Distribution Of Pb (II) Ions Into CHCl₃ Solution Of *N,N'*-Ethylenebis(4-Butanoyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-Oneimine) As Tris-Complex Species

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Abstract: *A study of the distribution of Pb(II) from aqueous media into chloroform solution of N,N'-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) H₂BuEtP and its mixture with (4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one) HBuP has been carried out. The pH₁/₂ of extraction of Pb(II) was slightly lowered from pH 5.88 ± 0.14 to 5.51 ± 0.13 when a mixture of the ligands was used. The physico-chemical properties were determined and the following values were recorded: partition coefficient (log K_D) 1.92 ± 0.25 (H₂BuEtP) and 1.82 ± 0.22 (H₂BuEtP-HBuP); extraction constant (log K_{ex}) -32.90 ± 0.07 (H₂BuEtP) and -9.79 ± 0.10 (H₂BuEtP-HBuP). Data analysis indicated that Pb(II) complexes distributed more effectively into chloroform solution of H₂BuEtP than into a solution of its mixture with HBuP, attributed to Pb(II) being extracted as the ion-pair tris-complex species $Pb(BuEtP)(BuEtP)_2^{4-}.4H^+$. Protonated Pb(HBuEtP).BuP species were extracted into organic solution mixture of the ligands. Extraction of Pb(II) from mineral acids, show that apart from sulphuric acid extraction is generally very poor, even when a mixture of H₂BuEtP and HBuP was used. However a mixture of the ligands is observed to be more effective in the extraction of Pb(II) from solution of anion than when H₂BuEtP is used alone. EDTA solution completely masked.the extraction of Pb(II) into organic solutions.*

Keywords- *acids, anions, extraction, lead(II), N,N'-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine)*

I.   Intrduction

Derivatives of 1-Phenyl-3-methyl-4-acyl-pyrazolone-5 are known for their complexation reactions with transition metals forming metal complexes with interesting coordination chemistry [1-4]. In continuation of our work on the synthesis and characterization [5] of derivatives of 1-phenyl-3-methyl-4-acylpyrazolone-5 we report the application of a Schiff base derivative of 4-butanoylpyrazolone as a potential extractant for metal ions. The synthesis provided an opportunity for a N=C-C-OH bonding moiety and extended the scope of coordination to involve tetradentate ligands from the initial bidentate 4-acylpyrazolone. Application of Schiff bases in selective adsorption of Yb(III) in the midst of a range of transition metal ions such as Eu(III), Gd(III), Nd(III), Tb(III) etc on a silica surface has been reported [6]. Earlier studies on isolation and characterization of metal complexes of Schiff bases have shown that they are capable of forming stable metal complexes [7,8] with Cu(II) and Ni(II) and unstable metal complexes with Mo(VI), Co(II) and Cd(II).

In this study the solvent extraction of lead(II) ions from aqueous media using *N,N'*-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) was investigated. Extraction of metal ions with Schiff base derivatives of 4-acylpyrazolone has attracted little or no attention in the literature. Thus the effect of pH, acids, anions and auxiliary complexing agents on the extraction of Pb(II) from aqueous solutions was investigated. The aim of the study was to see if there is a role played by the ability of Pb(II) to form both Pb-O and weak Pb-N bonds [9-10] in the extraction process.

II.   Materials and Method

2.1   Reagents and Apparatus

N,N'-Ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H₂BuEtP) (fig. 1) was synthesised by method described elsewhere [5]. The ligand was recrystallized from aqueous ethanol and its purity established by elemental analysis for C, H and N. Measurement of IR and NMR spectral data were carried out. All analysis and spectral measurement were done at the Institut fur Anorganische Chemie, Technische Universitat Dresden, Germany.
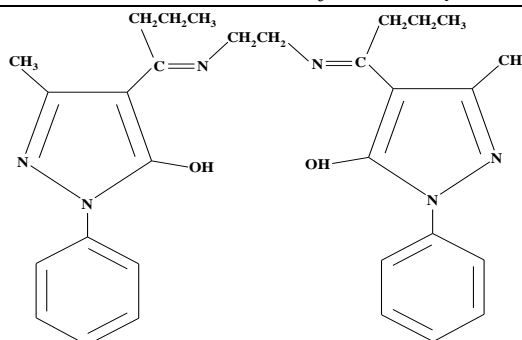
Figure 1; Structure of *N,N'*-Ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine)

