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Development of New Halogen-Free Hydrophobic Task-Specific Ionic Liquid

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Abstract: A new imidazolium based halogen free task-specific ionic liquid (TSIL) 1-decyl-3-methyl imidazolium dodecyl sulphate (C_{10}MimDs), was synthesized. The superior purity and structure of this IL was confirmed with ^{1}H-NMR, ^{13}C-NMR, FT-IR, UV, and mass indicating the helpfulness of this synthetic approach. The thermal stability was investigated using TGA and DTA spectra. The developed IL is new fluoride free hydrophobic TSIL which is economical and environmentally benign process and could be a good substitute of costly, toxic $PF6^{-}$, $BF4^{-}$ etc. anions based ILs. The results indicated that the synthesis procedure is valid and gives highly pure products.

Keywords: Halogen free task-specific ionic liquid, NMR, FT-IR, Mass, TGA.

INTRODUCTION

Recently, ionic liquids (ILs) appeared in the literature as a new class of solvents. ILs have gained wide popularity during the last decade because of their unique properties and this properties profiles originating from a complex interplay of Coulombic, hydrogen bonding, and van-der-Waals interactions of their ions.[1] The combination with the large number of anions that have proven to result in low melting salts yields an

enormous structural variability of ILs. Despite this great variability and the resulting diversity in some physicochemical properties, such as e.g. solubility, miscibility, melting point, viscosity, it is also important to state that their ionic nature also brings along some general limitations of ILs: for example, it will be hard to design and develop a highly volatile, non-conductive or absolutely non-polar IL. The details information on ranges of physicochemical and specific properties of ILs can be found in literature [2, 3]. The different characteristics allow for selecting the right IL for a given application.

While ILs with ‘‘cheap’’ anions, such as e.g. toluenesulfonates [4] octylsulfates [5] dodecyl/lauryl sulfate[6] and hydrogensulfates [6, 7] are used, for example, in potential bulk applications (e.g. in synthesis, catalysis, separation technologies, lubrication, formulation, antistatics, materials technologies, biomass applications), ILs with ‘‘expensive’’ functionalized [8] fluorinated [9] deuterated [10] or even chiral ions [11] are interesting for small scale applications with very high added value (e.g. in analytical applications, sensors, electrolytes, coatings). Selecting the most suitable cation/anion combination for a given application has become much easier over the recent ten years, with a much greater set of experimental data being published [12, 13]. More and more, ILs are used as solvent substitutes and as innovative liquid materials in academic and industrial research laboratories.

They have been applied in a broad variety of synthetic [14, 15], catalytic [16, 17], engineering [18, 19] and electrochemical applications [20-26]. Other reported applications deal with the role of ILs as active materials in sensors [27, 28] and analytical devices [29] or as performance additives for paints [30]. In particular, their extremely low vapor pressure at ambient conditions makes ILs extremely interesting for many technical purposes. Given the wide variety of different IL materials, the selection of the right cation/anion combination is a key factor for success for all different applications. In recent years some of the traditionally used "working horses", namely tetrafluoroborates and hexafluorophosphates, have been found to be of restricted suitability in practical and industrial use due to their sensitivity vs. hydrolysis forming highly toxic and corrosive HF [31]. Due to this reason bis (trifluoromethylsulfonyl) imide ($[Tf_2N]^-$) is mostly used today if a hydrophobic and hydrolysis stable IL is required [32, 33]. However, the relatively high price of this anion and related fluorinated anions will limit the use of these systems in large scale applications. Also the presence of fluorine may still be problematic for an environmental friendly disposal. Given this importance of the anion's chemical nature on the practical applicability of an IL, we focused on the development of new synthetic approaches towards modified anions in IL material development. The proposed synthetic approach to halogen-free task specific ILs comprises two steps. In the first step, imidazolium cation reacts with decyl alkyl chain to generate mim^+ cation halide anion and in the second step this materials reacts with dodecyl sulphate by metathesis reaction and remove halogen. In view of the emerging importance of benign and environmental friendly IL, the present work demonstrated the synthesis of halogen free TSIL based on 1-decyl-3-methyl imidazolium ($C_{10}Mim^+$) cation with dodecyl sulphate (DS^-) as the anion. The main advantage with Sodium Dodecyl Sulphate (SDS) over other alkyl sulphate which is made from synthetic alcohol, SDS is a naturally derived surfactant made from the whole natural coconut. This IL was characterized by spectroscopic methods like ^1H & ^{13}C-NMR, FT-IR, UV-vis., MS etc.

