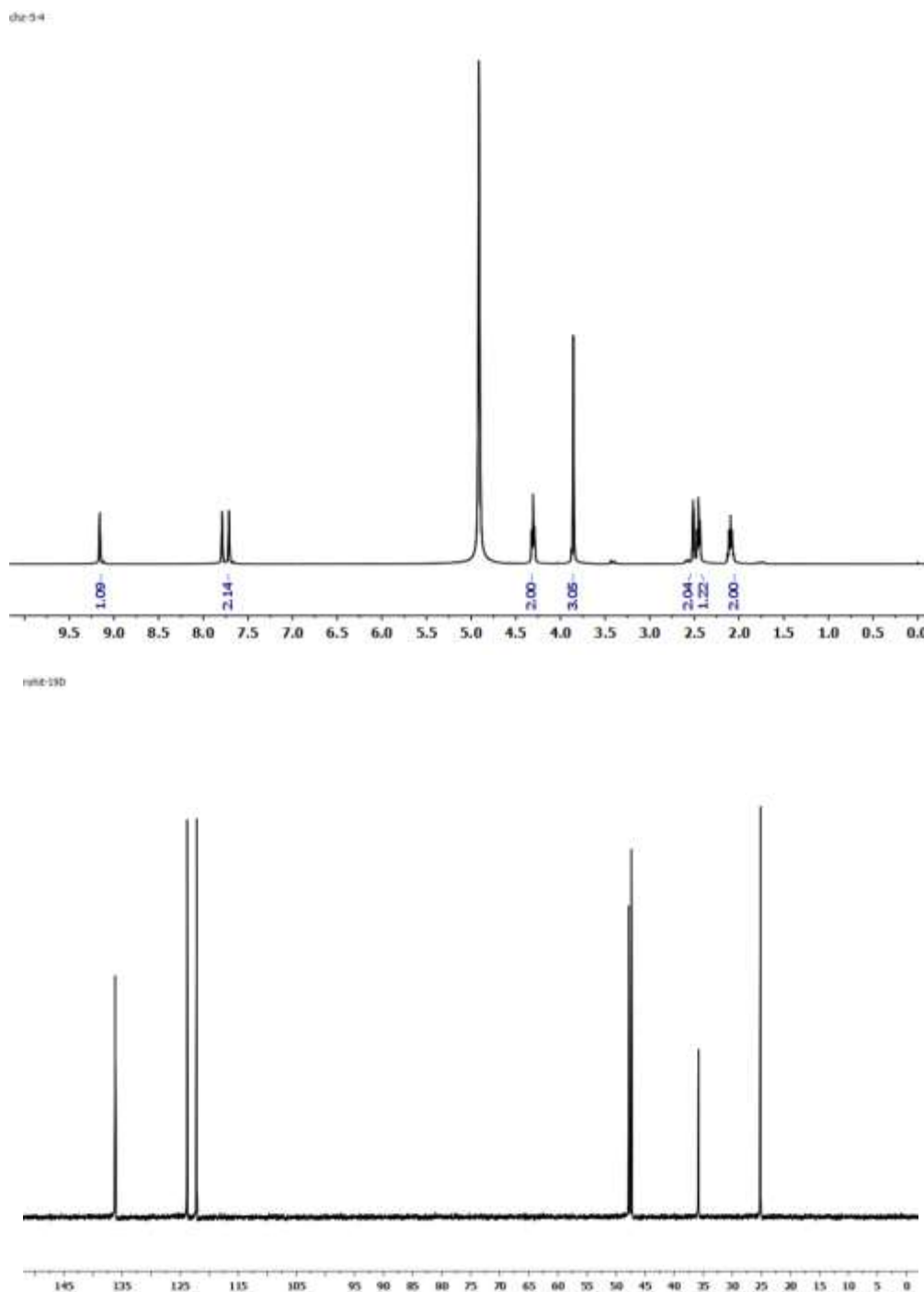


Fig. 5: ^1H and ^{13}C spectra of Component [D]: 1-Methyl-3-Propane Sulfonic acid imidazolium chloride

^1H -NMR (δ_{H}): (400 MHz; *d*-Acetone; Me_4Si): 0.85 (3H, $-\text{CH}_3$), 1.25 (18H, $-\text{CH}_2-$), 1.7 (2H, $-\text{CH}_2-$), 4.0 (2H, $-\text{CH}_2-$). **^{13}C -NMR:** δ_{C} : 13.1, 22.5, 26.2, 30.0, 32.5, 70.0 (**Fig. 6**).

