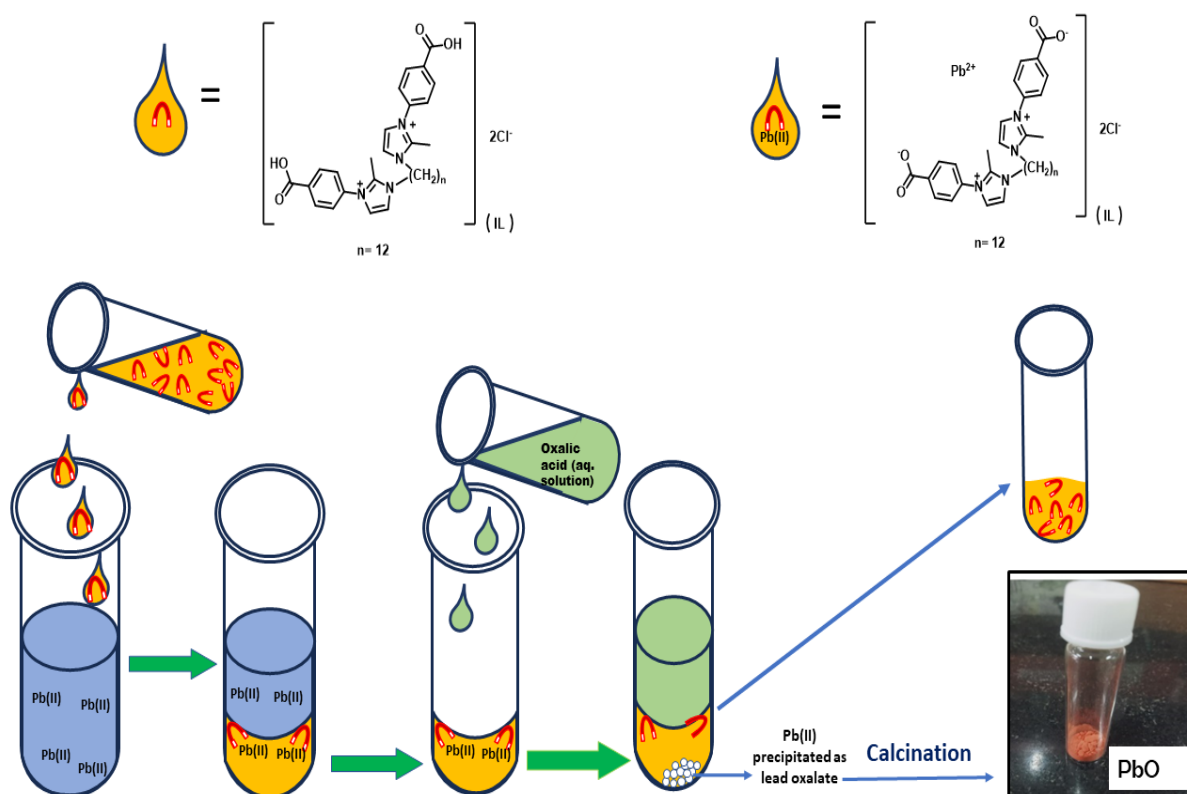# *Chapter-5*

Investigative study on the dual functional behaviour of dicationic ionic liquid as extractant and hydrophobic biphasic solvent for extraction of Pb(II) in water

Synopsis: Two imidazolium based dicationic ionic liquids, tailored with $(CH_2)_n$ bridging alkyl chains, n= 4 and n= 12 with inbuilt carboxylic acid functionalities, **IL-1** named 1,1'(butane-1,4-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium) chloride and **IL-2** named 1,1'(dodecane-1,12-diyl)bis(3-(4carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium)chloride were synthesized and investigated for Pb(II) metal ion extraction from aqueous solution. Greater than 90% extraction efficiency was observed with both the ionic liquids as biphasic extraction solvent. Regeneration of IL-2 with efficient back stripping of Pb(II) as oxalate salt concludes that use of long alkyl chain spacer in dicationic imidazolium based ionic liquids with inbuilt carboxylic acid functionalization served as a good choice for extraction of the Pb(II) metal ion from aqueous medium.

5.1 Introduction

Due to many environmental changes and pollution, toxic metals enter the ecosystem and their accumulation in living beings results in harmful consequences related to physiological disorder in living organisms [1]. Generally, water body contamination by toxic metals occurs due to release of untreated wastewater to the water bodies. Liquid-liquid extraction is one of the simple and economical process for removal of toxic metals from water bodies [2]. Nowadays one of the major environmental concerns for metal contamination is from effluent wastewaters coming from battery manufacturing industries. Dismantling and discarding of lead acid battery wastes with high lead content into the environment not only leads to problems related to human health but is also a major waste of lead resources. Therefore, from a sustainable point of view, recovery of lead from lead waste prevents metal contamination and damage to the environment [1]. Lead is one of most toxic metal among other heavy metals that affects central nervous system, kidney, liver. Therefore it was chosen to investigate the Pb(II) extraction from aqueous solution using our synthesized ionic liquids as extraction solvent [3].

Biphasic liquid-liquid extraction is a process for separation of metal ions which involves solvents that have restricted solubility in water [4]. The biphasic liquid-liquid extraction has always been an important process in hydrometallurgy [5,6]. These require

use of large volumes of volatile organic solvents which are generally toxic and have detrimental impacts on human health. Ionic liquids in this case come as a rescue as alternative solvent.

Ionic liquid (IL) has always been a significant alternative to volatile organic solvents. Ionic liquids are considered as better alternatives because of their properties like non-flammability, non-volatility, thermal stability [7,8]. As they are completely made up of ions and the ability to synthesize ILs with innumerable possibilities of organic cation with organic or inorganic anion combinations widens their applications towards different fields [9]. Therefore, several research works on organic syntheses, catalysis, electrolysis, extractions involve the use of ionic liquids as reaction media [10-12].

Apart from the ionic liquids, there exists other classes of metal extractants and among them chelating extractants are one of the important classes of extractants used for separation of specific metals or group of metals. Extraction system based on crown ethers, calixarenes, amino acids, organophosphorus extractants etc. are profusely available in literature [2,13]. The use of crown ethers is considered as good class of extractants for separation of metals from platinum group, however, their high cost compared to organophosphorus based extractants acts as a disadvantage for its use in large scale. Although, calixarenes represent another class of metal extractants, but their solubility in aromatic hydrocarbons is of environmental concern. For hydrometallurgical processes, organophosphorus extractants have occupied a significant importance because of their low cost, stability, high selectivity etc. [13,14]. However, their high toxicity acts as a disadvantage while extracting metals from aqueous medium. Use of polymeric sorbents for carrying organophosphorus extractant for prevention of leaching to aqueous medium is a way to minimize water solubility of such extractants. Yudaev et al. modified organophosphorus extractant into a magnetic sorbent based on polyvinyl alcohol, metallic iron and a polydentate phosphazene extractant that was used as solid phase metal extractant. This modification prevented negative impact of organophosphorus extractant on the environment [13]. Generally, in metal extraction, polymers are used as extractant under solid phase extraction. This type of extractants is insoluble, non-volatile and easily recyclable. However, the ions to be extracted are observed to have poor diffusion to the reactive group of polymers and also there is limiting set of varied functional groups available for industrially used polymer extractants [14]. Therefore, research related to minimize the disadvantages of different types of extractants & diluents in every possible

way is important field of interest. As compared to the above extractants, the use of ILs as an alternative extractant possess many prospectives to remove the drawbacks of metal extractions because of possible designing of target specific ILs along with safety parameters like lower vapour pressure, low melting points and non-flammability. Ionic liquids with phosphonium, ammonium, imidazolium are commonly used cationic cores for the metal extraction [15]. Ionic liquids with different heteroatom cationic cores are used for separation of rare earth elements and heavy metals and also extraction from wastewater. However, they are not used in large scale, since some of the hydrophilic ionic liquids are lost into aqueous phase during extraction process due to their solubility in water [15]. Many other extraction systems have been studied that utilizes ionic liquid together with other extractants for the metal extraction process. Dai et al. utilized [Rmeim][Tf$_2$N] and [Rmeim][PF$_6$], (([Rmeim]= 1-alkyl-3-methylimidazolium) ionic liquids for extraction of Sr^{2+} in presence of crown ether [16]. Various other room temperature ionic liquids together with crown ethers as extractants are used for extraction of metals like Na$^+$, K$^+$, Cs$^+$, Sr^{2+} [17-19]. Other examples like octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide (CMPO) is used as an extractant dissolved in [Bmim][PF$_6$] for extraction of rare earth metals from aqueous solution [20]. In industry, selective metal extraction is performed by employing liquid-liquid extraction technique, where solvent extractions are done using extractants like acidic, basic as well as neutral in nature [21-26]. IL-extractants especially the functionalized ILs are employed nowadays for the extraction of metal ions due to their sustainability and environmental-friendly nature compared to generally used organic extractants [27-29].

From this point of view, designing target specific ILs for metal extraction purpose is very essential with low solubility in water, low viscosity, high hydrophobicity to prevent such losses while extraction of metals from aqueous medium. In analytical chemistry, functionalized imidazolium based ionic liquids with cations incorporated with thiourea and urea were the first TSILs that were utilized for extraction of Cd^{2+} and Hg^{2+} from aqueous solutions [30]. 1,10-phenanthroline-2,9-dicarboxamides bis conjugated to imidazolium cations and bis[(trifluoromethyl) sulfonyl] imide anion is another TSIL which is dicationic and used for the extraction of trivalent f-ions from aqueous medium [31]. Regarding thermal stability and volatility, dicationic ionic liquids exhibits better stability and low volatility over the monocationic ones, although there are very few works available on dicationic ionic liquids being used as metal extracting solvents [32,33]. In the biphasic

liquid-liquid extraction, water solubility is an important parameter as solvent hydrophobicity plays an important role in phase separation after the extraction takes place [34,35]. Solvent extraction of metal cations from aqueous medium, uses hydrophobic ionic liquids as medium, however the hydrophobic ionic liquids are limited. The hydrophobicity in ILs is obtained using anion like hexafluorophosphate (PF$_6^-$) which eventually hydrolyses in acidic aqueous phase, and this acts as a disadvantage [7,9]. Anion like bis[(trifluoromethyl)sulfonyl]imide (Tf$_2$N$^-$) are also used to introduce hydrophobicity in the ionic liquids although use of such anion makes the synthesis process costly [9].
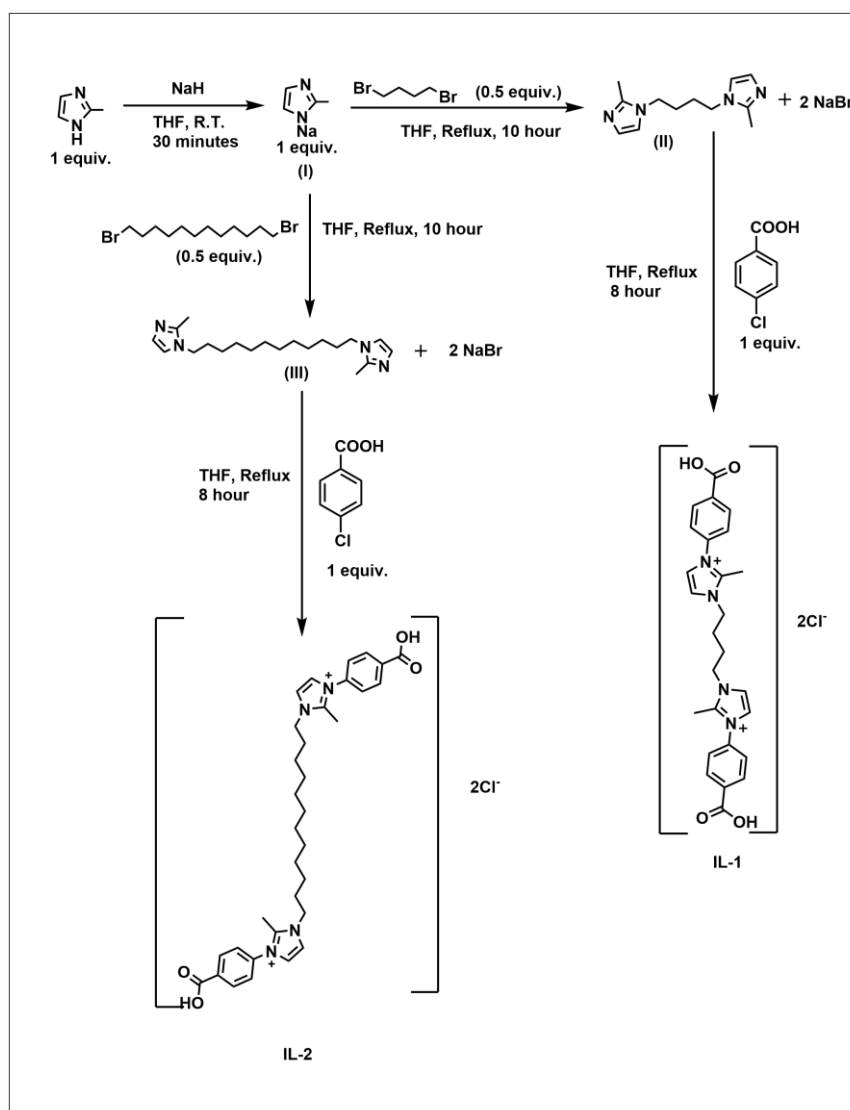
Scheme-5.1: Synthesis of **IL-1** and **IL-2**