Stock solutions of 0.05 M H₂BuEtP were prepared by dissolving appropriate mass of the ligand in CHCl₃. Those of 0.05 M 4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP) were also prepared by dissolving appropriate mass of the ligand in CHCl₃. Stock solutions of 1,000 mg/L of Pb(II) were prepared by dissolving appropriate mass of the metal nitrate (Pb(NO₃)₂) in 0.1 mL of 10 M HNO₃ and making up to mark in 50 mL volumetric flasks with deionized water. Buffer solutions were prepared with 0.1 M HCl/0.1 M NaCl (pH 1.0 – 3.0), 0.1 M acetic acid/0.1 M NaCl (pH 3.0 – 3.5), 0.1 M acetic acid/0.1 M Na-acetate (pH 3.6 – 5.6) and 0.1 M KH₂PO₄/0.1 M NaOH (pH 5.7 – 8.0). The actual pH of solutions were determined with a Labtech Digital pH meter.

A range of mineral acid, anion and complexing agent concentrations covering 0.001 – 2 M were prepared. This was done by diluting appropriate volumes of stock solutions of mineral acid or sodium salt of anion or complexing agent with deionized water.

2.2   Extraction Procedure

A 10 mL corked extraction bottle containing 2 mL aliquot of buffer solution and 50 mg/L of Pb(II) ions at a desired pH of solution was prepared. For extraction studies involving mineral acids, anion or complexing agents 2 mL aliquot of solution containing 50 mg/L of Pb(II) ions and the desired mineral acid, anion or complexing agent was prepared in a similar 10 mL corked extraction container. Two millilitre (2 mL) solution of 0.05 M concentration of H₂BuEtP or 0.05M H₂BuEtP:0.05 M HBuP (9:1 ratio by volume) in chloroform was pipetted into the aqueous phase in the extraction container. The immiscible phases were shaken mechanically for 30 minutes at a room temperature of 30 °C. A shaking time of 30 minutes was found suitable enough for equilibration. The two phases were allowed to settle and separated.

Concentration of Pb(II) ion in aqueous phase was determined with a Buck Scientific AtomicAbsorption Spectrophotometer (AAS) 205. Pb(II) ion concentration extracted into the organic phase was determined from the difference between the concentration of Pb(II) ion in aqueous phase before and after the extraction. Distribution ratio *D* was calculated as the ratio of metal ion concentration in the organic phase (*C_o*) to that in the aqueous phase (*C*). Thus D = *C_o*/*C*.

III.   Results and Discusion
3.1   Effect of buffer solution

Extraction of Pb(II) from aqueous phase into an organic phase '*(o)*' containing the ligand H₂BuEtP can be represented by equation:

$$Pb^{2+} + H_2BuEtP_{(o)} \rightleftharpoons Pb(BuEtP)_{(o)} + 2H^+ \qquad (1)$$
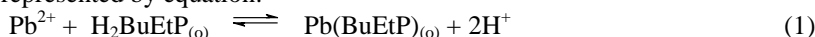
where H₂BuEtP is a tetradentate ligand. It shows that the reaction should take place in the metal:ligand mole ratio of 1:1. Thus the extraction constant K_ex can be represented by:

$$K_{ex} = \frac{[Pb(BuEtP)_{(o)}][H^+]^2}{[Pb^{2+}][H_2BuEtP_{(o)}]} \qquad (2)$$