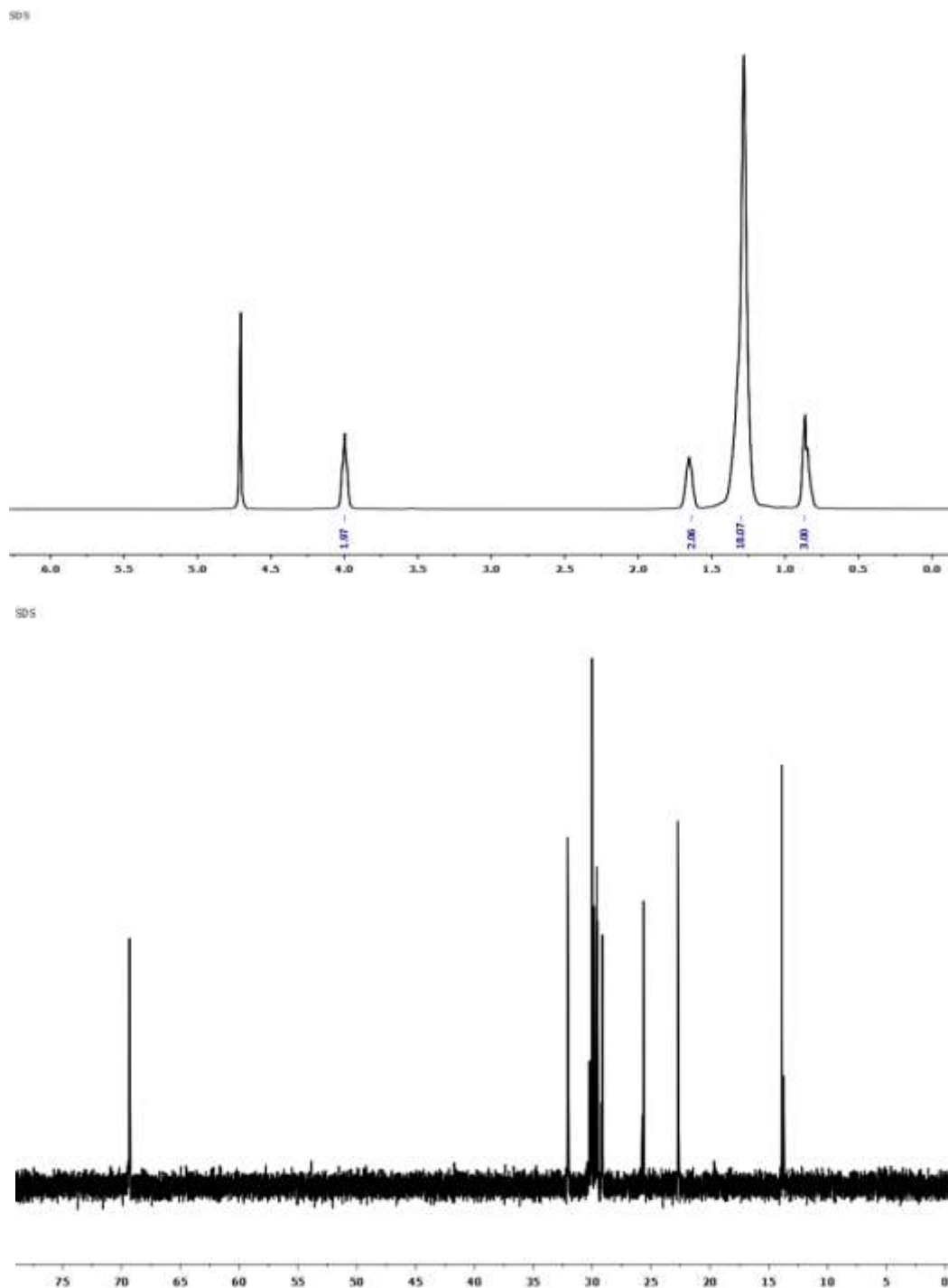


Fig. 6: ^1H and ^{13}C spectra of Component [E]: Pure sodium lauryl sulphate (SLS).

^1H -NMR (δ_H): (400 MHz; *d*-Acetone; Me_4Si): 0.85 (3H, $-\text{CH}_3$), 1.25 (18H, $-\text{CH}_2-$), 1.4 (2H, $-\text{CH}_2-$), 2.1 (1H, $-\text{CH}-$), 2.5 (2H, $-\text{CH}_2-$), 3.4 (2H, $-\text{CH}_2-$), 3.8 (3H, $-\text{CH}_3-$), 4.4 (4H, $-\text{CH}_2-$), 7.75 (2H, $-\text{CH}_2-$), 9.2 (1H, $-\text{CH}-$). **^{13}C -NMR: δ_C :** 13.1, 22.5, 26.2, 30.0, 32.5, 33.5, 36.0, 40.0, 47.5, 61.0, 122.0, 124.0, 137.5 (Fig. 7).

