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Extraction of the heavy metals from the aqueous phase in ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate by N-salicylideneaniline

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Abstract

The extraction behavior of heavy metals in aqueous phase by using the N-Salicylideneaniline (SA) extractant in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate was studied in room temperature. The extractant SA and the ionic liquid used were synthesized and characterized by the different methods of analysis like IR, ^{1}H-NMR,^{13}C-NMR and elementary analysis. The extraction mechanism of different metals with surfactant SA was studied by varying the experimental parameters, such as pH and concentration of ligand. The results showed that the pH of aqueous medium had a great effect on the efficiency of the process and on the percentage of extraction. The optimum pH for Ni^{2+}, Co^{2+} and Pb^{2+} was 4, 5 and 6 respectively, but the extraction process observed for Cu^{2+} was independent from the pH of solution. Using two different non-aqueous medium with the ligand to extract these metals under the same conditions shows that the extraction efficiency is higher in the ionic liquid then inthe chloroform. The association constants of complexes formed in ionic liquid for different metals are 2.74 10^7 for Ni^{2+}, 2.29 10^6 for $Co^{2+}$and 2.08 10^3 for Pb^{2+}. The stoichiometries of complexes between Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+} and the ligand were 1:2 for all metals used.

*Keywords***:** Liquid-liquid extraction, ionic liquid, N-salicylideneaniline, metal ions extraction

1. Introduction

The main objective of chemistry lies on research, discovery and exploitation of environmental appropriate methods. Today the new chemistry should aim at prevention; it must design and implement clean and safe processes, using less expensive raw materials and reducing the generation of wastes such as heavy metals. Liquid–liquid extraction has often been a good choice technique to separate heavy metals from industrial wastewater and in the development of separation process [1]**.**One of the biggest problems for traditional solvent extraction is employing organic solvent, which evaporates into the atmosphere with detrimental effect on the environment and human health [2]. The main focus of interest is the replacement of these often toxic volatile organic solvents, which are used extensively today. Among the various alternative considered strategies is the possibility of the use of ionic liquids. In recent years, ionic liquids have attracted much attention in different areas of chemistry due to their new chemical and physical properties [3, 4]. ILs has shown significant promise as media for organic synthesis and biphasic catalysis [5-12], extraction [13-18] and industrial processes [19]. The possible application of ionic liquid for liquid-liquid extraction of metals from wastewater based on combination with chelating agent is an important part when used in coupling with organic solvent to extract metals ions from water and are capable of metal and extraction with the final step in the extraction procedure that is referred to as the partition between the two phases [20]**.** The following are some examples of liquid-liquid extraction of metal ions from various solutions via ILs [21- 24]. The efficiency of extraction and selectivity can be affected by size of the chelate ring and type of its donor atoms, oxidation state and size of the metal ion, and pH of the solvent system [25]**.** In this work, the famous ligand N-salicylideneaniline in metal ion extraction was used in combination with ILs for the extraction Cu^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} by varying several parameters that can influence the extraction efficiency.

2. Materials and methods

2.1. Apparatus

A flame atomic absorption spectrometer (FAAS) model analyst Perkin Elmer (spectro AA 55B) was used for the determination of metal concentration using an air-acetylene flame. The pH values were measured by pHmeter (Tacussel model CPH 230 I). NMR spectra of ionic liquid and ligand were obtained in $CDCl_3$, ^1H NMR (250 MHZ), $^{31}P$and ^{19}F (400 MHZ) were recorded on a nuclear magnetic resonance spectrometer NMR model Bruker AC 250 and 400.Thermo scientific flash 2000, organic elemental analysis was used for identifying ionic liquid and extractant. Infrared spectra were recorded on a Fourier transform infrared spectrometer model Perkin Elmer (BX FT-IR). Heathrow scientific agitation HAS shaker was used for mixing.

2.2. Reagents and Materials

All reagents synthesis of IL including 1-méthylimidazole (99%), 1-chlorobutane (99%), and hexafluorophosphoric acid (60 wt% solution in water) were obtained from Acros Organics (Geel, Belgium). 1-methylimidazole, 1-chlorobutane and all solvents were distilled before use [26].

The ligand N-salicylideneaniline (SA)(Fig. 1) was synthesized according to the general condensation procedure [27].