MATERIAL AND METHODS

Reagent grade 1-methyl imidazole, 1-decyl chloride, sodium dodecyl sulphate, ethyl acetate were purchased from Sigma-Aldrich and used without further purification. Acetone, ethanol, methanol were purchased from Himedia. ^1H-NMR and ^{13}C-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 – 4000 cm^{-1}. UV-vis. spectra were recorded on a UV-160A spectrophotometer (Shimadzu Corporation, Japan) in water and methanol.

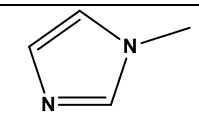
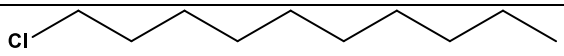
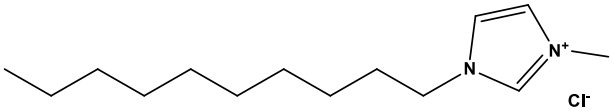
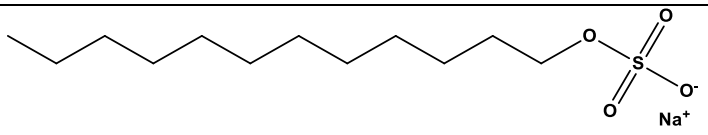
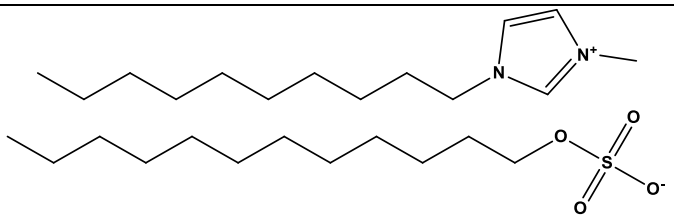
The TGA data were obtained at a heating rate of 5 ºC/min on a TGA-DTA instrument (TA instruments model 5000/2960 thermogravimetric analyser, USA).

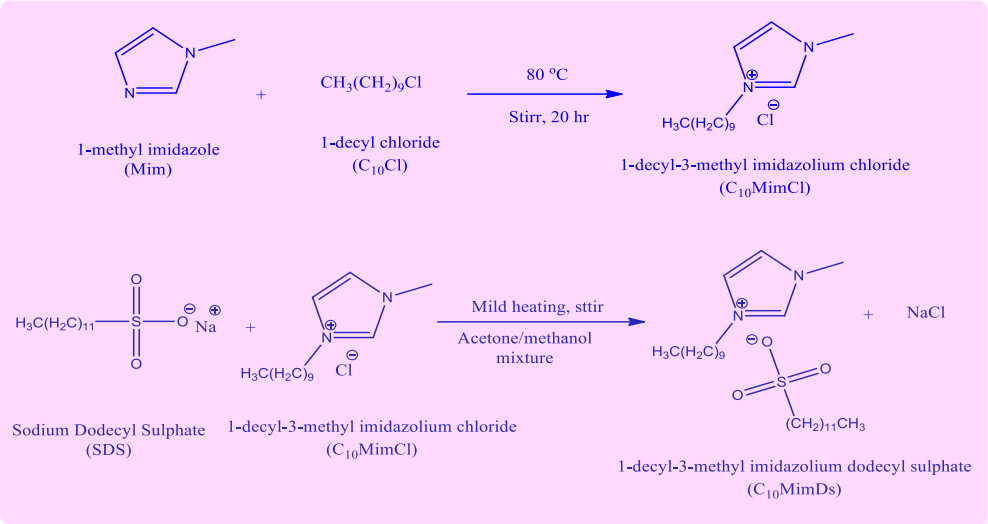
SYNTHETIC PROCEDURES

Synthesis of 1-decyl-3-methyl imidazolium dodecyl sulphate (C_{10}MimDs): In order to get desired IL, first 1-methyl imidazole was used as a starting material and reacted with 1-decyl chloride. Sodium dodecyl sulphate was then added to replace the chloride ions with dodecyl sulphate anions forming the desired IL **(Scheme 1)**.

The chemical structures, abbreviation, molecular weight of synthesized ILs and reagent used for synthesis are given in **Table-1**.

Table-1: Chemical structure, abbreviation and molecular weight of synthesized TSILs.