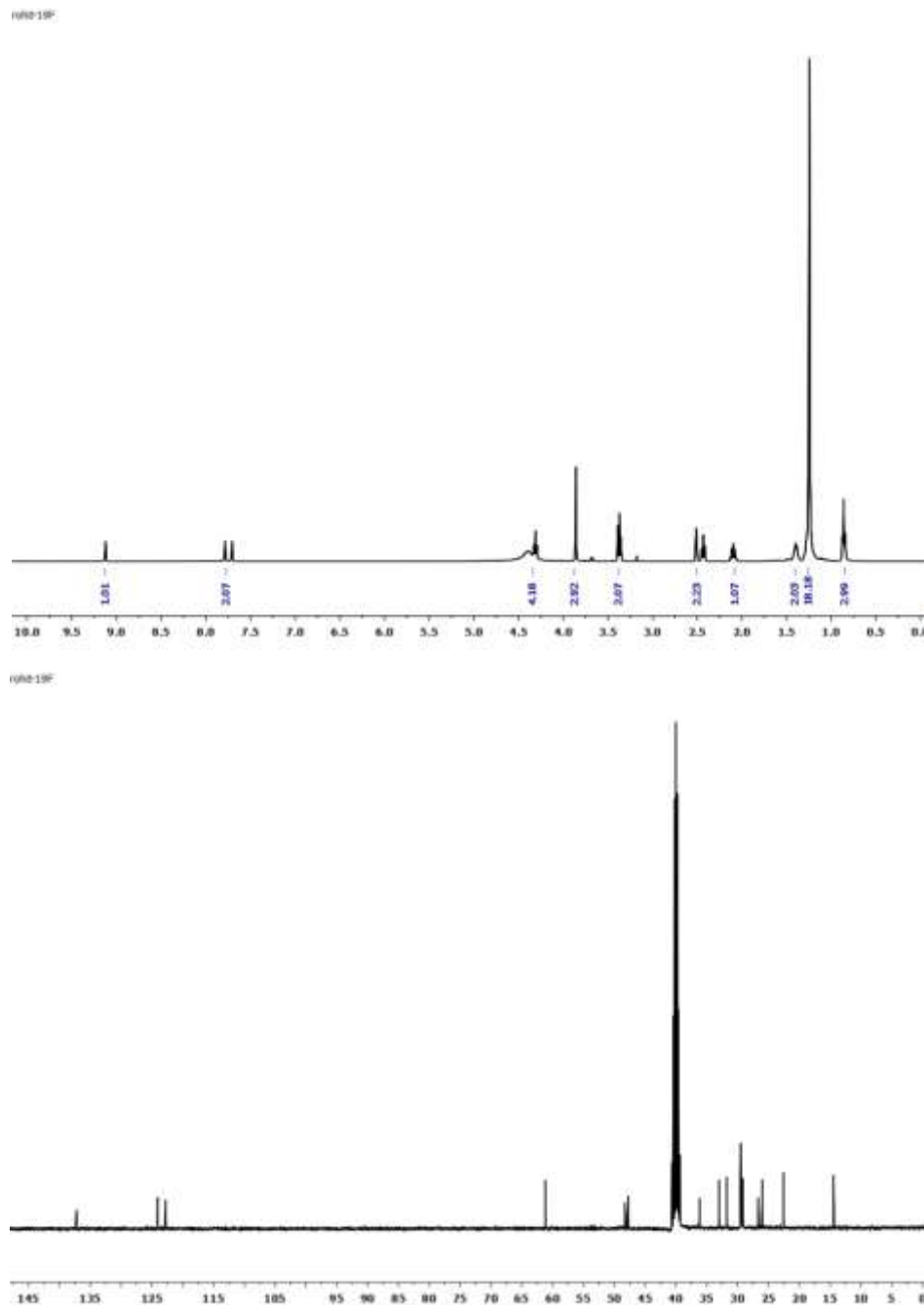


Fig. 7: ^1H and ^{13}C spectra of Component [F]: 1-Methyl-3-Propane Sulfonic acid imidazolium lauryl sulphate

¹H-NMR (δ_H): (400 MHz; *d*-Acetone; Me₄Si): 0.80 (3H, -CH₃), 1.20 (20H, -CH₂-), 2.1 (2H, -CH₂-), 2.5 (2H, -CH₂-), 3.7 (2H, -CH₂-), 3.8 (3H, -CH₃-), 4.3 (4H, -CH₂-), 7.75 (2H, -CH₂-), 9.2 (1H, -CH-). **¹³C-NMR**: δ_C : 14.1, 22.5, 26.3, 29.8, 32.0, 33.2, 36.5, 39.8, 47.4, 61.3, 122.5, 124.5, 137.3 (**Fig. 8**).