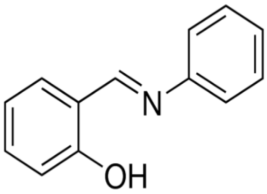

Figure 1.N-Salicylideneaniline

The product was recrystalized from ethanol to give yellow powder with a yield 90% and m.p of 49.5- 50 °C (lit. 51°C) [28]. The purity was checked by elemental analysis, IR and ^1H NMR analytical. For $C_{13}H_{11}NO$: C 79.19, H 5.57, N 7.12. Found: C 79.25, H 5.55, N 7.18. IR (KBr) δ 3440, 1613, 1480, 1395, 1277, 1031, 977, 894, 750 cm^{-1}. Spectral dada for SA ^1H-NMR (250 MHz, $CDCl_3$) δ 13.55 (s, 1H, OH), 8.65 (s, 1H, C (H) =N), 6.8-7.5 (m, 11H, ArH).

2.3. Synthesis of ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate

The structure of ionic liquid (Fig. 2), was confirmed by using ^1H, ^{19}F and ^{31}P NMR. The synthesis was based on the anion exchange from 1-butyl3-methylimidazolium chloride (BMIM, Cl) and HPF_6 acid. The ionic liquid was synthesized [29-32], purified and dried [33, 34]**.** The spectral data for (BMIM, PF_6): ^1H-NMR (250 MHz, $CDCl_3$) δ ppm: 0.93 (t,3H), 1.35 (q,2H), 1.90 (m, 2H), 4,00(s, 3H), 4.32(t, 3H), 7.66 (d, 2H), 8.88 (s, 1H); ^{13}C NMR (250 MHz, $CDCl_3$): δ 137.02, 124.38, 123.00, 49.85, 36.20, 32.30, 19.58, 13.30.^{31}P NMR ($CDCl_3$) δ ppm: – 144.20 (septet, PF_6^-); ^{19}F NMR ($CDCl_3$) δ ppm: –70.95, –72.85 (d, PF_6^-). Elemental analysis of IL found: C: 33.77; H: 5.91; N: 9.98; F: 40.10; P: 10.72.

2.4. Liquid-liquid extraction of metal ions in ionic liquid(IL) or chloroform

Different parameters are taken into consideration in the extraction of metals at room temperature indicating the concentration of ligand used, pH of solution and extraction time. All experiments were performed in duplicate.

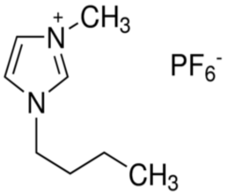

Figure 2. *Structure of 1-butyl-3-methylimidazolium hexafluorophosphate*

Extraction of metals was conducted with 3ml of metal solution concentration 30 mg/l and 1 ml ionic liquid containing the ligand 30mg. An optimal extraction time for different metals shaken was120 min for $Ni(NO_3)_2$, 30 min for $Co(NO_3)_2$, $Pb(NO_3)_2$ and $Cu(NO_3)_2$. They were stirred in a shaker and then centrifuged to separate two phases. The aqueous phase recovered and the concentration of each metal was measured by the use of atomic absorption spectrophotometer. The extraction efficiency and the distribution coefficient of metal ions were calculated by using Eq (1) and Eq (2) respectively.

$$\%E = \frac{(C_i)_{aq} - (C_f)_{aq}}{(C_i)_{aq}} \times 100 \qquad (1)$$

$$D = \frac{(C_i)_{aq} - (C_f)_{aq}}{(C_f)_{aq}} \times \frac{volmeofaqueousp\ \ hase}{volumeofILp\ \ hase} \qquad (2)$$

Where $(C_i)_{aq}$ and $(C_f)_{aq}$ represent the initial and final concentrations of metal ion in the aqueous phase, respectively

3. Results and discussion

The effect of several experimental parameters (pH, extractant concentration and extraction time) was investigated in order to find optimal operation conditions.