Entry	Reagents/ILs	Abbreviation	Mol. Wt. ($gm.mol^{-1}$)
1	 1-methyl imidazole	Mim	82.05
2	 1-decyl chloride	C_{10}Cl	176.13
3	 1-decyl-3-methyl imidazolium chloride	C_{10}MimCl	258.19
4	 sodium dodecyl sulphate	SDS	288.14
5	 1-decyl-3-methyl imidazolium dodecyl sulphate	C_{10}MimDs	488.36



Scheme 1: Reaction scheme for synthesis and modification of TSIL.

In the first step, 10.0 g (0.12 mol) of 1-methyl imidazole and 21.45 g (0.12 mol) of 1-decyl chloride was placed in two necked round bottom flask and stirred thoroughly while heating at 80 °C for 20 hrs under N_2 atmosphere. The resulting viscous liquid was cooled to room temperature washed several times with small portion (20 ml × 3) of ethyl acetate to remove unreacted starting material and dried under vacuum for 5-7 hrs. In second step, 1-decyl-3-methyl imidazolium dodecyl sulphate (C_{10}MinDs) IL was synthesized from the metathesis reaction between Sodium Dodecyl Sulphate (SDS) and 1-decyl-3-methyl imidazolium chloride (C_{10}MimCl) in acetone/methanol mixture under mild heating.

The IL-acetone/methanol mixture was filtered to remove sodium chloride (NaCl) and the filtrate was vacuum dried at 75 ± 0.1 °C. The resultant products are semi solid light yellow to brown waxy type material **(Figure 1)** which have partial solubility in water (~ 0.01 – 0.05% w/v). The solubility of synthesized ILs in various organic solvents is listed in **Table-2**.

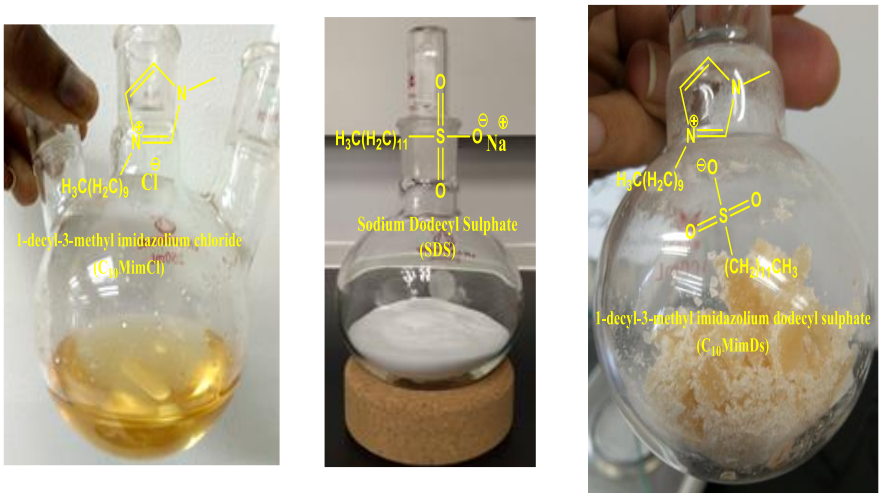


Figure 1: Physical appearances of synthesized TSILs (C_{10}MimCl, SDS, and C10MimDs).

RESULTS AND DISCUSSION

Characterization of IL: The synthesis of 1-decyl-3-methyl imidazolium IL with chloride ions and the modified (desired) IL with dodecyl sulphate anion follows the general reaction scheme presented in **Scheme 1.** The modified imidazolium based halogen-free IL is solid material having high purity and good yields. The purity of the products was identified based on several techniques.

Table-2: Solubility of synthesized ILs in various solvents.

Solvent	C_{10}MimCl	C_{10}MimDs
Water	√	⊄
Methanol	√	√
Ethanol	√	√
Acetonitrile	√	√
Acetone	√	√
Toluene	√	√
THF	×	×
Chloroform	√	√
DMF	√	√
Hexane	×	×

√ soluble × Insoluble, ⊄ Partially soluble

^{1}H NMR and ^{13}C NMR studies: The results of ^{1}H-NMR, ^{13}C-NMR spectra indicated the high purity of 1-decyl-3-methyl imidazolium chloride (C_{10}MimCl) and 1-decyl-3-methyl imidazolium dodecyl sulphate (C_{10}MimDs) ILs without unexpected signals from unreacted starting materials is shown in **(Figure 2** and **Figure 3)**. The spectral data confirmed that the synthesized ILs is pure.