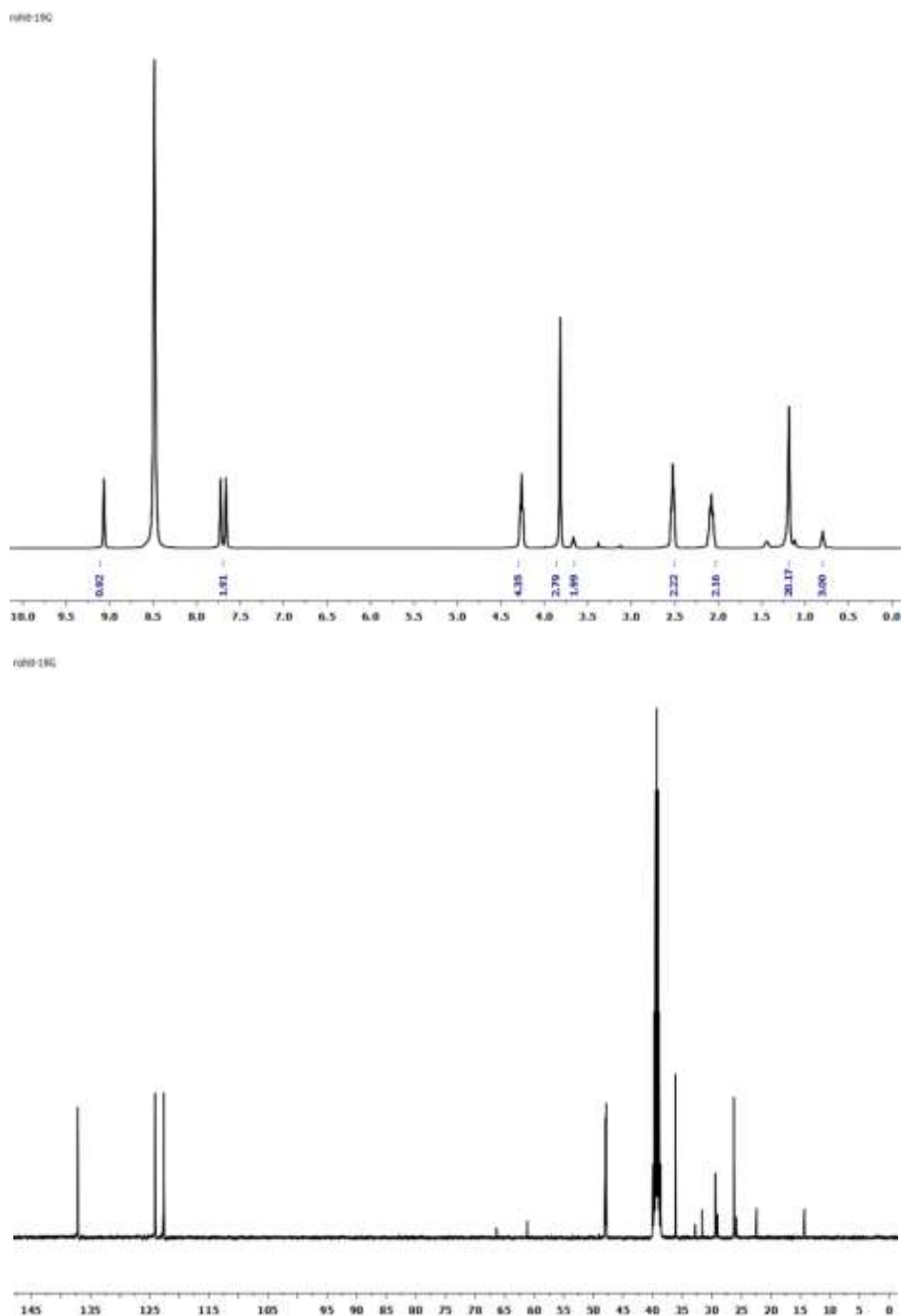


Fig. 8: ¹H and ¹³C spectra of Component [G]: 1-Methyl-3-Propane Sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate

MS studies

The important peaks of MS spectrum of the synthesized ILs relate to $241 (M^+ + 1)$, $240 (M^+)$, $204 (M^+ + 1)$, $204 (M^+)$, $364 (M^+ + 1)$, $363 (M^+)$ (**Fig. 9**).