3.1. Effect of pH on metal extraction

pH was the first parameter evaluated on the extraction of different metal ions. Thus in this study, the extractions of metals which were performed at different pH solution. The extraction percentage of Cu^{2+}, Co^{2+} and Ni^{2+}exceeds 80% when the pH = 3, or simply for Pb^{2+} is less than this value at the same pH From pH= 4 the extraction percentage is almost 100% for Cu^{2+} and Ni^{2+} and a little less for the Co^{2+} but for Pb^{2+} there is a dramatic increase from pH value and it can reach 90% at pH = 6. This means that the acidic medium does not have a remarkable percentage of extraction and this is confirmed by the existence of protons provided by HNO_3, the deprotonation of the ligand to form the complex or the decomposition ofPF_6^-, releasing HF in the presence of nitric acid or water in ionic liquid [35,36] and all this is confirmed by the equation (5) which indicates that the extraction of metals depends on the pH. Figure 3 shows the comparison of extraction of metal ions from aqueous phase into ionic liquid and into chloroform as a function of pH. Relying on the observations and the results, it is shown that the ionic liquid is better for metal extraction than chloroform. All this is confirmed by other results in the literature [13,15,17]. The most important remark that can be distinguished from this figure is that the extraction of the three metals Co^{2+}, Ni^{2+} and Pb^{2+} depends on the pH (5, 4 and, 6 respectively) but for Cu^{2+}already at pH = 3, the extraction rate is very high, so the extraction process is quite independent from pH and more at the ionic liquid phase we noticed the existence and the formation of a complex of a dark brown color. The complex might be the result of oxidation of the ligand by Cu^{2+} ion to form complex electron transfer as reported by Larkworthy et al [37]**.**The extraction of Cu^{+} was performed according to the hypothesis that Cu^{2+} is reduced to Cu^{+} during extraction. The color of the ionic liquid after extraction confirmed this assumption and the extraction between Cu^{2+} and Cu^{+} is not the same since the second depends on pH.

3.2. Effect of extractant concentration

The optimization of the extractant concentration is necessary to design the optimum extraction process and quick recovery of the metal. To achieve this aim, a series of experiments were performed in 3 ml of metal solution containing 3 ppm in 100 µl ionic liquid and various concentrations of extractant N-salicylideneaniline, over the range of 0.210^{-2} mM/L to 310^{-2} mM/L were subjected to the extraction process under pH = 4 and room temperature.