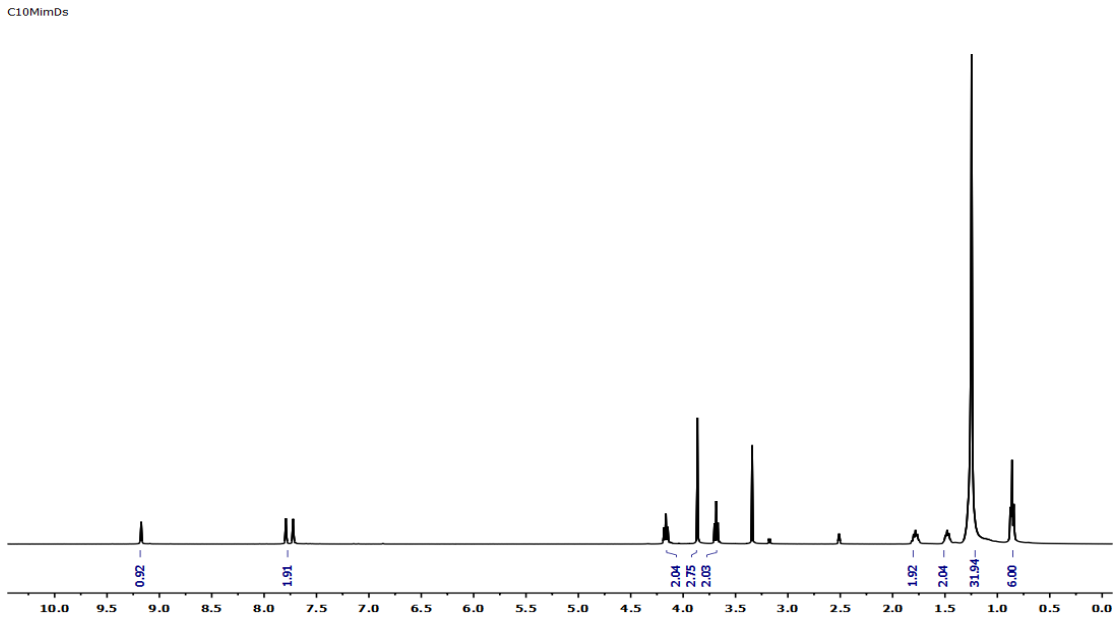


Figure 2: ^{1}H-NMR spectra of C_{10}MimDs.

[1]H-NMR (400 MHz, *d*-Acetone, TMS): δH 9.25 (1H, -CH-), 7.75 (2H, -CH-), 4.22 (2H, -CH_2-), 3.92 (2H, N-CH_2-), 3.75 (2H, -OCH_2-), 1.75 (2H, -CH_2-), 1.50 (2H, -CH_2-), 1.25 (32H, (-CH_2-)$_{16}$), and 0.82 (6H, (-CH_3)$_2$).