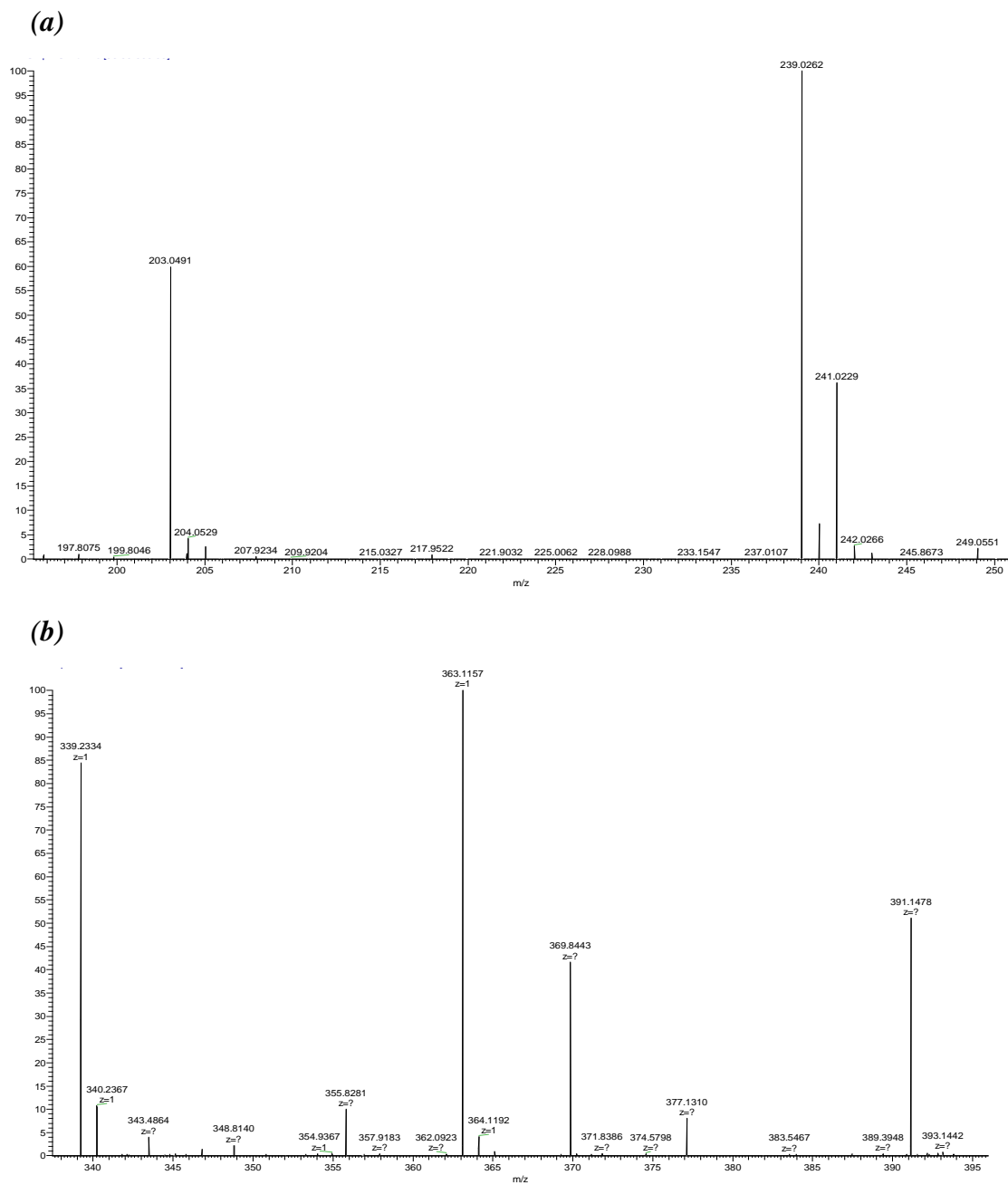


Fig. 9: Mass spectra of synthesized ILs (a) MIM-PS (component: D) and (b) MIM-PS-LS (component: G).

Determination of H_0 values of Brönsted acidic ILs: The measurement of the acidic scale of these Brönsted acidic ILs was conducted on an Agilent B453 UV-vis. spectrophotometer with a basic indicator according to the literature reported previously.^{27,28} With the increase of acidic scale of the acidic ILs, the absorbance of the unprotonated form of the basic indicator decreased, whereas the protonated form of the indicator could not be observed because of its small molar absorptivity and its location, so the $[I]/[IH^+]$ (I represents indicator) ratio could be determined from the measured absorbance differences after addition of Brönsted acidic ILs, and then the Hammett function, H_0 , was calculated by using Eq. (1). This value could be regarded as the relative acidity of the ILs;

$$H_0 = pK(I)_{aq} + \log \left(\frac{[I]}{[IH^+]} \right) \quad (1)$$

Under the same concentration of 4-nitroaniline (10 mg/L, $pK(I)_{aq} = 0.99$) and ILs (25 mmol/L) in dichloromethane, we determined the H_0 values of the Brönsted acidic ILs.