The distribution ratio $D = [Pb(BuEtP)_{(o)}]/[Pb^{2+}]$). Substitution into equation *(2)* gives:

$$Log\ D = log\ K_{ex} + log[H_2BuEtP] + 2pH \qquad (3)$$

Fig. 3a shows plot of influence of pH of aqueous phase on the distribution behaviour of Pb(II) into chloroform solution of H₂BuEtP. The plot shows that the distribution pattern did not agree with equation (1). Rather than a slope of 2 expected if two moles of hydrogen ions were displaced a slope of 6 was recorded in fig. 3a indicating that 6 moles of hydrogen ions may have been displaced during the extraction process. May we report that we observed a jump in extraction of Pb(II) from ≈ 0 % to > 98 % extraction at pH of 5.9 which gave a slope of 6. The buffer medium was changed from 0.1 M NaCH₃COO/CH₃COOH to 0.1M NaCitrate/Citric acid and the same result was obtained at pH 5.9. A slope of 2 was however recorded for plot of

extraction of Pb(II) ions into H_2BuEtP-$HButP$ mixture (fig. 3b). This indicated clearly that 2 moles of hydrogen ions were displaced during the extraction process. Fig. 3a and 3b are obviously indicating that different extraction mechanisms are taking place in both media. Slope analysis of the mode of interaction between Pb(II) ions and the ligands was carried out. Results presented in fig. 4a – c show that one mole of H_2BuEtP interacted with Pb(II) both in the presence and absence of HBuP. The interaction between Pb(II) and HBuP in the presence of a fixed H_2BuEtP concentration was also in the mole ratio of 1:1. Thus this established conclusively that one mole of H_2BuEtP reacted with Pb(II). Extraction studies with mixed ligands shows that one mole of H_2BuEtP and one of HBuP interacted with Pb(II) ions. Log D-log [Pb(II)] plots of fig. 5a,b had a slope of zero at all pH values studied indicating that 1 mole of Pb(II) was involved in the extraction process. Metal-ligand interaction during the extraction process therefore involved one mole of Pb(II) ion only. To explain the displacement of 6 moles of H^+ or the involvement of 3 moles of H_2BuEtP we are proposing that supramolecular species may have been formed during the extraction of Pb(II) into chloroform solution of H_2BuEtP alone. The extraction process can be represented as follows:

$$Pb^{2+} + 3H_2BuEtP_{(o)} \rightleftharpoons Pb(BuEtP)(BuEtP)_2^{4-}.4H^+_{(o)} + 2H^+ \qquad (4)$$
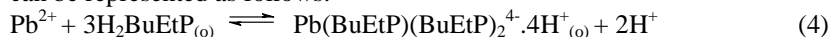
where $2H_2BuEtP$ is the excess. This is an indication that lead-trispyrazolonatoimine species may have been extracted and the suggested lead complex species for a 1:3 metal-ligand interaction is shown in fig. 2. Probably the complex formed is stabilised by both strong Pb-O and weak Pb-N bonds. Previous studies [9-10] have shown that lead has a high tendency of forming weak Pb-N bonds with the nitrogen group of pyrazolone moiety as suggested by fig. 2. A pK_a value of 6.8 ± 0.1 determined for the base shows that the Schiff base is a very weak acid. Hence electron shift on the pyrazoloimine species due to formation of weak Pb-N linkage may have provided the basis for ionization of the ligand. Releasing 4 additional protons during the extraction process forming ion-pair tris-complex species.

Figure 2,   Proposed structure of $Pb(BuEtP)(BuEtP)_2^{4-}$

Thus the extraction constant K_{ex1} can be represented by:

$$K_{ex1} = \frac{[Pb(BuEtP)(BuEtP)_2^{4-}{}_{(o)}][H^+]^6}{[Pb^{2+}][H_2BuEtP_{(o)}]} \qquad (5)$$

The distribution ratio $D = [Pb(BuEtP)(BuEtP)_2^{4-}{}_{(o)}]/[Pb^{2+}])$. Substitution into equation *(5)* gives:

Log D = log K_{ex1} + log[H_2BuEtP] + 6pH   (6)