In this report we have designed two dicationic carboxylic acid functionalized ionic liquids **IL-1** named 1,1'(butane-1,4-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium) chloride and **IL-2** named 1,1'(dodecane-1,12-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-

imidazol-3-ium)chloride as per reaction **Scheme 5.1**. Adjustment in physical properties of ionic liquid have been obtained by making alterations to the alkyl chain lengths incorporated into the IL. This allows fine-tuning of IL's hydrophobicity, viscosity as well as melting points [30,36]. The synthesized ionic liquids are immiscible in water which prevents its loss in aqueous medium along with the ionic liquid not polluting the aqueous medium. Although various ionic liquids are utilised for metal extraction provided but the extraction mechanisms are not very informative. In this report we studied the extraction ability of synthesized ILs for Pb(II) in aqueous solution and investigated the mechanism of metal ion extraction from aqueous medium thus providing a plausible mechanism

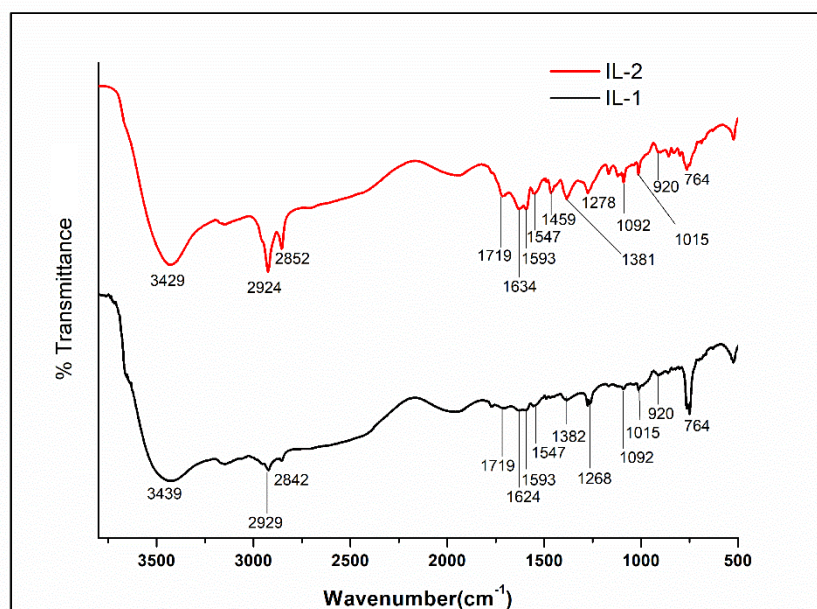## 5.2. Results and discussion

5.2.1. FT-IR analysis

Fig. 5.1: FT-IR spectra of **IL-1** and **IL-2**

The FT-IR spectra of **IL-1** and **IL-2** are represented in **Fig. 5.1**. The existence of -COOH functionality in both the ionic liquids can be observed from carbonyl stretch at 1719 cm^{-1} and broad O-H stretching in the region of 3300-3450 cm^{-1}. Peaks at 1268 cm^{-1} of **IL-1** and 1278 cm^{-1} of **IL-2** are found due to their C-O stretching vibrations. The frequencies at 1634 cm^{-1} and 1628 cm^{-1} in both the ionic liquids express existence of residual water molecules with H-O-H bending vibrations. The C=C stretching vibrations of imidazolium cation and phenyl rings can be assigned at 1593 cm^{-1} in addition to C-N stretch at 1547 cm^{-1}. Weak intensity C-C ring stretches are observed at the region of 1459 cm^{-1}. Aromatic

C-H and aliphatic C-H stretches of both the ILs are assigned at around 2924, 2852, 2892 and 2842 cm^{-1}. The methyl group at C-2 position of imidazolium cation shows C-H rocking at 1382 cm^{-1}. The methylene chain, bridging each of the IL between their imidazolium cations display single CH_2 rocking mode around 764 cm^{-1} and also the peaks around 1015–1350 cm^{-1} indicate twisting and bending modes of the methylene chain [37]. The intramolecular hydrogen bonding within the ionic liquid unit itself lowers the absorption frequency of the carbonyl stretch and this has been evidenced by the carbonyl stretch at 1719 cm^{-1} which is at lower frequency compared to typical monomeric carbonyl stretch found at 1740-1800 cm^{-1} [38] and this result proves the formation of di-cationic ionic liquids which are also dicarboxylic acid in nature.

5.2.2 NMR analysis

^{1}H and ^{13}C NMR analysis spectra of the **IL-1** and **IL-2** in DMSO-d_6 are presented in **Fig. 5.2 (a)**, (**b**) and **Fig. 5.3 (a)**, (**b**) respectively. For the **IL-1**, ^{1}H NMR spectrum displays two doublets each of 4 protons of two phenyl rings at 7.96 ppm and 7.53 ppm. A multiplet is seen at 6.87-7.12 ppm for 4 protons in two imidazolium rings. Two singlets each of 3 protons are observed at 3.92 ppm and at 1.65 ppm of the bridging methylene linkages. The six protons of two C-2 methyl groups of imidazolium cations are found at 2.34-2.38 ppm along with 2 protons of methylene bridge. The signals of protons of the carboxyl groups on the NMR spectrum are difficult to detect here in the spectrum. Although one broad peak of two –COOH protons is observed at 8.48 ppm. This difficulty in clear detection of -COOH protons might be due to the deuterium exchange involving DMSO-d_6. The ^{13}C NMR spectrum of **IL-1** shows characteristic carbonyl peak at 167.46 ppm in addition to other aliphatic and aromatic carbon peaks as mentioned in the supporting information of spectral data.

In case of the **IL-2**, the ^{1}H NMR spectrum shows one broad peak of two –COOH protons at 8.55, multiplet of 4 protons of the two imidazole rings at 6.87-7.15 ppm, two doublets each of 4 protons at 7.94 ppm and another at 7.54 ppm of the two phenyl rings. The eight proton signals at 2.33-2.37 ppm include two methyl group protons attached to the two imidazolium cations and two protons of the methylene linkages. The methylene protons of dodecyl chain are also observed as triplet at 3.87 ppm for two protons, one multiplet of 4 protons at 1.62-1.70 ppm and another singlet at 1.21 for 16 protons. From the spectrum **Fig. 5.3(a)**, deuterium exchange involving DMSO-d_6 results in unclear detection of -

COOH protons. The peaks correspond to total 24 protons of dodecyl bridging chain in its
^{1}H NMR confirms the formation of **IL-2** in support of the carbonyl carbon peak of -COOH
group at 167.34 ppm in its ^{13}C NMR spectrum. Like the **IL-1**, the ^{13}C NMR spectrum of
IL-2 also provides the aliphatic and aromatic carbon signals (**Fig. 5.3b**).
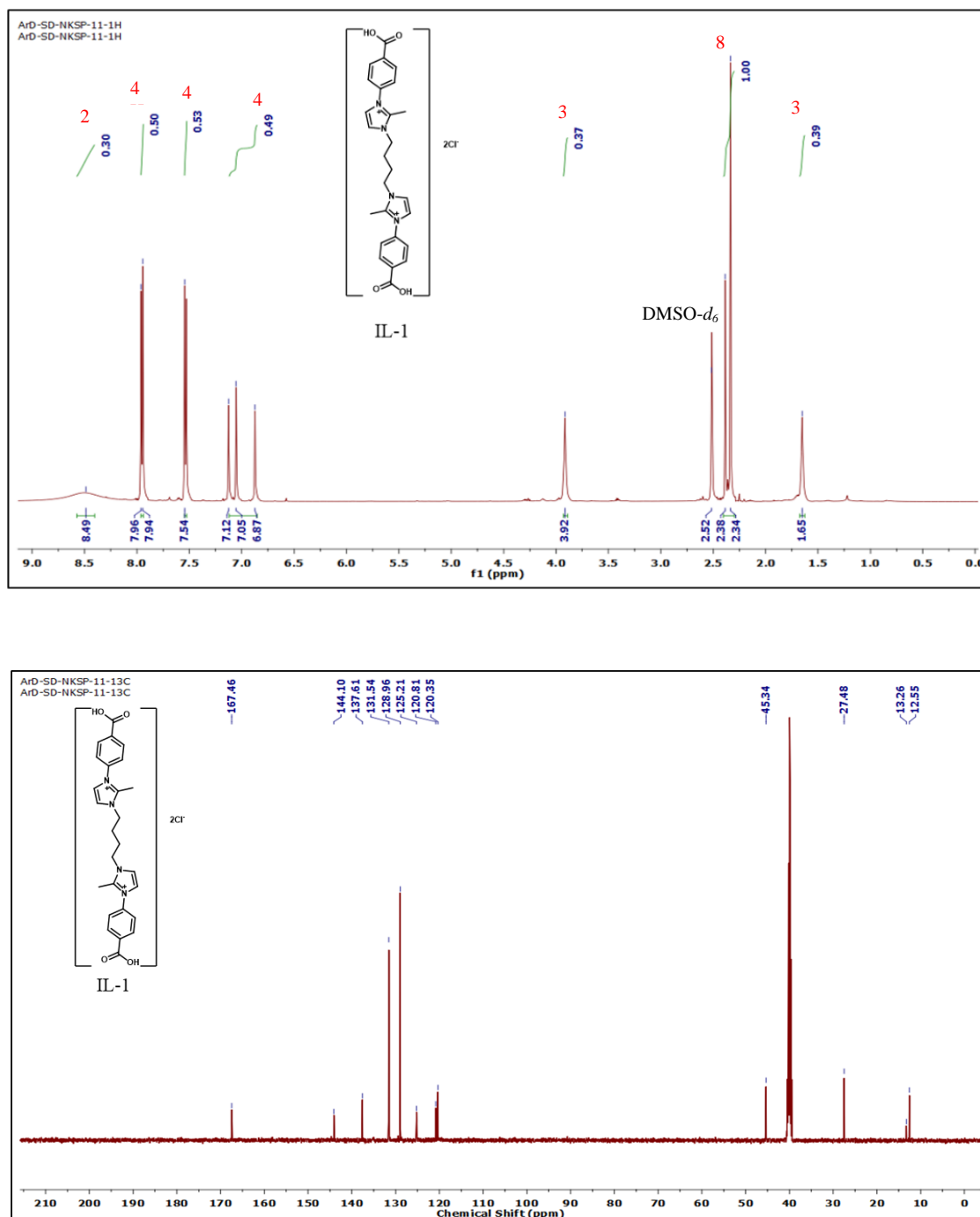