The maximal absorbance of the unprotonated form of the indicator was observed at 378 nm in water. When an acidic IL was added, the absorbance of the unprotonated form of the indicator decreased. As shown in **Fig. 10** the absorbance of the unprotonated form of the indicator on two acidic ILs decreased as follows: $[MIM-PS-LS]HSO_4 > [MIM-PS]Cl$. Ultimately, we obtained the acidity order of the two ILs with the following H_0 values (**Table 1**): $[MIM-PS-LS]HSO_4$ (0.93) $>$ $[MIM-PS]Cl$ (0.78), suggesting that the Brönsted acidity of $[MIM-PS-LS]HSO_4$ was relatively stronger than the $[MIM-PS]Cl$.

Table 1: Calculation and comparison of H_0 values of BAILs in water at 30 °C by using 4-nitroaniline indicator.

Entry	ILs	A_{max}	$[I]$ (%)	$[IH^+]$ (%)	H_0
1	No IL	1.708	100.0	0	-
2	$[MIM-PS]Cl$	0.654	38.3	61.7	0.78
3	$[MIM-PS-LS]HSO_4$	0.796	46.6	53.4	0.93

The acidity of the ILs depended both on the characteristics of the cations and anions. When the cations of the ILs were the same, the dependence of the acidity of the IL on anion was significant.

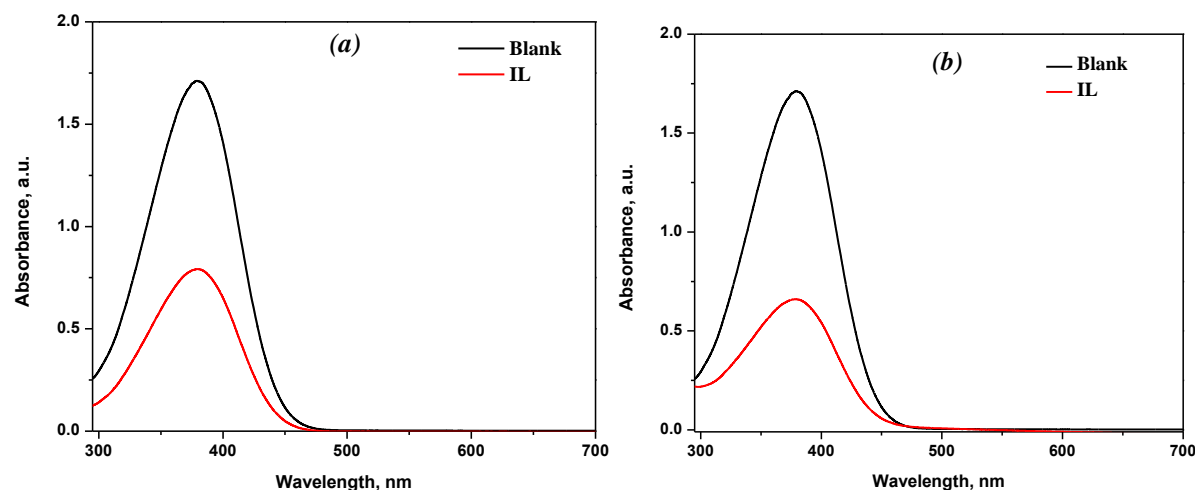


Fig. 10: Absorbance spectra of 4-nitroaniline after addition of BAILs in water, (a) [MIM-PS-LS]HSO₄ and (b) [MIM-PS]Cl.

pH measurements of Brönsted acidic ILs

The pH values of ILs in methanol were also detected; the data were listed in **Table 2**. As it is shown in **Fig. 11**, the IL MIM-PS-LS exhibited stronger acidity than MIM-PS in methanol.