where excess $2H_2BuEtP$ is constant and perhaps incorporated into K_{ex1}. The pseudo involvement of 2 moles of H_2BuEtP in the reaction process is established by fig. 2 which shows that of the 3 moles of H_2BuEtP in solution only one mole of H_2BuEtP interacted with Pb(II) ions forming Pb-O bonds. The partition coefficient K_{D1} is given by $K_{D1} = [Pb(BuEtP)(BuEtP)_2^{4-}.4H^+_{(o)}]/[Pb(BuEtP)(BuEtP)_2^{4-}.4H^+]$ for which a value of 1.92 ± 0.25 was determined for Log K_{D1} from the graph. The $pH_{\frac{1}{2}}$ was also found to be 5.88 ± 0.14. Data of all the extraction processes are contained on Table 1.
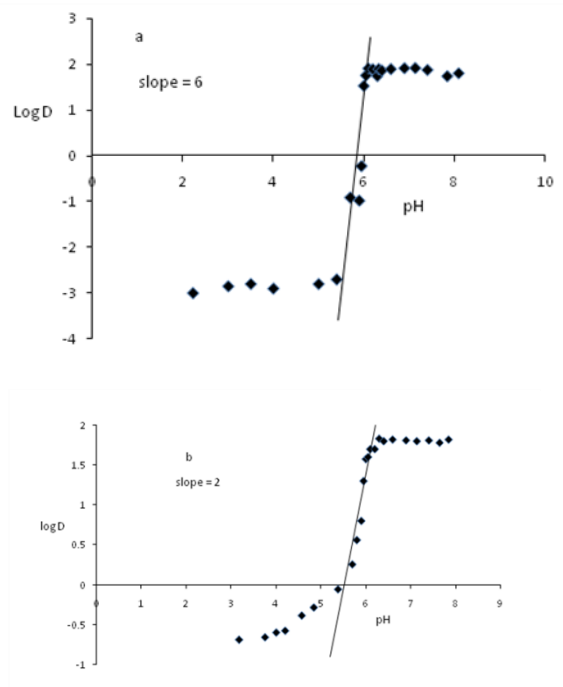
Figure 3: Plot of extraction of Pb(II) from buffer solutions into (a) chloroform solution of 0.05 M H_2BuEtP and (b) chloroform solution of 0.05 M H_2BuEtP-0.05 M HBuP in the 9:1 ratio by volume
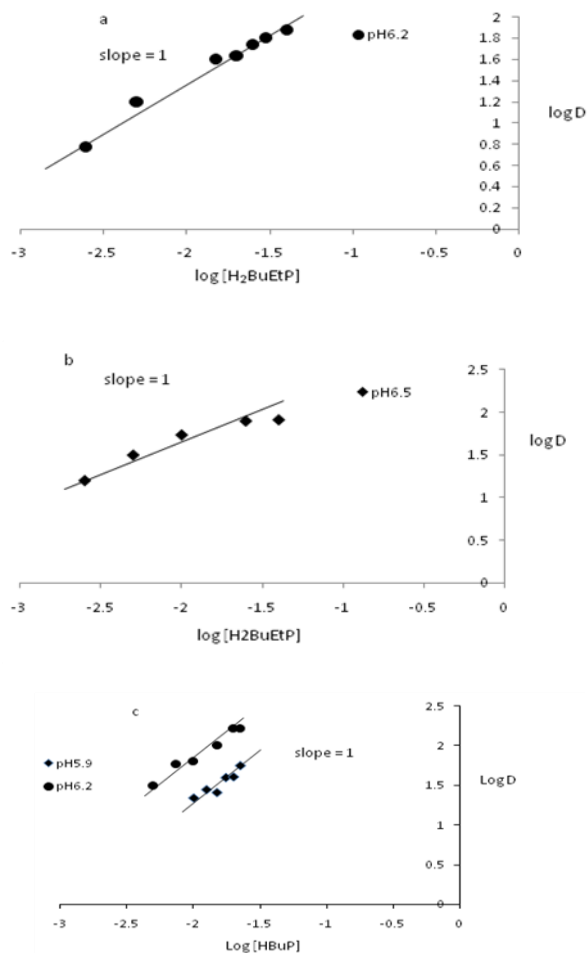