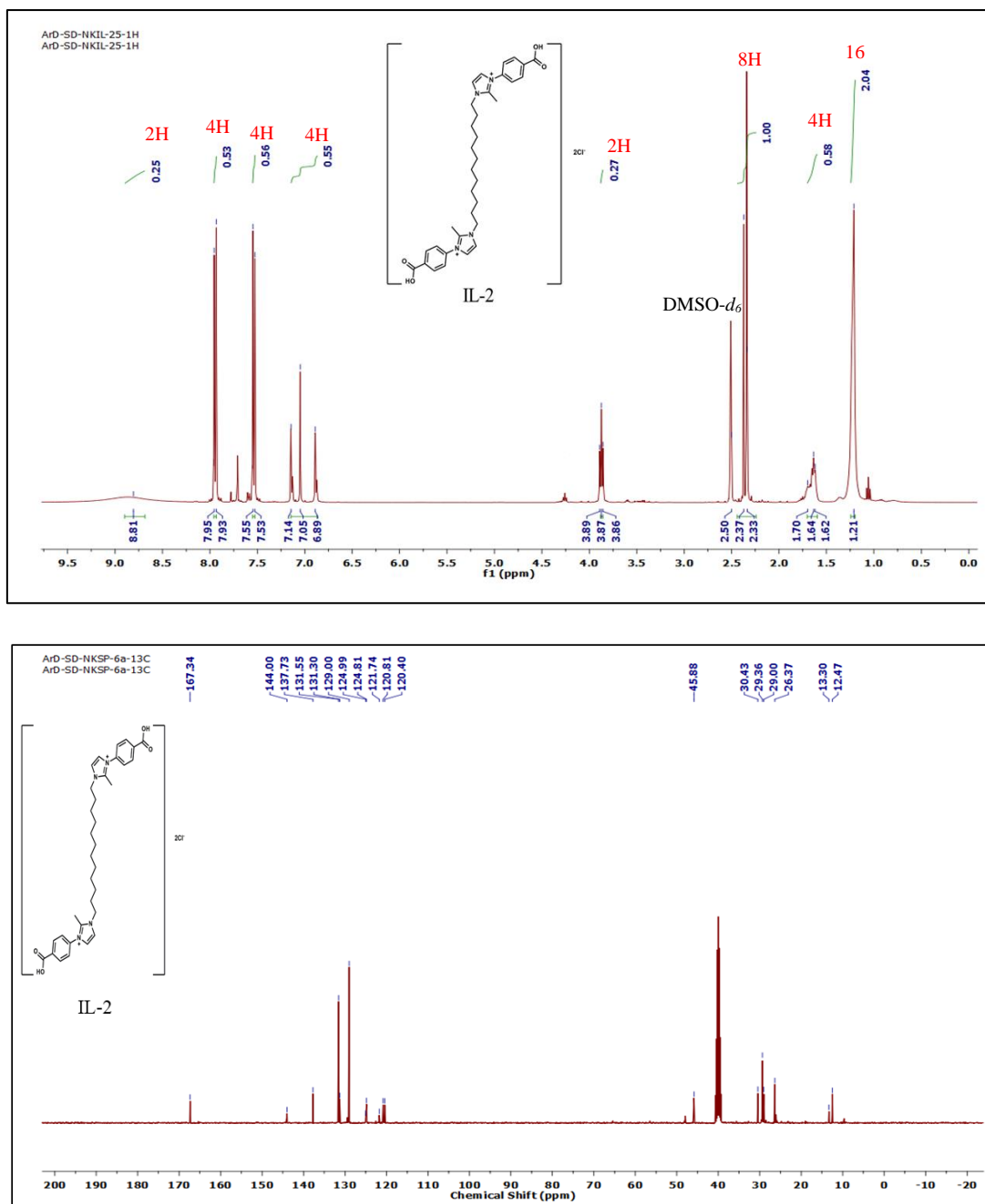**Fig. 5.2**: (**a**) ^{1}H NMR of **IL-1**, (**b**) ^{13}C NMR of **IL-1.**

Fig. 5.3: (**a**) ^{1}H NMR of **IL-2**, (**b**) ^{13}C NMR of **IL-2**

5.2.3 Elemental analysis

The formation of the two ionic liquids is also evidenced from their C, H, N elemental analysis data provided here: Calculated for **IL-1** (%): C 58.75, H 5.27, N 10.54 Found: C 57.24, H 5.31, N 10.02; CHN analysis: Calculated for **IL-2** (%): C 63.45, H 6.84, N 8.709 Found: C 58.87, H 6.90, N 7.88.

5.2.4 Thermogravimetric analysis

Thermogravimetric analysis (TGA) of the ionic liquids (ILs) displays that they do retain physisorbed water. The presence of longer methylene bridging chains provides hydrophobic nature by limiting uptake of water molecules in excess amount and this can be observed from their TGA plots. They start to decompose gradually around 200 ℃ and completely degrade below 300℃ in case of the **IL-1** and 350 ℃ in case of the **IL-2** (**Fig. 5.4**).
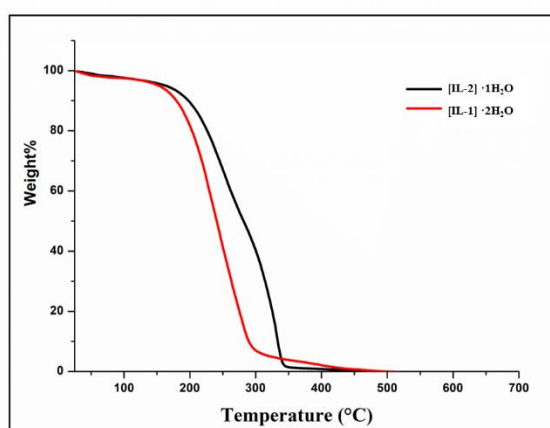

Fig. 5.4: TGA graph of **IL-1** and **IL-2**

5.3 Preliminary experimental results of metal extraction using IL-1 and IL-2

IL-1 is a room temperature ionic liquid whereas **IL-2** is sticky solid with paste like appearance at room temperature which has melting point at 54 ℃. This discrepancy in physical state can be considered for increasing chain length of the alkyl bridging groups with enhanced van der Waals interaction for the **IL-2** brought about by long non-polar alkyl chain [39].

After carrying out the extraction experiment of **IL-1** and **IL-2** with aqueous solution of Pb(II), as mentioned in the experimental section, it was allowed to settle for phase separation. The metal-IL complex formed being hydrophobic in nature remains soluble in ionic liquid phase. The aqueous layer is analysed by AAS for the unextracted metal content in water.

It was observed that Pb(II) provided a very good extraction percentages with **IL-1**. The same experiments were also conducted using melted **IL-2** and then addition of 20 mL of

7.25 mM Pb(NO$_3$)$_2$ aqueous metal salt solution, as the **IL-2** retains as pasty solid state at room temperature. The photographs of Pb(II) metal extraction by the **IL-1** and **IL-2** are given in **Fig. 5.5**. Also, the results of metal extraction with **IL-1** and **IL-2** are summarized in **Fig 5.6**. It was concluded that extraction percentage results of the Pb(II) is almost same with both the **IL-1** and **IL-2**, when the reaction is continued for 30 minute. **Fig. 5.5**(**a**) represents biphasic mixture of IL-1 and water without any metal content which depicts that IL-1 and water forms two immiscible phases with IL-1 being denser than water remains in the lower phase and water being less dense of the two remains as the upper phase. **Fig. 5.5**(**b**) represents biphasic mixture of **IL-1** loaded metal soluble in ionic liquid phase with aqueous metal solution of Pb(II) as the upper phase upon settlement of two separate layer after completion of extraction experiment. This picture depicts **IL-1** based extraction system with **IL-1** phase loaded with Pb(II). Similarly, **Fig. 5.5**(**c**) represents biphasic mixture of **IL-2** and water without any metal content which depicts that **IL-2** and water forms two immiscible phases with **IL-2** being denser than water remains in the lower phase and water being less dense of the two remains as the upper phase. **Fig. 5.5**(**d**) represents biphasic mixture of **IL-2** loaded metal soluble in ionic liquid phase with aqueous metal solution of Pb(II) as the upper phase upon settlement of two separate layer after completion of extraction experiment. This picture depicts **IL-2** based extraction system with **IL-2** phase loaded with Pb(II). **Fig. 5.5**(**e**) represents precipitation of lead oxalate after reaction of oxalic acid with Pb(II) loaded-**IL-2** phase.
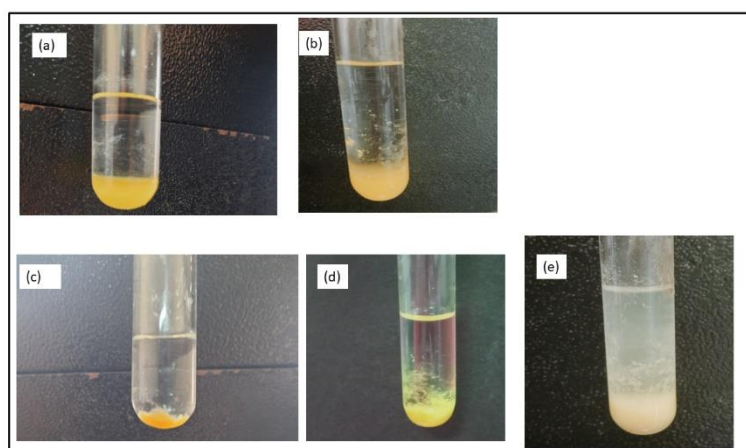

Fig. 5.5: (**a**) Biphasic mixture of **IL-1** and water, (**b**) biphasic mixture of **IL-1**-lead metal complex soluble in ionic liquid with aqueous Pb(II) metal solution, (**c**) biphasic mixture of **IL-2** and water (**d**) biphasic mixture of **IL-2**-lead metal complex soluble in ionic liquid

with aqueous Pb(II) metal solution (**e**) precipitation of lead oxalate after reaction of oxalic acid with metal loaded-**IL-2**.

5.4 Optimization of the extraction process and the biphasic extraction study

5.4.1 Optimization of reaction time on extraction of metal

To observe the effect of bridging methylene chain length on the metal extraction process, varying molar quantities of the **IL-1** and **IL-2** ranging from 0.05 mmol to 1.2 mmol were employed for the extraction of Pb(II) from 20 mL of 7.25 mM $Pb(NO_3)_2$ aqueous metal salt solution. The extraction process was carried out for 30 minute. The extraction results of Pb(II) using both the ILs are presented in **Fig. 5.6** (**a** and **b**). The extraction percentage of Pb(II) ion observed with 0.9 mmol of the **IL-2** is (92.6 $\pm$ 0.784) with 95% confidence interval. Whereas for **IL-1**, the extraction percentage obtained with 95% confidence interval is (91 $\pm$ 0.37) using similar mmol of ionic liquid. To know the optimum time for maximum extraction of the metal cation, the effect of reaction time was investigated for 20 mL of 7.25 mM $Pb(NO_3)_2$ aqueous solution. It was observed that the extraction efficiency of Pb(II) reached its maximum in 30 minute of reaction time and did not change when the stirring was done for another 15 minute for the **IL-1**. Therefore 30 minute was selected to be the optimal extraction time for maximum extraction of the metal ions from aqueous medium by the **IL-1** at room temperature. The histogram of extraction percentage of Pb(II) for 20 mL of 7.25mM $Pb(NO_3)_2$ aqueous solution using 0.9 mmol of **IL-1** with respect to stirring time is represented in (**Fig. 5.7**). The extraction percentage of Pb(II) using varying mmol of the **IL-1** and **IL-2** are tabulated in **Table-5.1**. The study of metal extraction with the ILs showed that almost 0.9 mmol of both the ionic liquids are sufficient to extract greater than 90% of the Pb(II) ion from 20 mL of 7.25mM aqueous solution of $Pb(NO_3)_2$ in 30 minute.