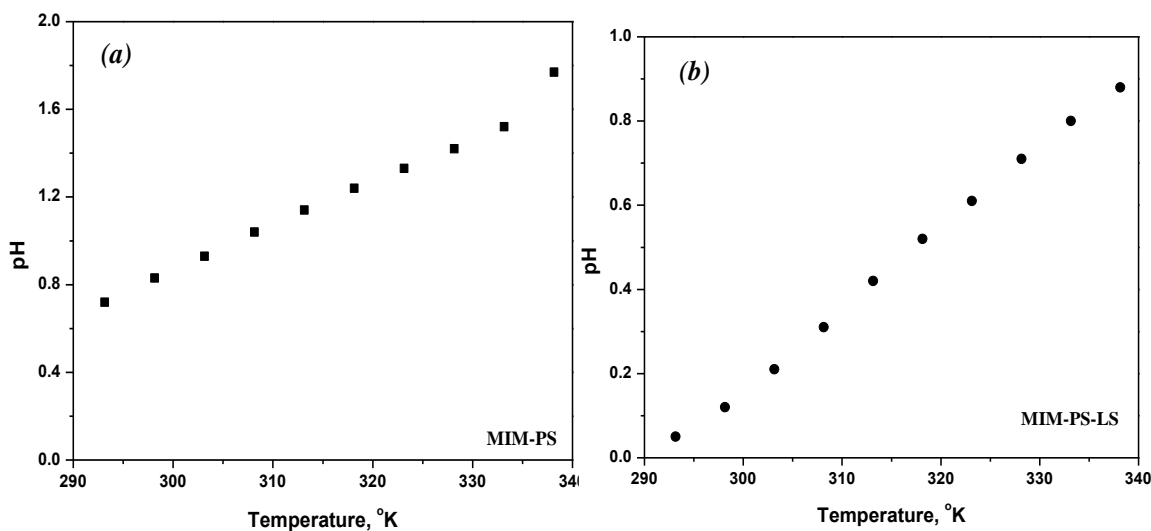


Fig. 11: Temperature dependent pH values of synthesized IL in methanol (a) MIM-PS and (b) MIM-PS-LS at the concentration of IL are 5 mmol/Lit.

The reason of this phenomenon is MIM-PS-LS has present hydrogen sulphate (HSO₄⁻) anion, while in MIM-PS chloride (Cl⁻) anion present, which also confirmed from Hammett acidity value.

Table 2: The pH values of MIM-PS and MIM-PS-LS in methanol at the concentration of 5 mmol/Lit.

Temperature (°C)	Temperature (°K)	pH (MeOH) MIM-PS	pH (MeOH) MIM-PS-LS
20	293.15	0.72	0.05
25	298.15	0.83	0.12
30	303.15	0.93	0.21
35	308.15	1.04	0.31
40	313.15	1.14	0.42
45	318.15	1.24	0.52
50	323.15	1.33	0.61
55	328.15	1.42	0.71
60	333.15	1.52	0.80
65	338.15	1.77	0.88

CONCLUSIONS

In conclusion, we have successfully synthesized a 1-Methyl-3-propane sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate (MIM-PS-LS) and 1-Methyl-3-propane sulfonic acid imidazolium chloride ILs. These ILs have been carefully characterized with ^1H -NMR, ^{13}C -NMR, FT-IR and mass analysis. The Hammett acidity of ILs $[\text{MIM-PS-LS}]\text{HSO}_4$ (0.93) > $[\text{MIM-PS}]\text{Cl}$ (0.78), suggesting that the Brönsted acidity of $[\text{MIM-PS-LS}]\text{HSO}_4$ was relatively stronger than the $[\text{MIM-PS}]\text{Cl}$. The results indicated that the synthesis procedure is valid and gives highly pure products. 1-Methyl-3-propane sulfonic acid imidazolium lauryl sulfonic acid hydrogen sulphate (MIM-PS-LS) IL contains the lauryl sulphate anion, which is ordinary surfactant; this IL might be find application in catalysis, organic synthesis, electrochemistry, chemical separation, solid support, metal extraction and also biological sides.

ACKNOWLEDGEMENT

Author thankful Ton Duc Thang University (TDTU-DEMASTED) for financial support.

CONFLICT OF INTEREST

Author declares there is no conflict of interest.

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