Figure 4: Log D-log [Ligand] plot of extraction of 50 mg/L of Pb(II) from buffer solutions into chloroform solutions of ligand: (a) [H_2BuEtP] was varied in the absence of [HBuP] (b) [H_2BuEtP] was varied, [HBuP] was kept constant (5×10^{-3} M) (c) [HBuP] was varied, [H_2BuEtP] was kept constant (2.5×10^{-2} M)
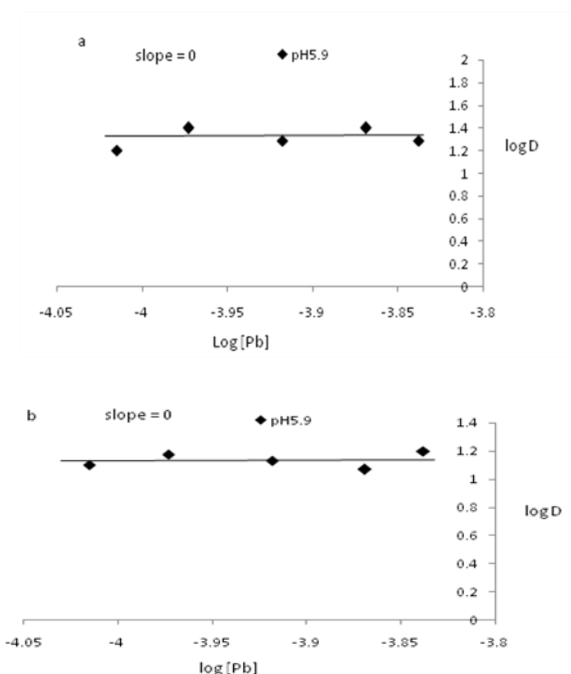
Figure 5: Log D-log [Pb(II)] plot of extraction of Pb(II) from buffer solutions into chloroform solutions of ligand (a) 0.05 M H_2BuEtP (b) (b) 0.05 M H_2BuEtP-0.05 M HBuP in the 9:1 ratio by volume

Table 1: Extraction data of the influence of pH of aqueous phase on the extraction of 50 mg/L of Pb(II) into chloroform solutions of 0.05 M H_2BuEtP and mixture of 0.05 M H_2BuEtP-0.05 M HBuP (9:1) ratio at room temprature of 30 ^{o}C

	Log K_{ex}	pH½	Log K_D	Species extracted
0.05 M H_2BuEtP	-32.90 ± 0.07	5.88 ± 0.14	1.92 ± 0.25	$Pb(BuEtP)(BuEtP)_2^{4-}.4H^+$
0.05 M H_2BuEtP-0.05 M HBuP (9:1) mixture	-9.79 ± 0.10	5.51± 0.13	1.82 ± 0.22	Pb(HBuEtP)(BuP)

3.2   Influence of addition of HBuP on the distribution of Pb(II)

Plots of the interaction between Pb(II) and H_2BuEtP in the presence of HBuP at pH 6.5 is presented in fig. 3b. The plot shows that one mole of H_2BuEtP reacted with Pb(II) in the presence of a fixed concentration of HBuP. Fig. 4c shows that one mole of HBuP interacted with one mole of Pb(II) in the presence of a fixed concentration of H_2BuEtP. One mole of Pb(II) reacted with H_2BuEtP in the presence and absence of fixed HBuP concentration (Fig. 5). A combination of the results of figures 3b, 4 and 5 suggests that the interaction between Pb(II) and H_2BuEtP in the presence of HBuP resulted in the displacement of a total of 2 moles of H^+ ions. This can be represented by,

$$Pb^{2+} + H_2BuEtP_{(o)} + HBuP_{(o)} \rightleftharpoons Pb(HBuEtP).BuP_{(o)} + 2H^+ \qquad (7)$$

Analysis of data is showing that extraction involving a mixture of the ligands probably gave a protonated mixed ligand lead(II) complex species. The suggested lead complex species is shown in Fig. 6 having Pb-N bonds [9-10].

Figure 6: Proposed structure of Pb(HBuEtP).BuP

Results also show that addition of HBuP into the organic phase did not offer any remarkable advantage in the extraction of Pb(II). This is reflected in the decreased value of the partition coefficient K_{D2} = [Pb(HBuEtP).BuP$_{(o)}$]/[Pb(HBuEtP).BuP] which recorded a value of 1.82 ± 0.22 (log K_{D2}, 1.82 ± 0.22 < log K_{D1}, 1.92 ± 0.25) and a pH$_{1/2}$ value of 5.51 ± 0.13 that is not statistically different from 5.88 ± 0.14. An increase in extraction constant K_{ex2} (log K_{ex2}, -9.67 ± 0.10 > log K_{ex1}, -32.90 ± 0.07) (Table 1) was however observed. The extraction constant K_{ex2} is given by:

$$K_{ex2} = \frac{[Pb(HBuEtP).BuP_{(o)}][H^+]^2}{[Pb^{2+}][H_2BuEtP_{(o)}]} \qquad (8)$$

where [HBuP] is constant and incorporated in K_{ex2}. The distribution ratio D_2 = [Pb(HBuEtP).BuP$_{(o)}$]/[Pb^{2+}], on substitution into equation *(8)* gives:

Log D_2 = log K_{ex2} + log[H$_2$BuEtP] + 2pH (9)

This agrees with the observed extraction behaviours obtained through graphical analysis.

3.3   Influence of mineral acids, anions and auxiliary complexing agents on the distribution of Pb(II)

Appreciable extraction into organic solutions of H$_2$BuEtP and a mixture with HBuP was observed for sulphuric acid solutions. For which extraction close to 90 % was obtained. However other results presented on Fig. 7 as plots of % extraction of Pb(II) ions from molar concentrations of mineral acids show that extraction is poor for acid concentrations > 0.1 M. Apart from sulphuric acid the study shows that extraction of Pb(II) is remarkably masked by both strong acids and weak acids such as acetic acid.
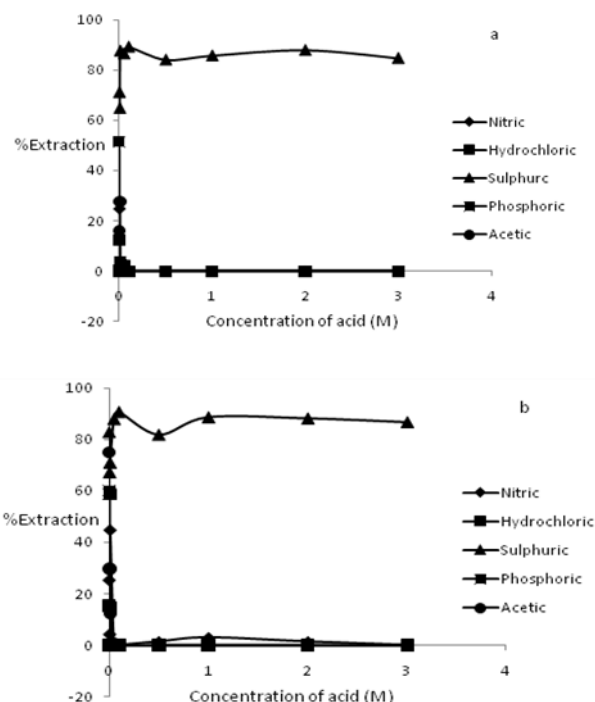

Figure 7: Plot of % extraction of 50 mg/L of Pb(II) from mineral acid solutions into (a) 0.05 M H$_2$BuEtP solution (b) 0.05 M H$_2$BuEtP-0.05 M HBuP (9:1) solution

The effect of anions on the distribution pattern of Pb(II) presented on Fig. 8 shows that extraction of Pb(II) is masked in chloride ion concentration > 0.1 M. Extraction is however remarkable for phosphate ion solution where 95 ± 5 % was recorded between phosphate ion concentrations of 0.1 and 0.5 M (Fig. 8a). When a mixture of H$_2$BuEtP and HBuP was used the extraction from acetate and nitrate ion solutions increased from 32 to 99 % and 30 to 97 % respectively at 0.5 M concentration of the two ions. Within experimental error the % extraction from phosphate ion solution could be said to be constant at close to 95 %. Fig. 8b shows that extraction was more remarkable using a mixture of the ligands rather than H$_2$BuEtP alone because the following increases in % extraction were observed: I$^-$ (10 % to 52%), Cl$^-$ (1 % to 70 %), SO$_4^{2-}$ (58 % to 88%) at 0.5 M concentration of ion.
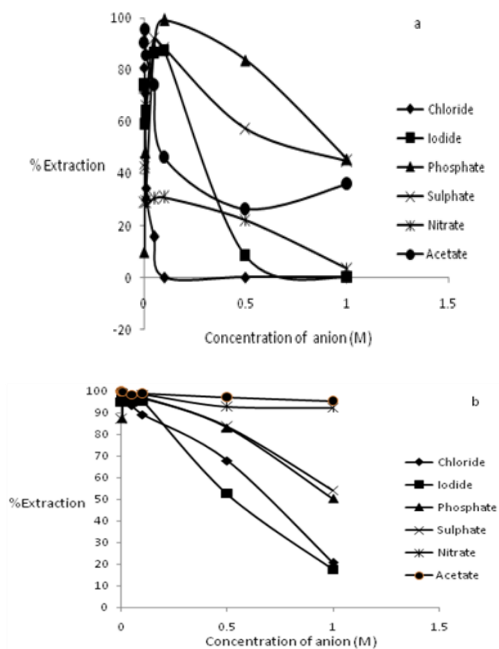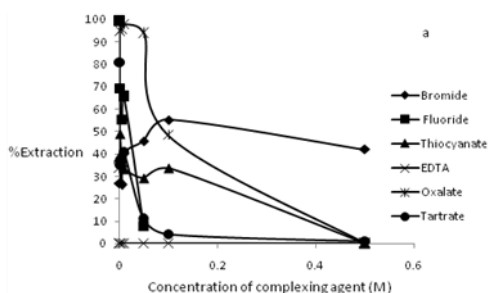