Table 5.1: Extraction percentage of Pb(II) from 20 mL of 7.25 mM Pb(NO$_3$)$_2$ aqueous solution using variable amount of **IL-1** and **IL-2** for 30 minute of reaction time

Entry	Variable amount of IL	Extraction % (Trial-1)	Extraction % (Trial-2)	Extraction % (Trial-3)	Average Extraction % Trial 1, 2, 3)	Standard deviation	95% confidence interval
1.	0.05 mmol IL-1	13.59	13.44	20.09	15.7	3.796	4.296
2.	0.1 mmol IL-1	34.11	35.37	38.41	35.9	2.210	2.501
3.	0.3 mmol IL-1	72.7	73.34	76	74	1.75	1.980
4.	0.5 mmol IL-1	88.41	88.68	89.21	88.7	0.406	0.460
5.	0.7 mmol IL-1	90.5	90.63	90.79	90.6	0.14	0.164
6.	0.9 mmol IL-1	91.01	90.67	91.34	91	0.335	0.379
7.	0.1 mmol IL-2	34.74	33.26	32.07	33.3	1.337	1.513
8.	0.3 mmol IL-2	72.75	68.68	70.02	70.4	2.074	2.347
9.	0.5 mmol IL-2	83.31	79.22	82.05	81.5	2.095	2.371
10.	0.7 mmol IL-2	89.9	88.8	89.46	89.3	0.553	0.626
11.	0.9 mmol IL-2	93.3	91.92	92.73	92.6	0.693	0.784
12.	1.2 mmol IL-2	93.59	93.6	93.6	93.59	0.005	0.006

All the metal solutions are diluted to a detectable limit of AAS and then the resultant value is multiplied with the dilution factors respectively.
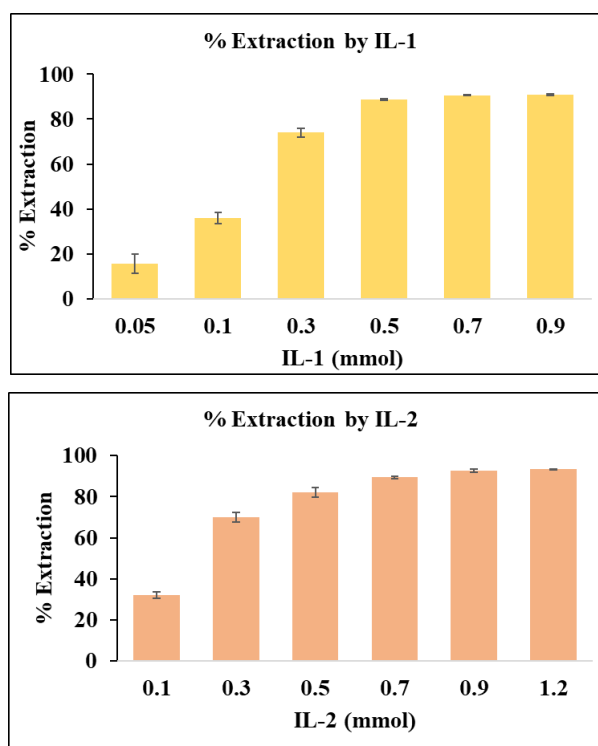
Fig. 5.6: Histogram representing extraction percentage of Pb(II) with **IL-1** and **IL-2** in 30 minute (reaction condition): 20 mL of 7.25 mM aqueous solution of $Pb(NO_3)_2$; molar quantity variation **IL-1** (0.05, 0.1, 0.3, 0. 5, 0.7, 0.9 mmol) and **IL-2** (0.1, 0.3, 0.5, 0.7, 0.9, 1.2 mmol); error bars arise from n = 3 independent trials.
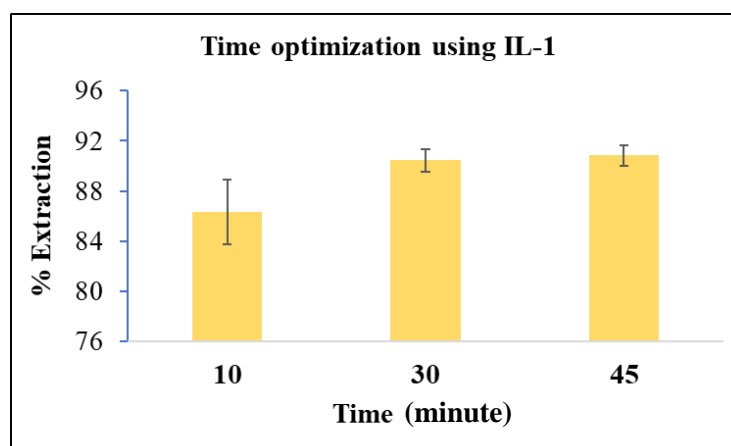

Fig. 5.7: Histogram representing extraction percentage of Pb(II) with respect to time (10 minute, 30 minute, 45 minute); error bars arise from n = 3 independent trials.

5.4.2 Effect of varying concentration of Pb(II) in aqueous medium on extraction process

This study was performed by keeping constant amount of the **IL-1** and **IL-2** (i.e., 0.2 mmol) to test the extraction efficiencies using varying concentration of $Pb(NO_3)_2$ i.e. 2.25

mM, 3.65 mM, 7.25 mM, 14.5 mM prepared as 20 mL of aqueous metal salt solution. The concentration of lead in the respective salt solutions before extraction were prechecked using AAS. The extraction efficiencies of Pb(II) ions in percentages using 0.2 mmol of **IL-1** and **IL-2** towards different concentration of $Pb(NO_3)_2$ aqueous solution are represented in **Fig. 5.8** (**a** and **b**). The extraction percentages of Pb(II) for three independent experimental trials for each prepared concentration using **IL-1** and **IL-2** are tabulated in **Table**-**5.2**. In case of the **IL-1** in **Fig. 5.8a**, it was observed that the percentage extraction efficiency decreases gradually from (76.7 ± 1.603) % to (43.47 ± 2.451) % with 95% confidence interval, as the Pb(II) concentration increases in 20mL of aqueous $Pb(NO_3)_2$ solution from 2.25 mM to 14.5 mM. This decrease in extraction percentage might have happened because of unavailability of enough coordination sites in the dicationic ionic liquids.

Table 5.2: Extraction percentage of Pb(II) using 0.2 mmol of **IL-1** and **IL-2** from varying concentration of 20 mL of aqueous molar solution of $Pb(NO_3)_2$ in 30 minute of reaction time

Entry	Variable Concentration of $Pb(NO_3)_2$ (in mM)	Extraction % using **IL-2** (0.2 mmol)			Average Extraction % (**IL-2**) for Trial-1, 2 and 3	95% confidence interval	Extraction % using **IL-1** (0.2 mmol)			Average Extraction % (**IL-1**) for Trial-1, 2 and 3	95% confidence interval
		Trial-1	Trial-2	Trial-3			Trial-1	Trial-2	Trial-3		
1.	2.25	73.02	73.54	71.74	73.0	1.048	77.73	77.35	75.1	76.73	1.602
2.	3.65	69.16	67.51	67.7	68.1	1.021	73.32	76.1	72.4	73.94	2.179
3.	7.25	67.37	66.04	62.9	65.4	2.597	65.77	63.5	65.5	64.94	1.416
4.	14.5	49.94	41.4	42.54	44.6	5.246	41.04	44.17	45.2	43.47	2.451

All the metal solutions are diluted to a detectable limit of AAS and then the resultant value is multiplied with the dilution factors respectively.
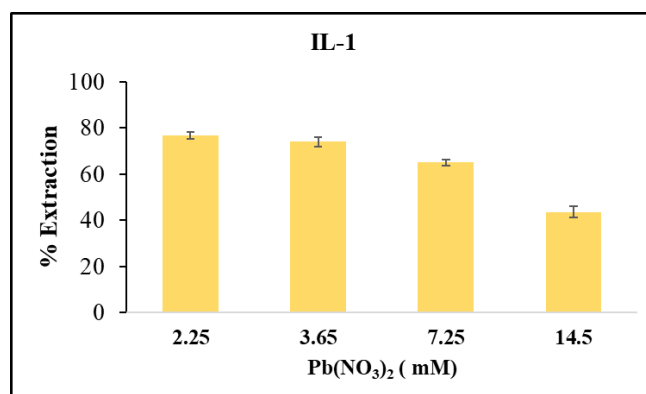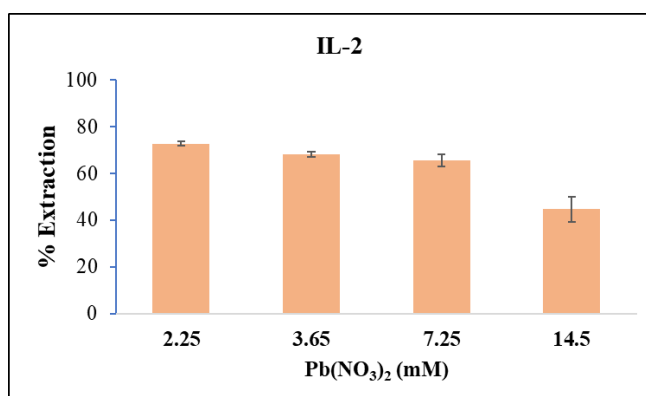
Fig. 5.8: Histogram representing extraction percentage using 0.2 mmol of (**a**) **IL-1** and (**b**) **IL-2** with varying Pb(II) metal concentration in 20mL of aqueous Pb(NO$_3$)$_2$ metal salt solutions (2.25 mM, 3.65 mM, 7.25 mM, 14.5 mM); error bars arise from n = 3 independent trials.

The results observed for the **IL-2** are represented in **Fig. 5.8b**. It was observed that with consideration of 95% of confidence interval, 0.2 mmol of the **IL-2** can extract (73 ± 1.048) % of Pb(II) ions from 20mL of 2.25 mM aqueous solution of Pb(NO$_3$)$_2$. And 0.2 mmol of the **IL-1** can extract up to (76.7 ± 1.603) % of Pb(II) ions at room temperature from 20 mL of 2.25 mM aqueous solution of Pb(NO$_3$)$_2$.