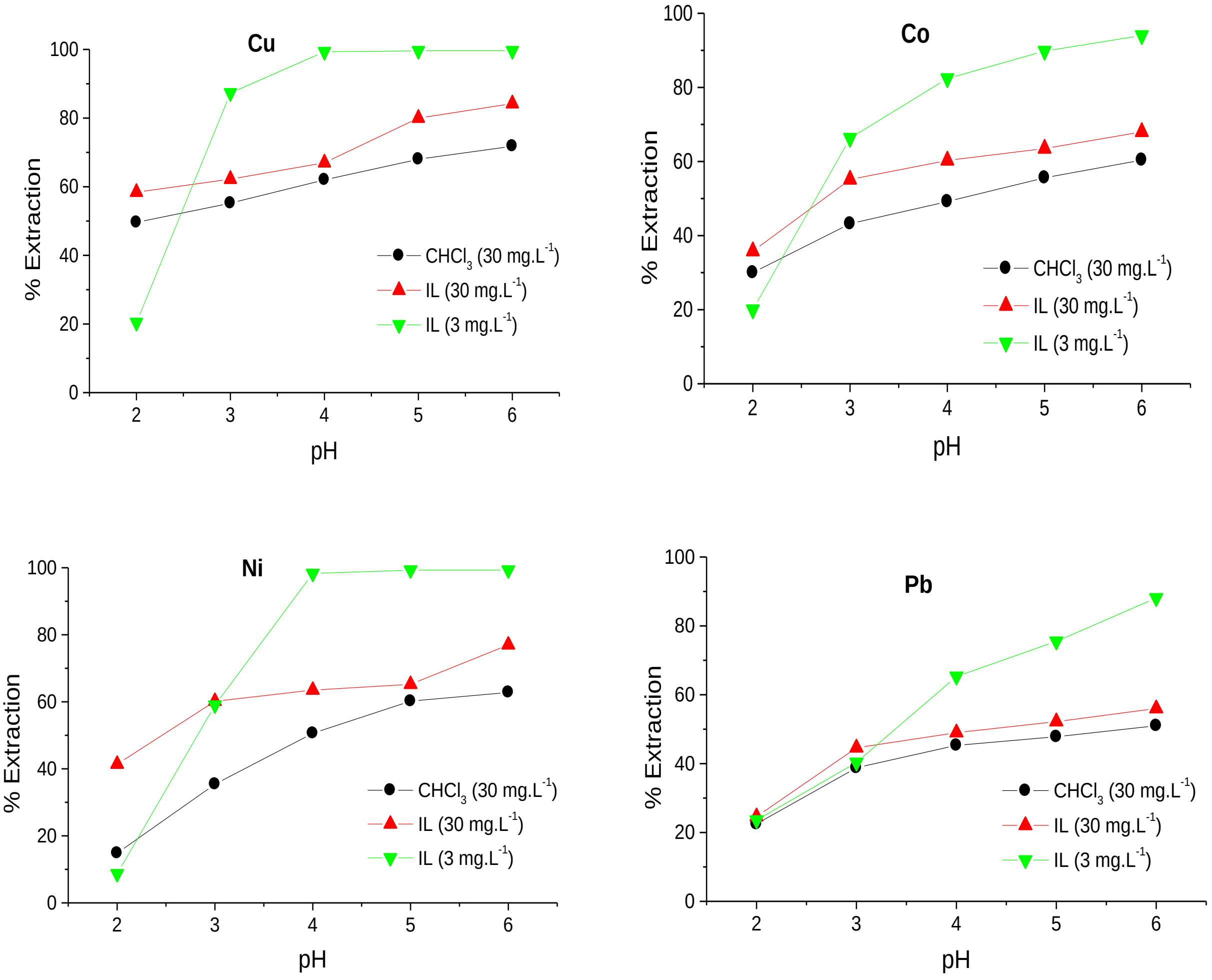

Figure 3: Effect of pH on the extraction of Cu^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} in different solvents: ionic liquid (3 mg.L^{-1}), ionic liquid (30 mg.L^{-1}) and chloroform ($CHCl_3$) (30 mg.L^{-1}) ([L] = 1.510^{-2}mM, 25°C).

The results are shown in (Fig.4) it is shown that the extraction's percentage of different metal ions increases with the increasing of ligand's concentration. At an extractant concentration higher than 110^{-2} mM/L the extraction percentage and efficiency showed insignificant changes. The concentration of the extractant (SA) that provides the highest extraction and efficiency 100% with a small amount of extractant and complete extraction is about 1.510^{-2} mM/L. Thus, this concentration was used in subsequent experiments.

3.3. Effect of extraction time on extraction efficiency

The extraction efficiency is a function of time which differs from one metal to another, the comparison of the four metals after an hour of contact between the two phases gives a slight increase for Ni^{2+}, Co^{2+} and Pb^{2+} contrary to Cu^{2+} were was a decrease, nevertheless, after 30 minutes, this metal's extraction rate is high compared to the three other metals, this can be explained by the dissolution of the copper complex in the aqueous phase. By contrast, the extraction efficiency of Pb^{2+}, Ni^{2+} and Co^{2+} was up to one hour of contact, this means that complex formation reached its maximum efficiency, but after that time, the three metals have a slight decrease may be due to some degradation of the complex (Fig. 5).

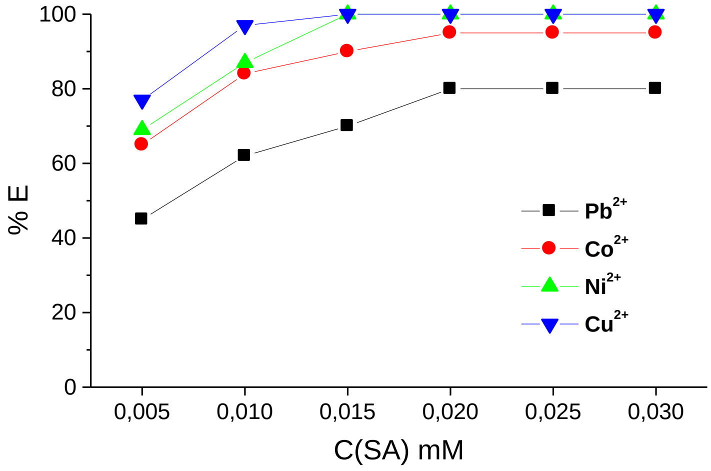

Figure 4: Plots of the extracted ratios (E %) for Pb^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} at 0.1 M HNO_3 as function SA concentration.