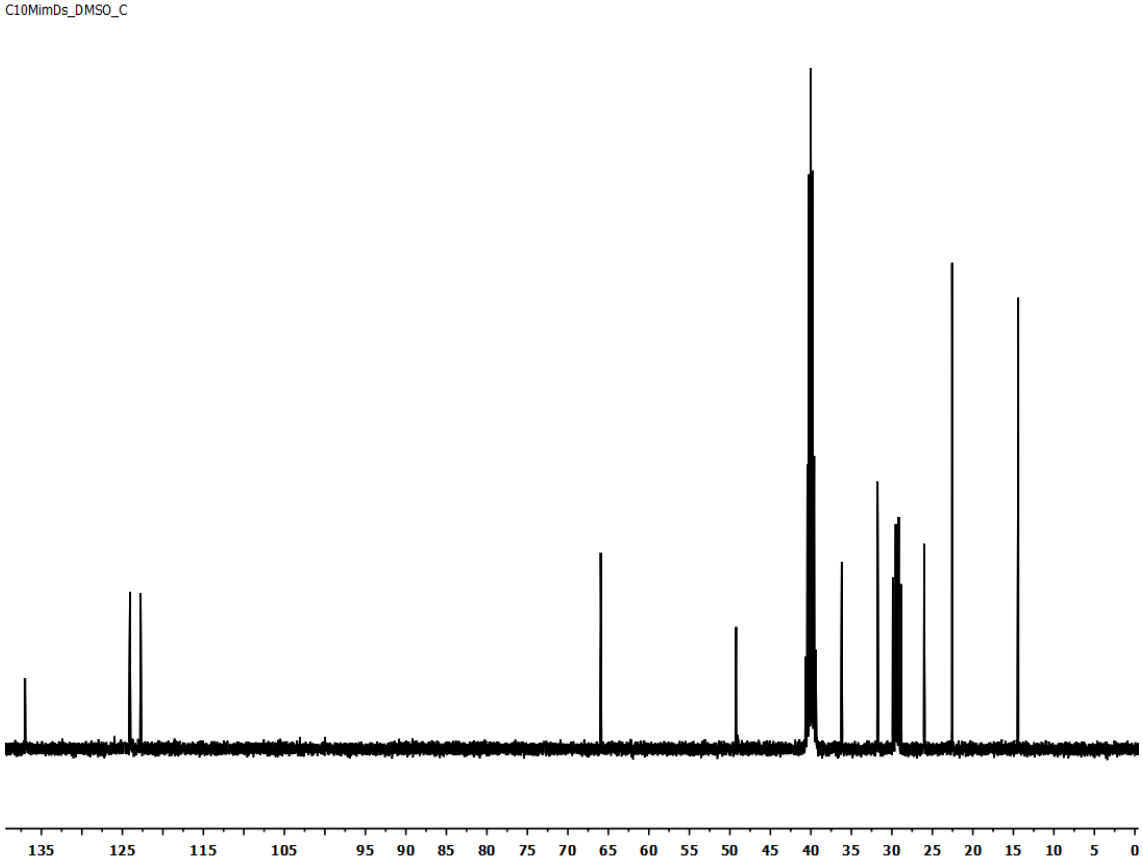


Figure 3: ^{13}C-NMR spectra of C_{10}MimDs.

[13]C-NMR: δC: 14.5, 22.5, 26.0, 29.5, 31.5, 37.0, 40.0, 49.1, 66.5, 122.5, 124.0, 137.5.

FT-IR studies: Careful examination of the FT-IR results **(Figure 4)** showed all functional groups expected for ILs. FT-IR (KBr, cm^{-1}) υ_{max}:

C_{10}MimCl: 3450, 3147, 3071, 2927, 2873, 2082, 1642, 1573, 1466, 1370, 1177, 1042, 851, 750. **C_{10}MimDs:** 3450, 3146, 2927, 2857, 2284, 1648, 1573, 1466, 1236, 1042, 851, 790, 630.

The corresponding FT-IR spectral data of ILs are presented in **Figure 4**. The strong absorptions at 1236 cm^{-1} in C_{10}MimDs IL assign to the stretching and bending for S–O bond of sulphate, which is absent in C_{10}MimCl. In addition, C=N and C=C vibrations are observed at 1573 and 1466 cm^{-1}, respectively for both of C_{10}MimCl and C_{10}MimDs. The band at 1236 cm^{-1} appear in C_{10}MimDs is due to R-SO_3^- which confirmed the synthesis of C_{10}MimDs. The broad and strong bands at 2800–3500 cm^{-1} can be arising from the stretching of the hydroxyl group in the IL as well as some moisture present in IL.

The bands at 630-851 cm^{-1} in both C_{10}MimCl and C_{10}MimDs are due to C-H bending of aromatic substitution of three adjacent hydrogen atoms.