5.4.3 Extraction studies based on FT-IR, TGA and EDX results of the metal-IL complexes soluble in ionic liquid phase

The above results of metal extraction (**Fig. 5.6**) with both the **IL-1** and **IL-2** exhibited extremely good performances in case of the Pb(II). Hence, FT-IR spectra (**Fig.5.9)** of the ionic liquid phase of extracted metal, depicted that the coordination of the Pb(II) ion into the ionic liquids occurred via -COOH groups of the ionic liquid after deprotonation of the functional group. In both the ionic liquids, the -COOH functional groups are the only single coordinating site for metal ions. In the FT-IR spectra of parent ionic liquid (**Fig. 5.1**), we observed that each molecule of ionic liquid because of the presence of two carboxylic acid functionalities, stays as a single unit with extensive intra molecular hydrogen bonding. Absorption band at 1719 cm^{-1} corresponds to the protonated acid function -COOH, but this red shift in carbonyl frequency from usual is the evidence of the hydrogen bonded dicarboxylic acid. Another absorption peak of low intensity peak at 1634 cm^{-1} in the parent ionic liquid corresponds to the deprotonated COO$^-$ form of the ionic

liquid present in the ionic liquid phase. The presence of deprotonated form of ionic liquid in the parent ionic liquid is because of formation of H_3O^+ due to presence of residual water molecules in ionic liquid phase. In the FT-IR spectra (**Fig.5.9**) of metal loaded phases of ionic liquid, it was observed that the peak at 1719 cm^{-1} starts disappearing and the peak intensity at 1634 cm^{-1} increases. The disappearance of peak at 1719 cm^{-1} in the metal loaded ionic liquid phase indicates maximum amount of loading of Pb(II) occurs with 0.9 mmol of the **IL-1** from 20 mL of 7.25 mM aqueous solution of Pb(NO$_3$)$_2$. The coordination of metal ions via protonated ionic liquid hinders the electrostatic interaction between the positive metal ion and the positive charge on imidazolium rings. However, the deprotonated carboxylate coordinating functional group of the organic cation is a zwitterionic structure which electrostatically attracts the metal cation. This deprotonated form thus provides less hindrance towards the metal coordination than the protonated form of the ionic liquid [40]. Metal loaded ionic liquid phase with prominent appearance of characteristic peaks of ionic liquid cation indicates that no degradation of ionic liquid into the aqueous phase occurred (**Fig. 5.9**).
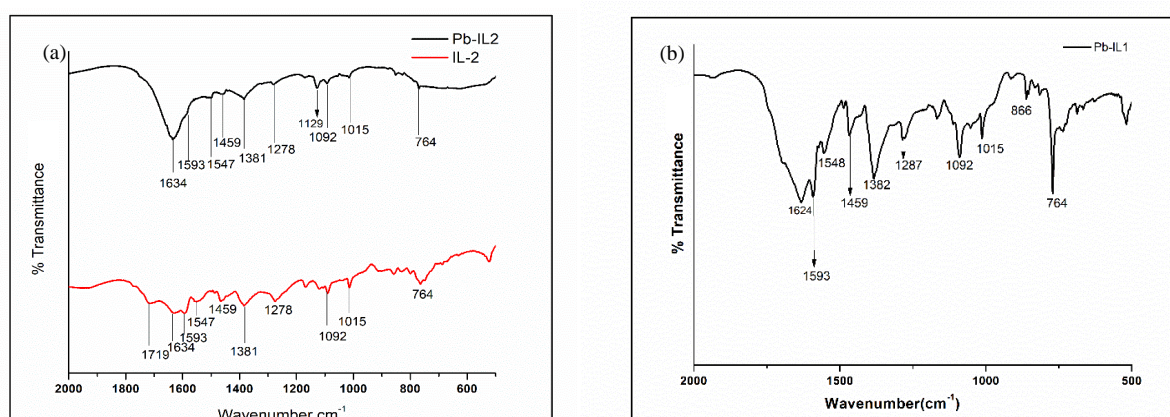

Fig. 5.9: (**a**) FT-IR spectra of **IL-2** and Pb-IL2 complex loaded in ionic liquid phase (**b**) FT-IR spectra Pb-IL1 complex loaded in ionic liquid phase.

From the TGA data, (**Fig. 5.10**) it is observed that in the lead loaded ionic liquid phases, the degradation below 300 ºC and 350 ºC in **IL-1** and **IL-2** respectively is because of the ionic liquid part only. Remaining weight percentage of 35 to 40% above the given temperatures in both the thermogravimetric plots respectively are because of presence of metal oxide formed at high temperature. Thus, degradation of metal loaded ionic liquid phase is not complete below 350 ºC which is a contrast to the complete degradation observed from both the thermogravimetric plots of parent ILs below 350 ºC (**Fig. 5.4**), which proves the complexation of Pb(II) with the ionic liquid phase.
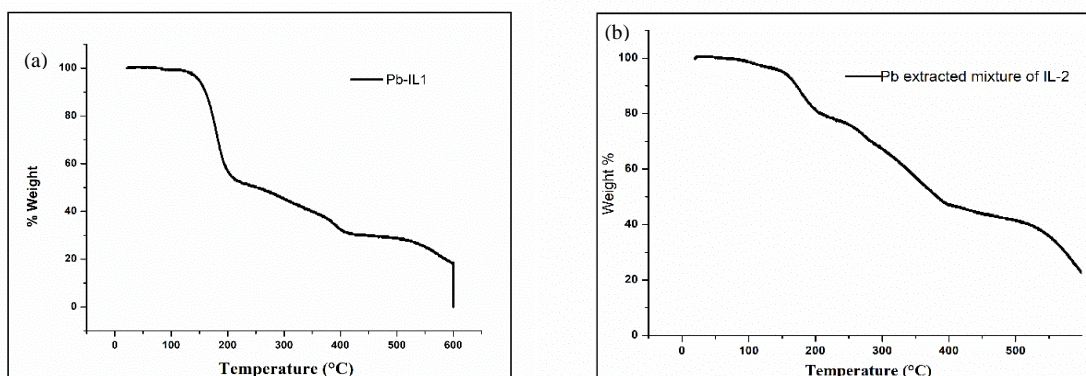
Fig. 5.10: TGA plots of metal loaded ionic liquid (**a**) **IL-1** and (**b**) **IL-2.**
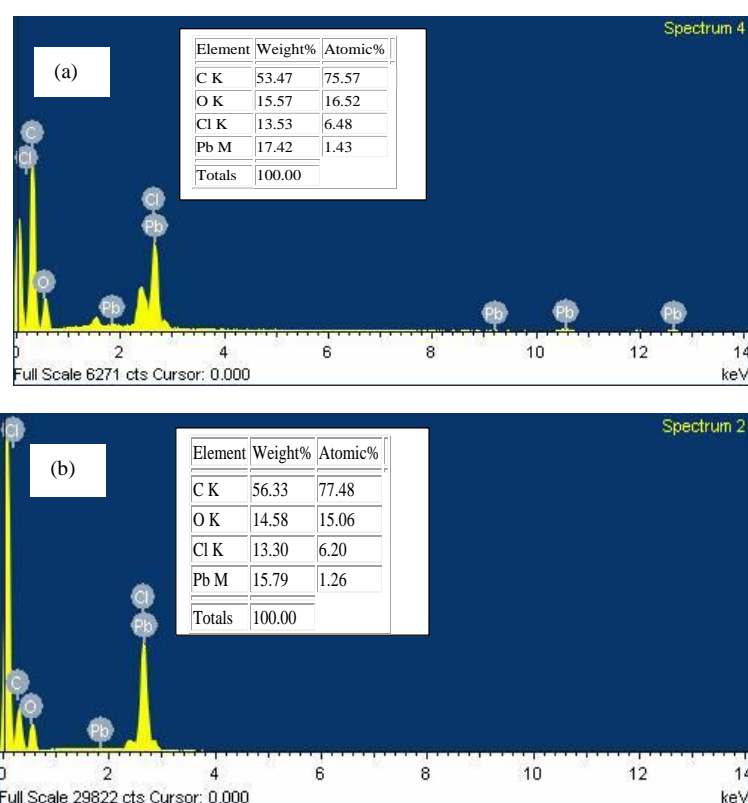

Fig. 5.11: EDX spectra of (**a**) Pb loaded **IL1**; (Pb-IL1) and (**b**) Pb loaded **IL2**; (Pb-IL2).

Also, the EDX spectra of Pb-IL1 (**Fig. 5.11a**) and Pb-IL2 (**Fig. 5.11b**) given above confirms the incorporation of Pb(II) into the ionic liquid phase. Although in both the EDX spectra, nitrogen atom cannot be detected and the reason for this can be viewed as low abundance of this element in surface of the ionic liquid phase. Presence of nitrogen was confirmed from the CHN analyses results.

The content (%) of elements for **IL-1** loaded with Pb(II) according to EDX are included in **Fig. 5.11**(**a**). During any EDX measurement, different areas were focused on the surface which results in many different spectra for the same compound. Spectrum-4 (**Fig. 5.11a**) is a particular focused area of the **IL-1** and percentage content of those elements has been presented for the same. Here, it can be seen that O:Cl ratio is approximately 2:1 in the whole structure for that particular area. Quantitative analysis of light elements like oxygen, nitrogen is very difficult to obtain using EDX only. Therefore, EDX cannot provide exact quantitative composition result for the **IL-1** loaded with Pb(II).The content (%) of elements for **IL-2** loaded with Pb(II) according to EDX are included in **Fig. 5.11**(**b**). Similarly, in spectrum-2, a particular area of **IL-2** has been focused and the result of elemental % content is shown for that focused area only, not the whole complex. However, different area may have different % element content.

5.5 The plausible mechanism study for metal extraction from FT-IR results

Literature search [41,42] suggests the presence of various mechanisms of extraction of metal from aqueous phase to the ionic liquid phase via anion exchange, neutral and cation exchange. From the FT-IR study **Fig. 5.9**, we came to know that the metal complex formation is occurring via deprotonation of the carboxylic acid functional group in the ionic liquid. **Fig. 5.12** represents variation of log D (distribution ratio) against log [IL], in which [IL] depicts amount of ionic liquid in mmol. We observe that with increase in ionic liquid concentration, the distribution ratio increases which means that there is a linear relation between ionic liquid and extraction efficiency. Slope analysis of the graph between logarithm of distribution ratio D, and logarithm of [**IL-1**] and [**IL-2**] respectively were performed. A linearly dependent curve was observed with slope= 1.5 with **IL-1** and slope= 1.39 with **IL-2** respectively. If we approximate the slope to 1, then it indicates that 1:1 complexation has occurred. This suggests that ionic liquids being dicationic in nature, 2 protons were released from 1 unit of both the ILs respectively against 1 unit of Pb(II) ion extracted. Disappearance of protonated -COOH peak at 1719 cm^{-1} in Pb-IL complexes soluble in ionic liquid phase indicates complete deprotonation of the -COOH groups (**Fig. 5.9**) and metal exchange in place. From the combined results of slope analysis (**Fig. 5.12**) and FT-IR analysis results of Pb-IL complexes (**Fig. 5.9**), a plausible structure of Pb-IL

complex, is proposed in **Fig. 5.13**. The extraction mechanism and plausible structure are proposed below.

$$M^{2+}_{(aq)} + H_2R_{(IL)} \longrightarrow MR_{(IL)} + 2H^+_{(aq)}$$
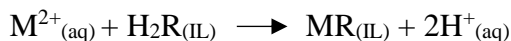
$$K_{ex} = [M]_{(IL)} [H]^2 \big/ [M]_{(aq)} [RH_2]$$

$$K_{ex} = D [H]^2 \big/ [RH_2]$$

$$\log[D] = \log K_{ex} + 2pH + \log [RH_2]$$

Here, K_{ex} is equilibrium constant, and D is distribution ratio of metal concentration, RH_2 represents one unit of the ionic liquid in protonated form with 2 protons of the -COOH groups.
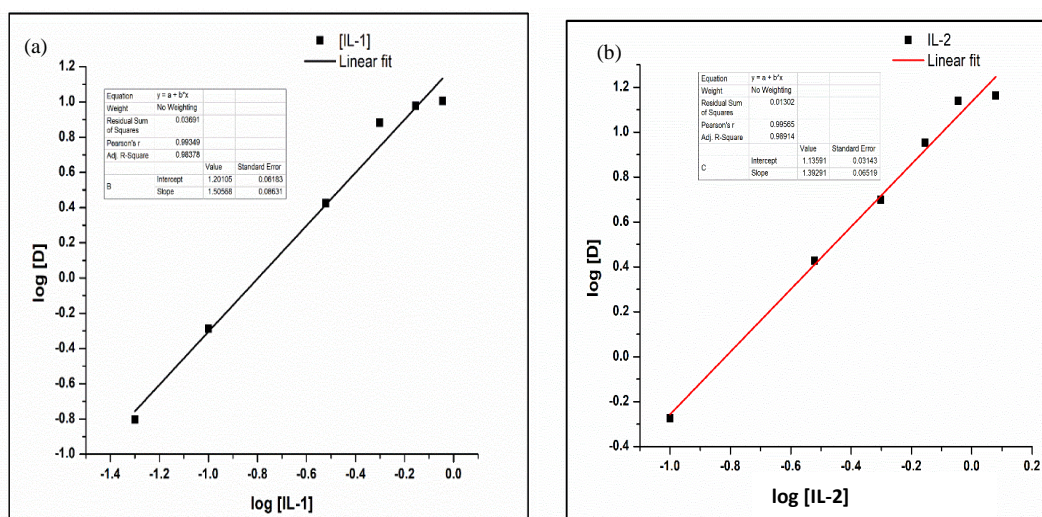