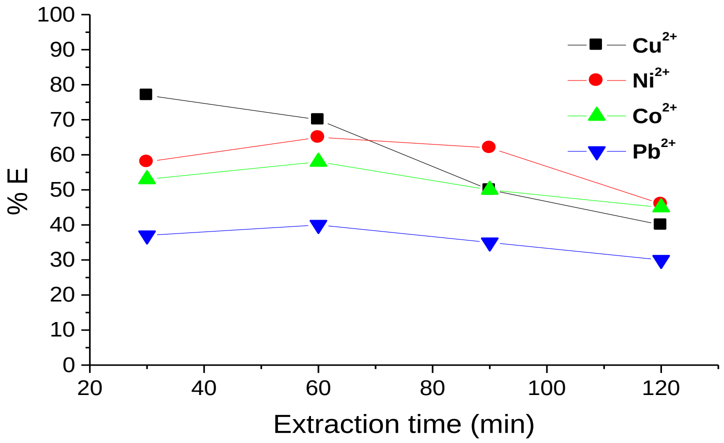

Figure 5: Effect of extraction time on metal ion extraction ($[L]_{IL}$ = 30 mg, [M] = 30mg, 3ml, pH 4)

3.4. Extraction mechanism, Stoichiometry of the extracted species and association constants in ILs

The phenomenon of mechanism extraction always makes the study of the used parameters and the reaction molecules to give an extraction capacity of metals in a high affinity and to achieve this, it is necessary to consider all species in the different environments. Before were known the ionic liquids, the extraction of metals was very simple with traditional organic solvents. Previous studies show that ionic liquids carrying two opposite charges are much more extractable metals about traditional solvents by anionic or cationic effect (Eq. 3.).

In our study, there is drastic enhancement of extraction of heavy metal by extractant SA in the presence of the ILs in comparison with traditional solvents or nonionic medium. The extraction of metal's mechanism is changed by the existence of nitric acid medium in the formation of the neutral metal nitric complex by SA in the organic medium. (Eq.4.).

On the other hand, several studies [38, 39] have shown that the mechanism of ion pairs with their complexes depends on the nature of the ion pairs, so in the presence of the latter, the extraction efficiency and the change of ion pairs have no influence on the extraction of metals which will change whatever parameters such as a concentration that can influence the precipitation and can cause the extraction of the metal, so the mechanism of ion pairs complexes is rarely findable. In RTIL based extraction of metal ions by neutral extractants there has been a report of different types of extraction mechanism for different types of extractant.

$$M_{aq}^{n+} + q(SA)_{IL} + q(bmim^{+})_{IL} \leftrightarrow (MSA^{n+})_{qIL} + q(bmim^{+})_{aq} \tag{3}$$

$$Mn^{+} + nNO_3^{-} + mSA \leftrightarrow [M(NO_3)_n(SA)_m] \tag{4}$$

Regarding the nitrate ions with the mechanism of ion and its reduction to the aqueous medium may associate extracting species in the ionic liquid phase and therefore it is assumed that the mechanism of ions association is almost negligible.

In liquid-liquid extraction, the system can be represented by the following reaction:

$$M_{aq}^{n+} + aHL_{IL} \overset{K_{ex}}{\longleftrightarrow} [ML_a(HL)_{a-b}]_{IL} + bH^{+} \tag{5}$$

Where M^{n+}_{aq} and HL_{IL} are the metallic solute and extracting ligand, respectively, in the aqueous and ionic liquid phase. $[ML_a\,(HL)_{a\text{-}b}]_{IL}$ is the complex in the ionic liquid phase, so

$$K_{ex} = \frac{[ML_a(HL)_{a-b}]_{IL}[H^{+}]^{b}}{[M^{+}]_{aq}\,[HL]_{IL}^{a}} \tag{6}$$

The distribution ratioD is given by

$$D_M = \frac{[M]_{IL}}{[M]_{aq}} \tag{7}$$

$$D_H = \frac{[H^{+}]_{IL}}{[H^{+}]_{aq}} \tag{8}$$

$$D = \frac{[ML_a(HL_b)]_{IL}}{[M^{+}]_{aq} + [ML_a(HL_b)]_{IL}} \tag{9}$$

And substitution of K_{ex} gives D:

$$D = \frac{[ML_a(HL)_{a-b}]_{IL}}{[M^{+}]_{aq}\,[HL]_{IL}^{a}}\,[HL]_{IL}^{a}[H^{+}]_{aq}^{-b} \tag{10}$$

$$D = K_{ex}\,[HL]_{IL}^{a}[H^{+}]_{aq}^{-b} \tag{11}$$

Or$logD = logK_{ex} + a.\,log[HL]_{IL} - b.\,log[H^{+}]_{aq}$ (12)