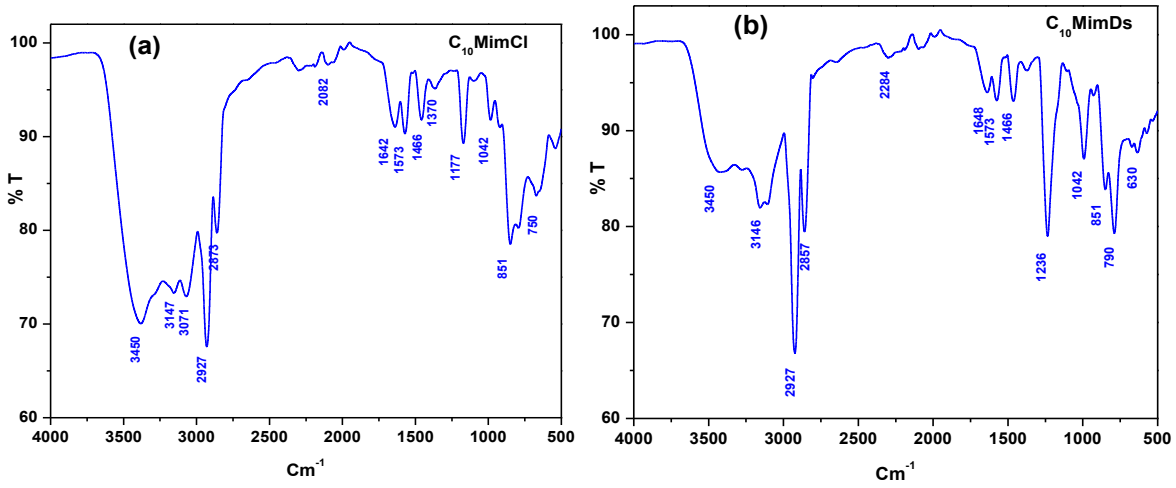


Figure 4: FT-IR spectra of synthesized ILs (a) C_{10}MimCl and (b) C_{10}MimDs.

UV-vis. Spectra: In the quest of understanding the optical properties of the ILs, the absorbance behaviour of the ILs with chloride and sulphate forms were examined. UV-vis. spectra were another evidence to confirm that IL was really synthesized. For this purpose, UV-visible absorption spectra of 0.001M C_{10}MimCl, C_{10}MimDs and SDS in water were measured and shown in **Figure 5**. A strong absorption in deep UV region (230-380 nm) with decreasing trend towards the visible part was observed for both ILs. The absorption tail is considerably long and extends beyond 380 nm. Since both ILs have almost identical absorption profile, the absorption centre should be the imidazolium cation [34]. The maximum absorptions of C_{10}MimCl (254 nm), SDS (260 nm) and C_{10}MimDs (256 nm) appeared at 2.14, 1.96 and 0.051 in methanol respectively, while C_{10}MimCl (254 nm), SDS (256 nm) and C_{10}MimDs (255 nm) appeared at 1.94, 1.84 and 0.25 in water respectively. The difference between maximum absorptions of C_{10}MimCl and C_{10}MimDs confirmed the production of the IL.

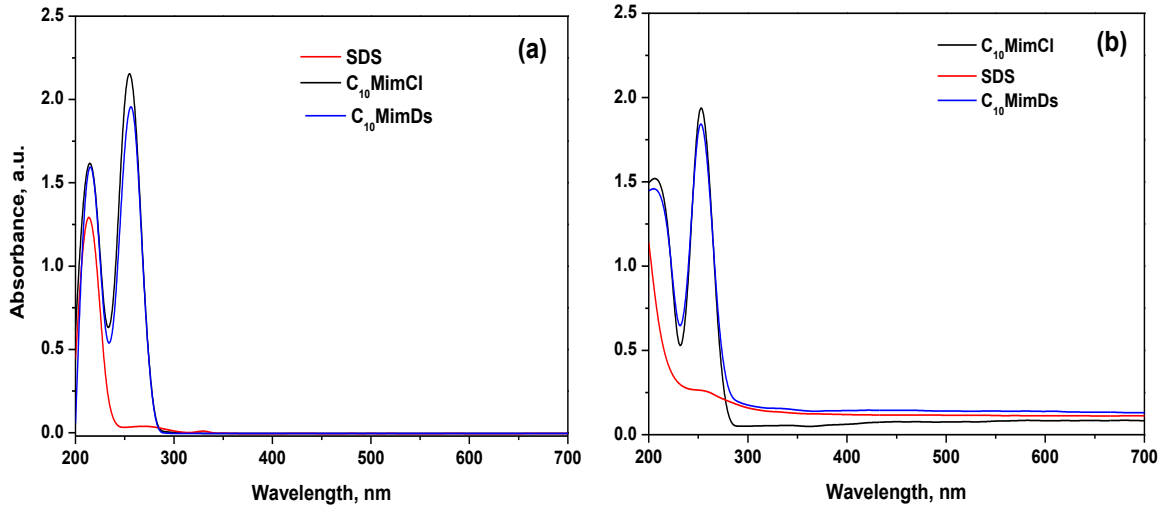


Figure 5: UV-vis. spectra of C_{10}MimCl, SDS and C_{10}MimDs in (a) methanol and (b) water, at room temperature in DMSO (the concentration of these compounds in water and methanol are 0.005 mol/L).