Fig. 5.12: (**a**) Graph between log D and log [**IL-1**] for the extraction of Pb(II), (**b**) Graph between log D and log [**IL-2**] for the extraction of Pb(II). Reaction condition: 20 mL of 7.25 mM aqueous metal solution of Pb(NO$_3$)$_2$, **IL-1** = 0.05, 0.1, 0.3, 0.5, 0.7 0.9 mmol, **IL-2** = 0.1, 0.3, 0.5, 0.7, 0.9, 1.2 mmol. Reaction time = 30 minute.
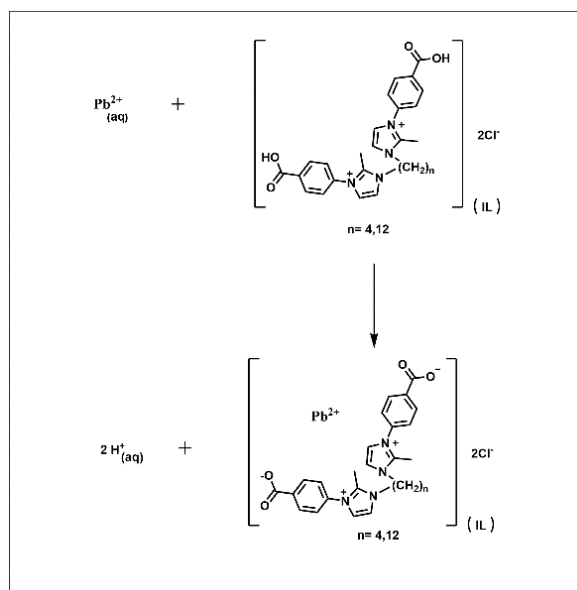
Fig. 5.13: Proposed structure of the Pb-IL complexes formed.

5.6 Results of back-stripping methods for Pb-IL1 and Pb-IL2

During the back-stripping of metal loaded ionic liquids with HCl, the recovery of original ionic liquids was not possible. This might have happened because there is a possibility of the ILs getting leached into the aqueous phase when reacted with HCl.

It was observed that the back-extraction was possible only with oxalic acid. Precipitation of metal oxalate started after continuous stirring of the metal loaded ionic liquid soluble in dichloromethane (DCM) with oxalic acid solution (2M) for 1 hour at room temperature. The ionic liquid being soluble in DCM, retained in DCM whereas the metal oxalate is isolated as the solid phase. The metal oxalate precipitate thus obtained was washed with distilled water for 5 to 6 times and dried in oven at 50 ºC and subjected for FT-IR (**Fig. 5.14**) analysis to know existence of functional groups of the oxalate salt. The organic DCM layer collected earlier was washed several times with deionized water. Finally, the IL after evaporation of DCM was recovered and dried in vacuum. The purity of IL was examined using FT-IR. We observed that the peak at 1719 cm^{-1} in **IL-2** which disappeared after metal ion exchange appeared in the FT-IR spectrum of the back stripped ionic liquid (IL-2R), with slow fading of peak of deprotonated COO$^-$ peak at 1634 cm^{-1} (**Fig. 5.15**). The absence of peak at 1593 cm^{-1}, 1459 cm^{-1}, 1381 cm^{-1}, 1092 cm^{-1}, 1015 cm^{-1} (**Fig. 5.14**) indicates absence of any kind of ionic liquid impurity in the hydrated lead oxalate salt. This result infers that the metal cation is stripped back in exchange of proton from the oxalic acid. The lead oxalate salt obtained after treating Pb(II) loaded **IL-2** with oxalic

acid was then calcined at 500 ℃ and then the calcined sample was analysed using PXRD which expressed the formation of mixture of α-PbO and β-PbO in **Fig. 5.16**. Decomposition of lead oxalate to lead oxide at 500 ℃ resulted in appearance of α-PbO and β-PbO phase and the diffraction patterns in the spectrum was marked according to JCPDS no: 01-0797 for α-PbO and JCPDS no: 38-1477 for β-PbO phase. Conventionally, α-PbO exists as major phase at lower calcination temperature and as the temperature rises, it gets transformed into β-PbO phase [43]. In **Fig. 5.16**, maximum diffraction patterns of PbO are present for β-PbO phase and very few are present for α-PbO. The occurrence of both the phases in **Fig. 5.16** infers that at 500 ℃, most of the α-PbO phase has been transformed into β-PbO which resulted in a mixture of both the phases with β-PbO existing as the major phase. Thus, the extracted metal can be transformed into its oxide via calcination. **Fig. 5.17(a)** displays oxalate salt of lead obtained after reaction of oxalic acid solution with Pb-IL2 containing ionic liquid phase and **Fig. 5.17(b)** displays PbO obtained after calcination of the oxalate salt of lead. Presence of only Pb and O in the calcined sample was also confirmed by EDX, **Fig. 5.18**.
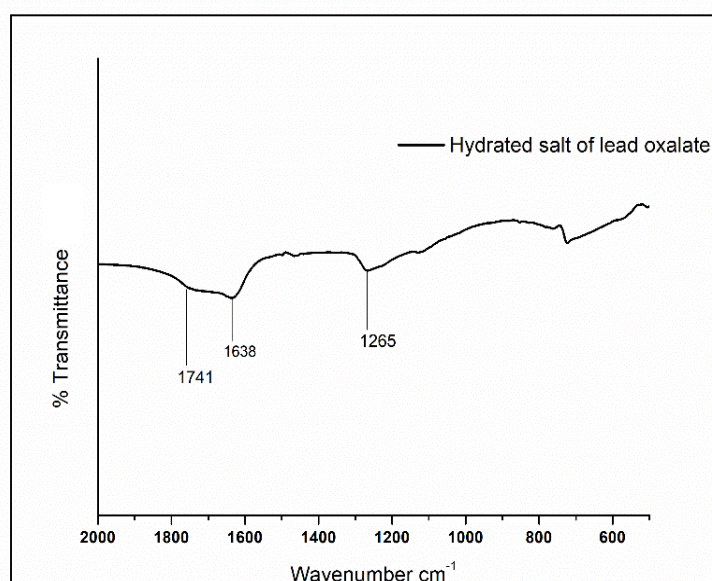

Fig. 5.14: FT-IR spectrum of oxalate salt of lead obtained by oxalic acid precipitation method with Pb-IL2 loaded ionic liquid phase.
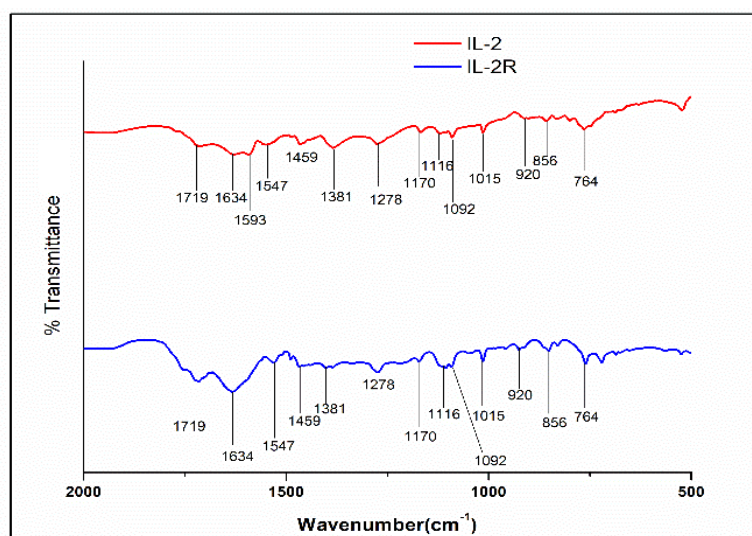
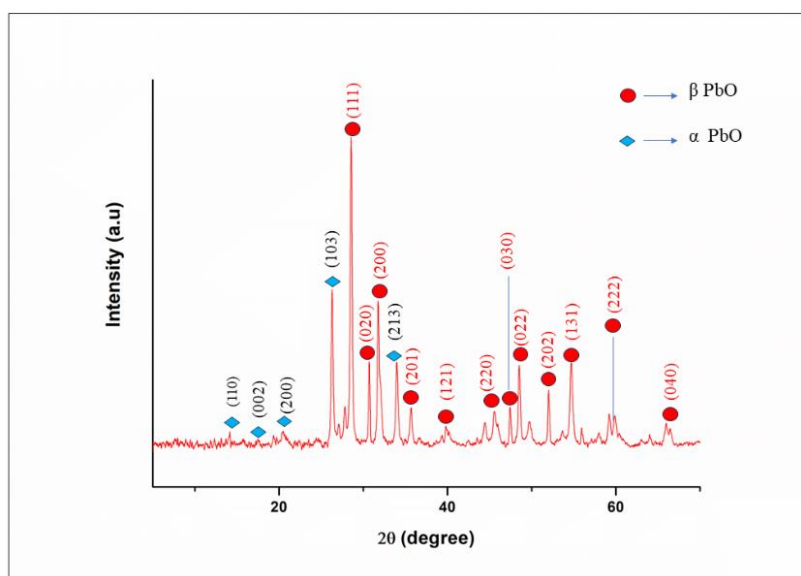**Fig. 5.15**: FT-IR spectra of regenerated ionic liquid (**IL-2**) compared to the fresh **IL-2**

Fig. 5.16: PXRD of PbO containing both the α as well as β phase obtained after calcination at 500ºC.
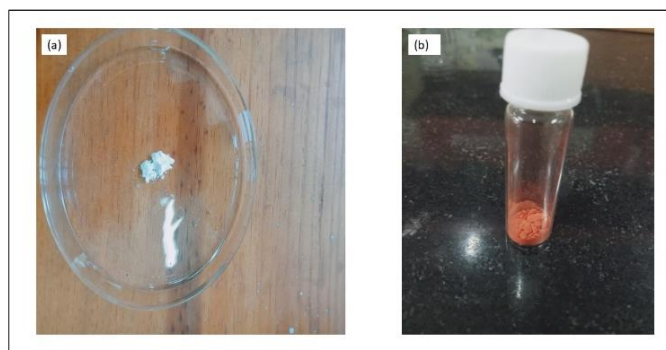
Fig. 5.17: (a) Oxalate salt of lead obtained after reaction of oxalic acid solution with Pb-IL2 containing ionic liquid phase (b) PbO obtained after calcination.
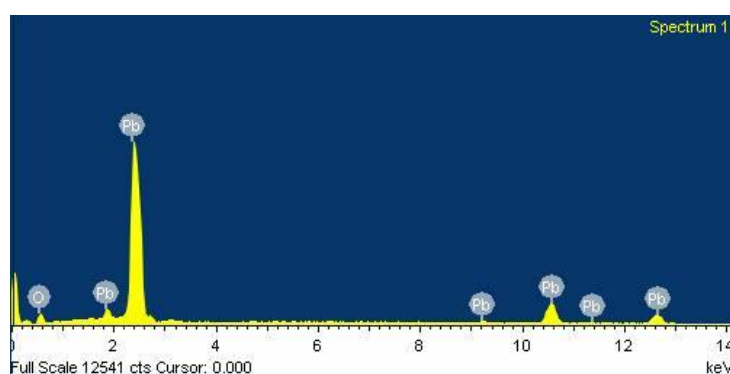

Fig. 5.18: EDX spectrum confirming formation of PbO after calcination at 500ºC.