The logarithm of D is written as a function of the extracting ligand concentration [HL], and pH of aqueous phase.

$$logD = logK_{ex} + a.\,log[HL]_{IL} + b.\,pH \tag{13}$$

The equation (13) confirms that the extraction depends on the pH of the solution. In general, the separation efficiency for metal is based on the distribution ratio or extraction percentage, which can be predicted from extraction constant and the formation of constant. Then the distribution ratio of different metals about ligand in IL can be expressed in general with the extraction constant.

To determine the composition or the number of ligands used in metal complex, the extraction constant and the stoichiometry of the extracted species, the slope analysis method is suitable to identify these parameters and can be carried out by plotting log D_M=f(log$[HL]_{IL}$) by using the developed (Eq.12). So from the curve logD=f(log[HL]), we can determine the complex formed by the metal and the ligand extract. Slopes Values found from (Fig.6) for the extraction of the different metals Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+} are 2.04, 2.11, 1.98, and 1.87 respectively which is the stoichiometry of complexes 1:2 for all ions corresponding to the formula $[CuL(HL)]^{+}$, $[CoL(HL)]^{+}$, $[NiL(HL)]^{+}$, $[PbL(HL)]^{+}$.

The stoichiometry examination of the metal complex by using the method of slope determines the constant extraction K_{ex} based on the equation of log D as a function of the concentration of free ligand at equilibrium in the ionic liquid and pH constant, The calculated values of K_{ex} are listed in Table1.The association constant is a very essential parameter to develop efficient extraction of metals and is determined by the relation between the extraction constant and the distribution constant for metal ions. Based on the achieved results and the different reactions exercised after two medium in aqueous phase or ionic liquid in the following reactions 3.4.1, 3.4.2, 3.4.3 and the most interesting training stable complex metal-Nsalicylideneaniline in the ionic liquid for different metals by calculating constants associations in table1.the mechanism extraction which differs Cu^{2+} versus Cu^{+} is not available because the difference of extraction efficiency is caused by other factors such as the coordination of the metal in the ionic liquid and the existence of a redox reaction the Cu^{2+} to Cu^{+} and can give the possibility that N-salicylideneaniline are oxidized by Cu^{2+}, therefore the possibility that the mechanism extraction is influenced by environmental factors which may exist.

Table 1: Extraction constants and association constant of metal complex from water into IL

Metal	K_{ex}	K_{ass}
Ni^{2+}	0.6110^{8}	2.6410^{7}
Co^{2+}	0.4610^{7}	2.2910^{6}
Cu^{2+}	1.8910^{8}	-
Pb^{2+}	0.4110^{4}	2.0810^{3}

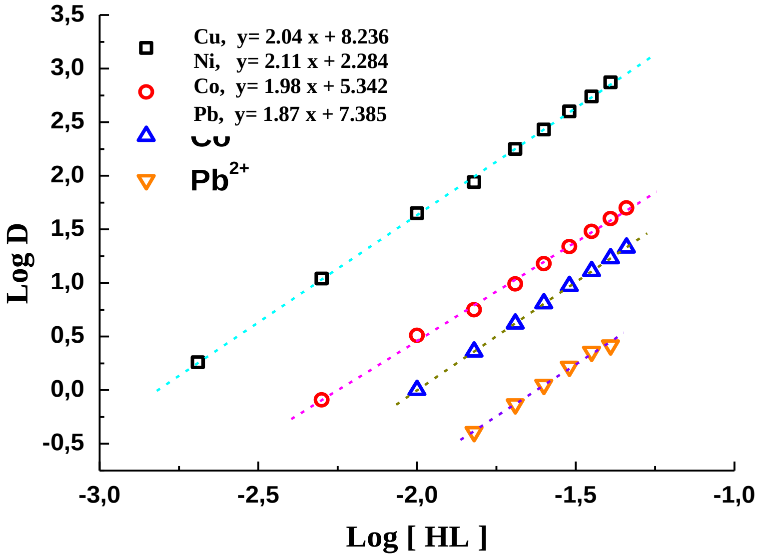

Figure 6: Plots of log D as a function of log concentration of free ligand in ionic liquid (V_{IL}= 100µL, V_M = 1mL, [M] = 3 mg, pH 4, 5)