Figure 8: Plot of % extraction of 50 mg/L of Pb(II) from solutions of anions into (a) 0.05 M H$_2$BuEtP solution (b) 0.05 M H$_2$BuEtP-0.05 M HBuP (9:1) solution

The influence of auxiliary complexing agents on the extraction of Pb(II) is presented on Fig. 9. Extraction of Pb(II) from EDTA solution into both solutions of Schiff base and its mixture with HBuP is completely masked giving a < 0.1 % extraction. The extraction from oxalate ion solutions decreased drastically from 95 % to 20 % when the concentration increased above 0.1 M. Figure 8b shows however that the extraction increased remarkably when organic solution of mixture of the ligands was used for the following ions: F$^-$ (10 % to 65 %), tartrate (5 % to 95 %), Br$^-$ (55 % to 95 %), SCN$^-$ (30 % to 95 %) at 0.1 M solution of the ions.
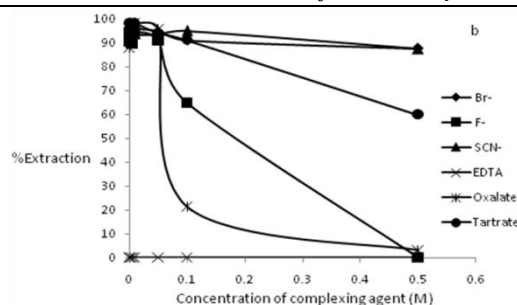
Figure 9:Plot of % extraction of 50 mg/L of Pb(II) from solutions of auxiliary complexing agents into (a) 0.05 M H$_2$BuEtP solution (b) 0.05 M H$_2$BuEtP-0.05 M HBuP (9:1) solution

IV.   Conclusions

Distribution of Pb(II) from buffered media into chloroform solutions of H$_2$BuEtP alone and its mixture with HBuP studied showed that the pH$_{\frac{1}{2}}$ was slightly lowered when a mixture of the ligands was used. The values recorded for partition coefficient (log K$_{D1}$) 1.92 ± 0.25 and (log K$_{D2}$) 1.82 ± 0.22 for the complexes indicated that Pb(II) distributes more effectively into H$_2$BuEtP solution rather than into solution of its mixture with HBuP. This has been attributed to the Pb(II) tris complex species shown to have been extracted by slope analysis into H$_2$BuEtP solution. Hence the analysis shows that species with both strong Pb-O and weak Pb-N bonds were extracted into the organic phase. And the suggested formulae are Pb(BuEtP)(BuEtP)$_2$$^{4-}$.4H$^+$ and protonated Pb(HBuEtP).BuP species were proposed as extracted species. Studies of the influence of mineral acids, anions and complexing agents on the extraction process show that apart from sulphuric acid, extraction is generally very poor for acid solutions even when mixture of H$_2$BuEtP and HBuP was used. Extraction of Pb(II) from EDTA solution is completely masked.

V.   Acknowledgment

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