The above results of ionic liquid recovery were observed in case of the **IL-2**. However, in case of the **IL-1**, the regeneration of the ionic liquid turned out to be difficult. After oxalic acid treatment of the metal loaded ionic liquid phase (Pb-IL1), EDX spectrum of oxalate salt showed presence of C, O, Pb, N elements with absence of chlorine (**Fig. 5.19**), which gives the possibility for exchange of two chloride anions with oxalate anions without disturbing the metal complexed dicationic imidazolium bridged cationic structures of the **IL-1**. For further confirmation, the TGA analysis of oxalate salt obtained by reacting Pb(II) loaded **IL-1** was done (**Fig. 5.20**) and compared with the chloride ion containing Pb-IL1 complex which represented identical degradation pattern up to 200 ºC. This indicates that whole of Pb(II) complexed cationic structure of the ionic liquid was exchanged with the oxalate anion which thus restricts the recovery of the used ionic liquid (**IL-1**). In **IL-2** with long bridged alkyl spacer (n=12), the imidazolium cation lies one above the other in a π-π stacking arrangements with the alkyl spacer chain folded in between the imidazolium dications. Presence of metal cation after extraction may destabilize the π-π stable confirmation which is why the back stripping of Pb(II) cation in exchange of 2 protons from oxalic acid becomes comparatively achievable when the metal

loaded-IL2 is reacted with aqueous solution of oxalic acid and thus results in regeneration of the **IL-2** in a much easier way. However, the **IL-1** with n=4, is observed to arrange itself in linear configuration. The extraction of Pb(II) cation does not have any effect on the overall linear configuration of the imidazolium cation on both ends. Therefore, the release of Pb(II) cation from the extracted phase is difficult which results in Pb(II) loaded dication complexation with the oxalate anion. This restricts the recovery of **IL-1** [44].
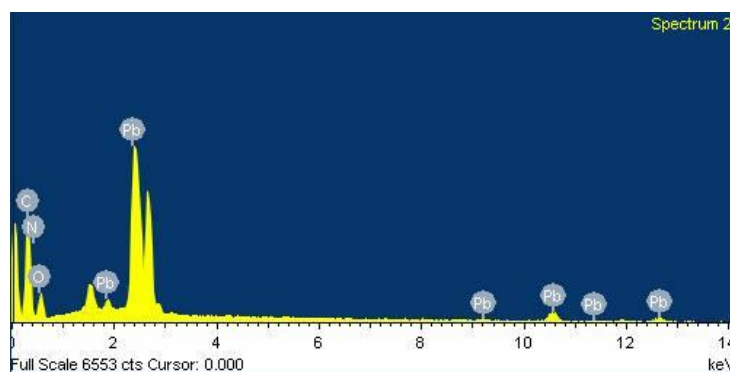
Fig. 5.19: EDX spectra of oxalate salt of lead obtained by oxalic acid precipitation method with Pb-IL1.
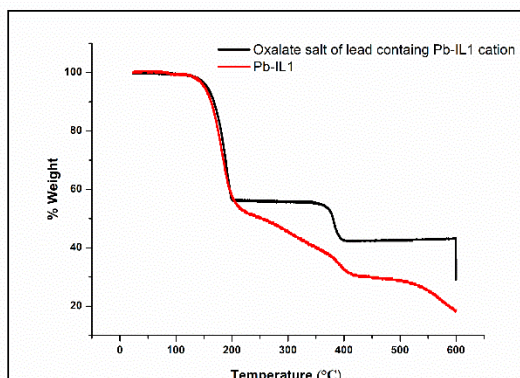
Fig. 5.20: TGA plots of Pb(II) loaded **IL-1** and oxalate salt of Pb(II) loaded **IL-1**.

5.7 Results discussing comparative and selective extraction experiments of Pb(II) in presence of Ni(II) and Co(II)

The results for **comparative extraction** experiments are represented in **Table 5.3** and **Fig. 5.21.** A histogram (**Fig. 5.22**) has been provided with error bars displaying the extraction in the order Pb(II) >> Ni(II)> Co(II). The tendency of **IL-2** to extract greater than 85% of Pb(II) is believed to have expansive use in analytical chemistry.

Fig. 5.21: Photographs displaying comparative extraction experiments of Pb(II), Co(II), Ni(II) using **IL-2**.

Table 5.3: Extraction percentages for comparative extraction experiments

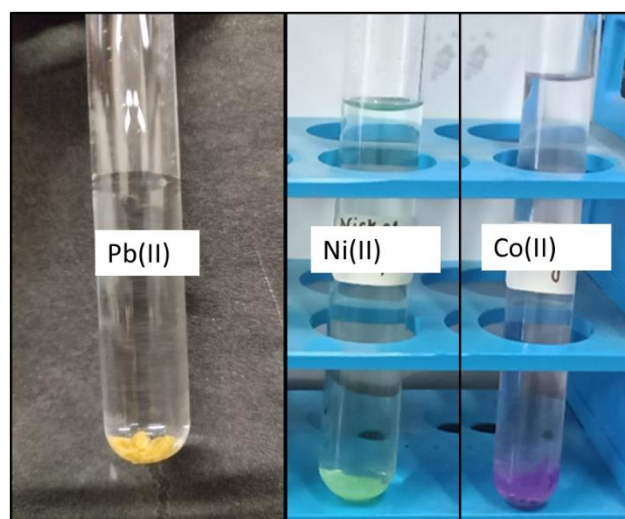| Entry	Metal	Extraction % (**IL-2**) (Trial-1)	Extraction % (**IL-2**) (Trial-2)	Extraction % (**IL-2**) (Trial-3)	Standard deviation	95% confidence interval
1.	**Pb(II)**	93.3	91.9	92.7	0.6934	0.7874
2.	**Ni(II)**	66	70	71	2.645	2.993
3.	**Co(II)**	41	41	39	1.154	1.306

All the metal solutions are diluted to a detectable limit of AAS and then the resultant value is multiplied with the dilution factors respectively.

Fig. 5.22: Histogram displaying comparative extraction percentages of Pb(II), Ni(II) and Co(II) using 0.9 mmol of **IL-2**; error bars arise from n = 3 independent trials.

The results for **selective extraction** experiments are displayed in **Fig. 5.23** and **Table 5.4**. A histogram (**Fig. 5.24**) has been provided with error bars displaying the extraction

percentages. The results obtained from AAS showed that Ni(II) and Co(II) were also coextracted with Pb(II). Although the extraction efficiencies were in the order Pb(II)> Ni(II) > Co(II). It was observed that at an average of (67.6 ± 5.695) % extraction of Pb(II) from the mixture was obtained with (15.6 ± 6.232) % extraction of Ni(II) and (6.3 ± 1.72) % extraction of Co(II). The selectivity results of **IL-2** with Pb(II) extraction in presence of other metal cations can be justified with the lowest enthalpy of dehydration of Pb(II) [45,46]. The driving force towards Pb(II) complexation with COO$^-$ may be the result of energetically favoured cation desolvation of Pb(II) compared to Co(II) and Ni(II). The tendency of **IL-2** to extract greater than 65% of Pb(II) from a multi-metal solution is believed to have expansive use in analytical chemistry.

Fig. 5.23: Photographs displaying selective extraction experiments from mixture of Pb(II), Co(II), Ni(II).

Table 5.4: Extraction percentages for selective extraction experiments from multi-metal solution

Entry	Metal	Extraction % (**IL-2**) for Trial-1	Extraction % (**IL-2**) (Trial-2)	Extraction % (**IL-2**) (Trial-3)	Standard deviation	95% confidence interval
1.	**Pb(II)**	67.2	73	63	5.033	5.695
2.	**Ni(II)**	22.1	12	13.5	5.50	6.232
3.	**Co(II)**	8	6.3	5.1	1.527	1.728

All the metal solutions are diluted to a detectable limit of AAS and then the resultant value is multiplied with the dilution factors respectively.
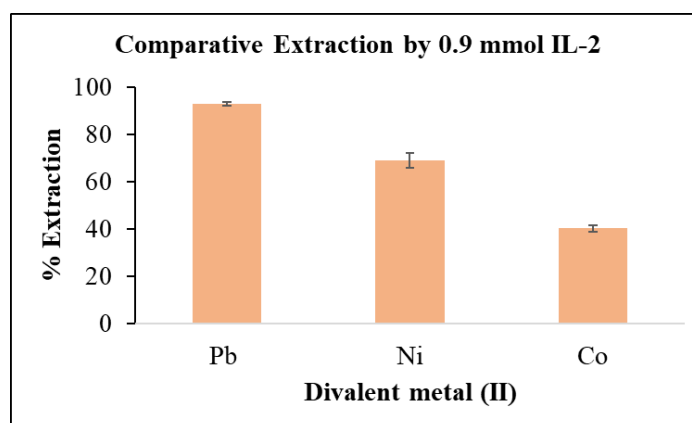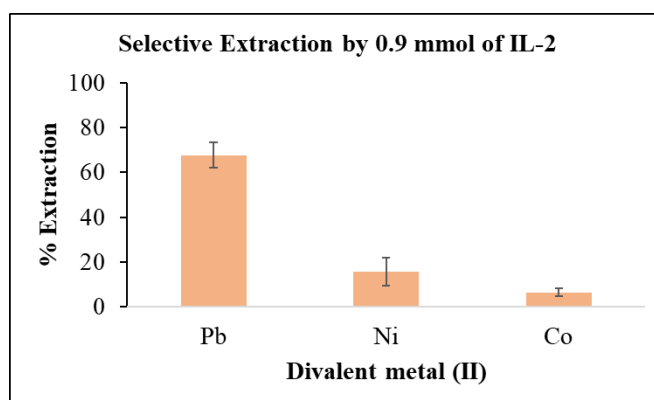
Fig. 5.24: Histogram showing selective extraction experiments from mixture of Pb(II), Co(II), Ni(II); error bars arise from n = 3 independent trials.

5.8 Recyclability and reusability of IL-2

The ionic liquid after the back extraction is collected in DCM layer is evaporated in rotary evaporator and the FT-IR results of IL-2R shows the retainment of all the peaks like original **IL-2** before extraction. The recovered ionic liquid is again used for one more cycle of metal extraction. It was observed that the extraction efficiency decreases from 93% to 71%. This might have happened because the 100% stripping of Pb(II) from **IL-2** did not occur. However, the whole process of metal extraction from aqueous phase and the extracted metal getting converted to its oxide form is a value-added method. In case of **IL-1**, the ionic liquid could not be recovered using oxalic acid. Thus, recyclability and reusability test could not be performed using **IL-1**.