From the results obtained above the mechanism extraction process can be described by the following reaction:

3.4.1. Extraction of Co^{2+}

In aqueous phase to ionic liquid

$$(Co^{2+})_{aq} + 2(HL)_{IL} \leftrightarrow [Co(L)(HL)]_{IL} + (H^{+})_{aq} \tag{14}$$

$$K_{ex,Co^{2+}} = \frac{[Co(L)\ \ (HL)\ \ ]_{IL}[H^{+}]_{aq}}{[Co^{2+}]_{aq}\,[HL]_{IL}^{2}} \tag{15}$$

The metal ion and ligand in ionic liquid

$$(Co^{2+})_{aq} + 2(HL)_{IL} \leftrightarrow [Co(L)(HL)]_{IL} + (H^{+})_{IL} \tag{16}$$

$$K_{ass,Co^{2+}} = \frac{[Co(L)\ \ (HL)\ \ ]_{IL}[H^{+}]_{IL}}{[Co^{2+}]_{IL}\,[HL]_{IL}^{2}} = \frac{K_{ex,Co^{2+}}D_H}{D_M} \tag{17}$$

3.4.2. Extraction of Ni^{2+}

In aqueous phase to ionic liquid

$$(Ni^{2+})_{aq} + 2(HL)_{IL} \leftrightarrow [Ni(L)(HL)]_{IL} + (H^+)_{aq} \quad (18)$$

$$K_{ex,Ni^{2+}} = \frac{[Ni(L)\ \ (HL)\ \ ]_{IL}[H^+]_{aq}}{[Ni^{2+}]_{aq}\,[HL]_{IL}^2} \quad (19)$$

The metal ion and ligand in ionic liquid

$$(Ni^{2+})_{IL} + 2(HL)_{IL} \leftrightarrow [Ni(L)(HL)]_{IL} + (H^+)_{IL} \quad (20)$$

$$K_{ass,Ni^{2+}} = \frac{[Ni(L)\ \ (HL)\ \ ]_{IL}[H^+]_{IL}}{[Ni^{2+}]_{IL}\,[HL]_{IL}^2} = \frac{K_{ex,Ni^{2+}}D_H}{D_M} \quad (21)$$

3.4.3. Extraction of Pb^{2+}

In aqueous phase to ionic liquid

$$(Pb^{2+})_{aq} + 2(HL)_{IL} \leftrightarrow [Pb(L)(HL)]_{IL} + (H^+)_{aq} \quad (22)$$

$$K_{ex,Pb^{2+}} = \frac{[Pb(L)\ \ (HL)\ \ ]_{IL}[H^+]_{aq}}{[Pb^{2+}]_{aq}\,[HL]_{IL}^2} \quad (23)$$

The metal ion and ligand in ionic liquid

$$(Pb^{2+})_{IL} + 2(HL)_{IL} \leftrightarrow [Pb(L)(HL)]_{IL} + (H^+)_{IL} \quad (24)$$

$$K_{ass,Pb^{2+}} = \frac{[Pb(L)\ \ (HL)\ \ ]_{IL}[H^+]_{IL}}{[Pb^{2+}]_{IL}\,[HL]_{IL}^2} = \frac{K_{ex,Pb^{2+}}D_H}{D_M} \quad (25)$$

Conclusion

The extractability of metal ions from medium with the extracting ligand, N- salicylideneaniline in biphasic system consisting of ionic liquid and an aqueous phase was studied using the liquid- liquid extraction process. ILs are environmentally benign because of their nonvolatile, nonflammable properties and limited pollution. This fact is particularly attractive because the green chemistry concept can be employed here. The use of chelate N- salicylideneaniline in two different middle ionic liquids and chloroform for the extraction of Cu^{2+}, Co^{2+}, Ni^{2+} and Pb^{2+} gives a high extraction efficiency in the ionic liquid compared to chloroform. The ligand SA form a more stable complex with 2:1 for different metals, and the latter were extracted with a stoichiometry of ML_2whatever their exchange mechanism and results for the association constant for the metal complex in the ionic liquid are 2.7410^7 for Ni^{2+}, 2.2910^6 for Co^{2+} and 2.0810^3 for Pb^{2+}.

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