Study on thermal gravimetric analysis (TGA): The thermal stability was determined over a temperature range from of 40-700 °C.

The corresponding diagram for TGA and DTGA analysis of the C_{10}MimDs is presented in **(Figure 6)**.

In general most of ILs have a high thermal stability and often begins to decompose around ~ 200 °C. As it can be seen in **Figure 6**,

TGA and differential thermal analysis (DTA) of the IL showed the major weight loss (87.7%) at 409 °C was observed. In TGA curve, it was found that an initial 3.6% below ~242 °C occurs which is attributed to the removal of water.

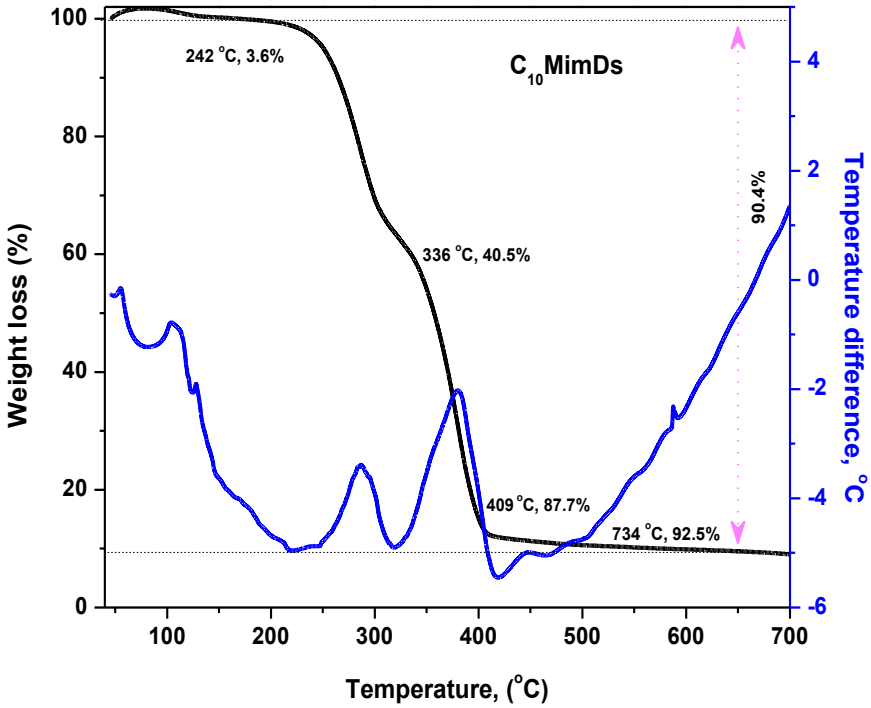


Figure 6: TG-DTA curve of synthesized IL.

This might be because of hygroscopic nature of IL. This weight loss was followed by a shouldering from 242 °C – 409 °C with complete decomposition of organic moiety. No further decomposition or degradation was observed. This gives a high thermal stability for the IL under study.

Recent reports have shown that the presence of a halide anion reduces the thermal stability of an imidazolium IL with onset occurring at least at a temperature of about 100 °C below other imidazolium salts [35]. Thus in IL, replacement of Cl^- anion in C_{10}PyCl by dodecyl sulphate anion induces enhancement in their thermal stability. The derivative thermogravimetric analyses (DTGA), of the IL indicate the presence of both the decomposition peaks as observed in the TGA.

MS studies: The important peaks of MS spectrum (**Figure 7**) of the synthesized IL relate to 224.21 (M^+ + 1), 223.21 (M^+, 1-Decyl-3-methyl imidazolium cation ($C_{10}Mim^+$)), 265.14 (M^-, Dodecyl sulphate anion (Ds)).