5.9 Conclusions

In this work, **IL-1** named 1,1'(butane-1,4-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium) chloride and **IL-2** named 1,1'(dodecane-1,12-diyl)bis(3-(4 carboxyphenyl)-2-methyl-1*H*-imidazol-3-ium)chloride were synthesized, characterized and used as organic phase as well as extractant to extract Pb(II) from aqueous solution of $Pb(NO_3)_2$. The results from extraction studies performed on this report comprises of optimization of Pb(II) extraction, comparative extraction of Pb(II), Ni(II) and Co(II); selective extraction studies from multi-metal solution of Pb(II), Ni(II) and Co(II). Both comparative and selective extraction experiments showed the highest extraction percentage for Pb(II) in comparison to Ni(II) and Co(II), using very less amount **IL-2**. It was observed that Pb(II) could not be extracted selectively from a multi-metal solution as other metals Ni(II) and Co(II) are also co-extracted along with Pb(II). However, extraction

capacity of **IL-2** is also good for other divalent metal cations like Ni(II) from aqueous metal solution as observed from comparative metal extraction study. The results obtained from FT-IR spectra suggested metal exchange via deprotonation of carboxylic acid functionalized IL forming a hydrophobic metal-IL complex, which being hydrophobic in nature solubilizes in ionic liquid phase. The hydrophobicity in both the ionic liquids are introduced because of hydrophobic alkyl spacer ligands added while designing cationic part and extended intramolecular hydrogen bonding. The **IL-2** was extracted back in DCM and evaporation of the solvent under reduced pressure reproduced the **IL-2** back which could be reused in the next cycle. Moreover, the metal oxalate salt obtained via oxalic acid precipitation method is also calcinated to its oxide. Thus, the metal extracted from water is converted into its oxide form thus reducing the metal waste which can be used in fields like in battery uses. None of the compound goes into the sink as the extracted metal is also converted into its oxide in its purest form. The task-specific ionic liquid designed is quite efficient for extraction, as metal is extracted at a high extraction percentage and the back extraction with oxalic acid do not destroy the TSIL (**IL-2**). Thus, this method of using **IL-2** as hydrophobic metal extractant along with its easy recyclability proves **IL-2** to be good choice. So, planning to investigate extraction from aqueous solutions with higher lead (II) content can be helpful and useful as an alternative solution for extraction using conventional volatile organic solvent. The recyclable nature of hydrophobic carboxylic acid functionalized **IL-2** would be a promising extraction system for rare earth elements and other divalent metal cations too. Moreover, presence of -COOH group in **IL-2** makes it applicable to be used as acid catalyst for catalytic reactions too. Further development and modification in attached functional groups to improve the extraction as well as stripping processes is currently underway in our laboratory. Most importantly, use of non-fluorinated functionalized ionic liquids like **IL-2**, is in a way safer than use of fluorinated ILs and is a promising candidate for use as an extractant in biphasic aqueous system.

5.10. Experimental section

5.10.1 Procedure for synthesis of IL-1 and IL-2

An equimolar mixture of 1 mmol of 2-methylimidazole and 1 mmol of NaH was stirred in dry tetrahydrofuran (THF, 95%) (10 mL) as solvent at room temperature for 30 minute. Drying of tetrahydrofuran solvent was done by refluxing with sodium wire and benzophenone under nitrogen atmosphere for several hours until the solvent turns deep

blue in colour and then distilled under nitrogen atmosphere. The sodium salt of 2-methylimidazole **(I)** was obtained in 30 minute and after complete conversion of the 2-methylimidazole to its sodium salt, the residue was filtered and washed 2-3 times with tetrahydrofuran (THF) and dried in vacuum oven for 2 hours at 50 ºC. Hereafter, 1 mmol of the sodium salt of 2- methylimidazole was treated with (0.5 mmol) of 1,4-dibromobutane in THF (20 mL) and the mixture was refluxed for 10 hours and then filtered. Similarly, in another batch, 1 mmol of the sodium salt of 2- methylimidazole was treated with (0.5 mmol) of 1,12-dibromododecane in THF (20 mL) and the mixture was refluxed for 10 hours and then filtered. The respective filtrates were evaporated in reduced pressure and then washed thoroughly with diethyl ether for three times and then again evaporated under reduced pressure to get the respective intermediates 1,4-bis(2-methyl-1H-imidazol-1-yl) butane **(II)** & 1,12-bis(2-methyl-1H-imidazol-1-yl) dodecane **(III)** as brown sticky solids.

Subsequently, p-chlorobenzoic acid (1 mmol) was added to the solution of intermediate **II/III** respectively in THF (20 mL) respectively and the reaction mixture was stirred at reflux temperature for 8 hours. The solvent THF was removed under rotary evaporator at 60 ºC, and highly viscous residue was obtained at room temperature. Then it was washed three times (3×5 mL) with water to remove any water-soluble impurities and then again drying them at 70ºC in vacuum give us the **IL-1** which is viscous liquid at room temperature and **IL-2** which is sticky solid with paste like consistency at room temperature.

5.10.2 Extraction experiments using prepared ionic liquids

The biphasic metal extraction experiments were done in water with the **IL-1** and **IL-2** in 50 mL round bottom flask. With the density of **IL-1**(1.40g/cm^3), and **IL-2** (1.28g/cm^3), certain mmol of ionic liquids were measured for the extraction experiments against constant volume of 20 mL of varying millimolar aqueous solution of $Pb(NO_3)_2$. **IL-1** is liquid at room temperature and **IL-2** is pasty solid at room temperature but melted at 54 ºC before reaction. The reaction mixtures were stirred using a magnetic stirrer for another 30 minute at room temperature to continue the extraction of metal ion by the ILs. The pH of the aqueous metal solution, Pb(II) was measured and found to be 4.5 before carrying out the extraction experiments.

Thereafter, the biphasic liquid-liquid mixture was allowed to settle down for few minute to complete the separation of layers. The upper aqueous phase of known volume of solution was taken out by syringe and treated with 0.2 M HNO$_3$ (1 mL) before the analysis and diluted to detectable limit of the AAS spectrometer and the unextracted metal ion concentration in the aqueous layer was detected by Atomic Absorption Analysis. The results obtained were multiplied by dilution factor to get the actual metal ion concentration. For this purpose, initially 20 mL of 7.25 mM of Pb(NO$_3$)$_2$ aqueous metal salt solution was prepared. Then the prepared aqueous metal solution was mixed well with 1 mmol of the **IL-1** as mentioned in the above written procedure. By observing initial good result of extraction for the Pb(II) ion as heavy metal, we continued the study further for this metal ion varying the mmol of ionic liquids and the concentration of metal salt solution to get best extraction performances. 20 mL of 7.25mM Pb(NO$_3$)$_2$ aqueous metal salt solution was kept constant against varying the **IL-1** amount from 0.05 mmol to 0.9 mmol and the extraction efficiency (E%) of the **IL-1** was determined. Similarly, 0.2 mmol of **IL-1** was then kept constant varying the Pb(II) concentration in the aqueous phase using varying millimolar solutions of Pb(NO$_3$)$_2$ salt i.e. 2.25 mM, 3.65 mM, 7.25 mM, 14.5 mM prepared as 20 mL of aqueous metal salt solution. In the same manner, the whole set of experiment was repeated with **IL-2**.

The following formulas are used for calculations of E% (Extraction Efficiency), D (Distribution ratio):

E% = [(C$_i$)$_{aq}$ − (C$_f$)$_{aq}$ /(C$_i$)$_{aq}$]× 100   Equation (5.1)

D = [(C$_i$)$_{aq}$ − (C$_f$)$_{aq}$ /(C$_f$)$_{aq}$]   Equation (5.2)

Here C_i and C_f are the initial and final concentration of metal ions in aqueous medium.

5.10.3 Back-stripping experiments using IL-1 and IL-2

Back-extraction experiments were studied for metal loaded ionic liquids with oxalic acid (2M) solution and 2M solution of HCl. Back extraction with HCl was performed by treatment of metal loaded ionic liquids with 2M HCl solution. And the precipitation stripping method was performed by treatment with 2M aqueous oxalic acid solution. Metal loaded ionic liquid soluble in dichloromethane (DCM) was stirred with oxalic acid solution (2M) for 1 hour at room temperature.
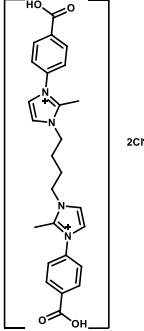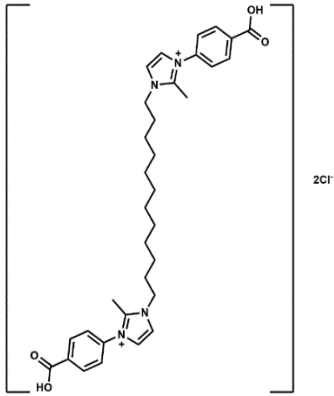
5.10.4 Comparative and selective extraction experiments of Pb(II) in presence of Ni(II) and Co(II) using IL-2

Three different metal solutions were prepared for the **comparative extraction experiments**. Solution 1 consists of 7.25 mM PbNO$_3$ at pH 4.5; Solution 2, contains 7.25 mM NiNO$_3$·6H$_2$O at pH 4.5; Solution 3, 7.25 mM CoCl$_2$·6H$_2$O at pH 4.5. The metal solutions are then poured into three different reaction vessels containing 0.9 mmol of **IL-2**. The reaction vessels were properly closed and stirred in magnetic stirrers at 600 rpm for 30 minute. After that the systems were allowed to settle for another 15 minute. The aqueous phase was collected, and the percentage extraction of different metals were determined by AAS.

In order to evaluate the **selective extraction efficiency** of **IL-2** towards Pb(II) from a multi metal mixture of Pb(II), Ni(II), Co(II) following experimental method was performed. Three different solution were prepared containing the following metal ion concentrations: Solution 1: 21.75 mM Pb(NO$_3$)$_2$ at pH 4.5; Solution 2: 21.75 mM Ni(NO$_3$)$_2$·6H$_2$O at pH 4.5; Solution 3: 21.75 mM CoCl$_2$·6H$_2$O at pH 4.5. All the above three solutions were prepared as 10 mL of metal salt solution separately. 10 mL of each solution (1, 2, 3) were transferred into another reaction vessel, Solution: 4. The resultant 30mL Solution 4 now has molarity of 7.25 mM of Pb(NO$_3$)$_2$, Ni(NO$_3$)$_2$·6H$_2$O and CoCl$_2$·6H$_2$O each respectively. In order to check the selectivity of **IL-2** towards Pb(II) in presence of Co(II) and Ni(II), 0.9 mmol of **IL-2** was used for extraction. The reaction vessels were properly closed and stirred in magnetic stirrer at 600 rpm for 30 minute. After that the system was allowed to settle for another 15 minute. The aqueous phase was collected, and the percentage extraction of different metals were determined by AAS.

5.11 Spectral data of IL-1 and IL-2

Table 5.5 Spectral data of IL-1 and IL-2:

Structure	Spectral data
  IL-1	White coloured viscous liquid at room temperature. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.49 (s, b, 2H), 7.96(d, 4H, 10 Hz), 7.53(d, 4H, 10 Hz), 6.87-7.12 (m, 4H), 3.92 (s, 2H), 2.34- 2.38(m, 8H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.55, 13.26, 31.23, 27.48, 45.34, 120.35, 120.81, 125.21, 128.96, 131.5, 137.61, 144.10, 167.46. CHN analysis: Calculated for **IL-1** (%): C 58.75, H 5.27, N 10.54; Found: C 57.24, H 5.31, N 10.02.
  IL-2	White coloured pasty solid at room temperature and turns viscous liquid at 54ºC. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.81 (s, b, 2H), 7.95 (d, 4H,10 Hz), 7.55 (d, 4H, 10 Hz), 6.89-7.4 (m, 4H), 3.87(t, 2H, 10 Hz), 2.33-2.37(m, 8H), 1.62-1.70 (m, 4H), 1.21(s, 16H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 12.47, 13.30, 26.37, 29.0, 29.36, 30.43, 45.88, 120.40, 120.81, 121.74, 124.81, 124.99, 129.00, 131.30, 131.59, 137.73, 144.00, 167.34. CHN analysis: Calculated for **IL-2** (%): C 63.45, H 6.84, N 8.709; Found: C 58.87, H 6.90, N 7.88.

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