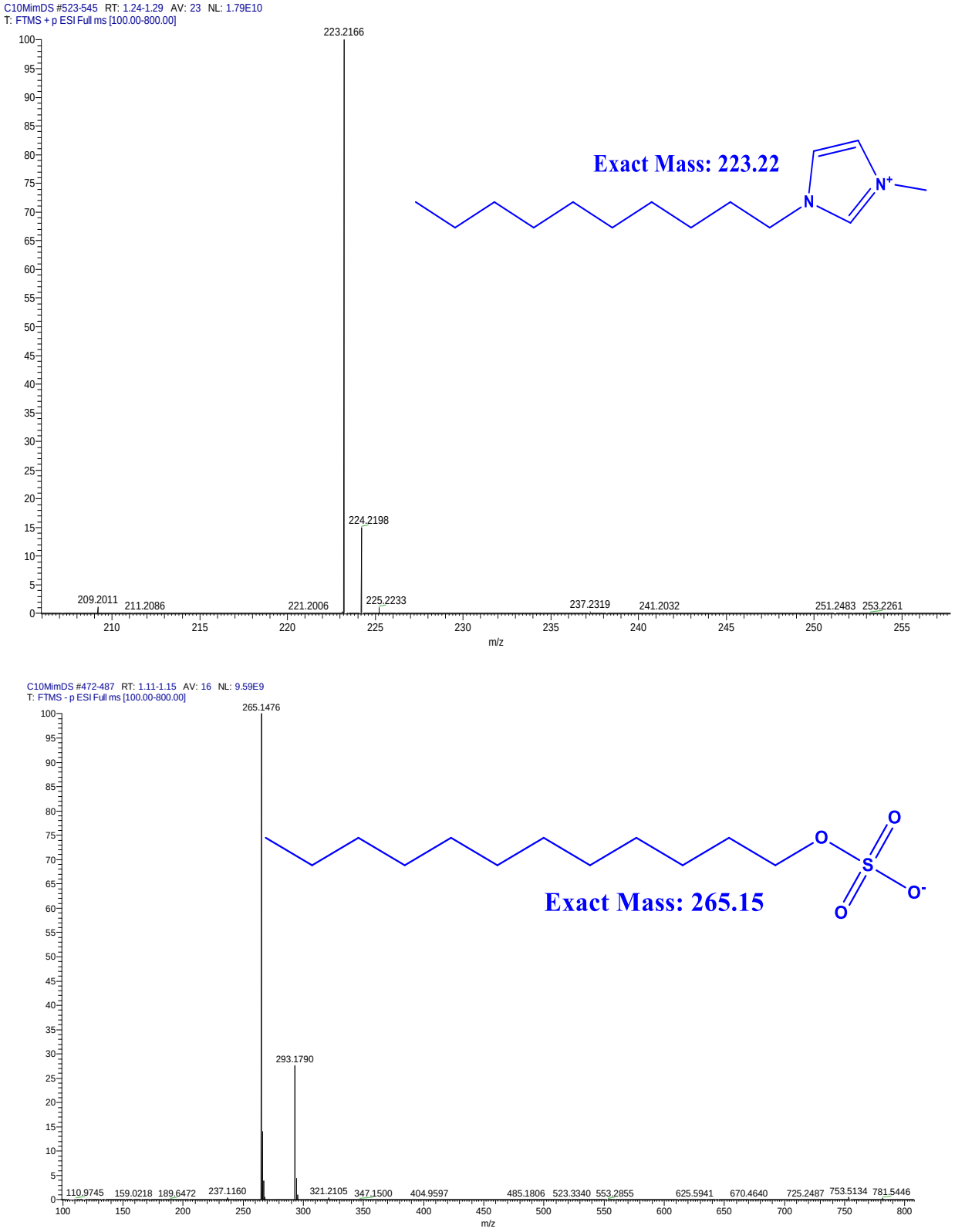


Figure7: Mass spectra of synthesized IL C_{10}MimDs.

CONCLUSIONS

In conclusion, we have shown the synthetic procedure for the preparation of C_{10}MimDs from SDS and C_{10}MimPyCl. The IL has been carefully characterized by ^{1}H & ^{13}C-NMR, FT-IR and MS analysis. The thermal stability was checked by TGA methods. In short, here we have developed economical and environmentally benign process for the preparation of new fluoride free hydrophobic C_{10}MimDs TSIL which could be a good substitute of costly, toxic PF_6^-, BF_4^- etc. anions based ILs. The results indicated that the synthesis procedure is valid and gives highly pure products. The synthesized IL contains the dodecyl sulphate anion, which is ordinary surfactant; this IL might be find application in shape directing agent in the synthesis of nanoparticles, purification of waste water, removal of metal ions and dyes from aqueous solutions, chemical separation, and also biological sides.

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CONFLICT OF INTEREST

Author declares there is no conflict of interest regarding this publication.

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