Kinetic studies on the recovery of Pb^{2+} and UO_2^{2+} from aqueous solutions into chloroform solution of *N,N'*-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) schiff base

Chukwu Uche John[1, *], Godwin Jackson[2], Onuigbo Somadina Benson[1]

[1]Department of Pure and Industrial Chemistry, University of Port Harcourt, Choba, Port Harcourt, Rivers State, Nigeria
[2]Department of Chemical Sciences, Niger Delta University, Wilberforce Island, Bayelsa State, Nigeria

Email address:
Lydiuche@yahoo.com (C. U. John), godwinj2012@gmail.com (G. Jackson), benzene83@yahoo.com (O. S. Benson)

Abstract: The kinetic studies on the recovery of UO_2^{2+} and Pb^{2+} from aqueous solutions into chloroform solution of *N,N'*-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) schiff base H_2BuEtP has been investigated and the rate of reaction found to be first order with respect to both metal ions (UO_2^{2+} and Pb^{2+}). The rate of extraction was equally dependent on the inverse of hydrogen ion concentration for both metal ions. The rate constant K_f was equally calculated from intercepts of plots to be $0.491 min^{-1}$ for UO_2^{2+} and $0.411 min^{-1}$ Pb^{2+} metal ions. Optimum percentage extraction of 99.714% was observed for Pb^{2+} metal ion at 30mins equilibration time and 98.216% for UO_2^{2+} metal ion at 20mins equilibration time. The study on mechanism of extraction for the metal ions from the aqueous phase into the organic phase showed that the formation of the first chelate ring of mono-pyrazolonato metal complex is the rate determining step which involved a slow bond-weaking effect by the bidendate H_2BuEtP on the water molecule.

Keywords: Kinetic Studies, Reaction Rate, Schiff Base, Chloroform, Uranium VI, Lead II

1. Introduction

The extraction of metal ions from aqueous pH medium using multi-dentate ligands has received quite some attention in recent times [1-5]. The continuous search for better and more efficient ligands has led to the synthesis and characterization of several ligands and Schiff bases [6-7] of which 1-phenyl-3-methyl-4-acyl-pyrazolone-5 and its derivatives have been studied and reported [8]. The role of these organic extractants in the recovery of several metals has equally been reported by several authors [9-10]. The schiff base *N,N'*-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H_2BuEtP) which was first synthesized and characterized by Uzoukwu, *et, al*. [7] has been used in the extraction of few metal complexes. This schiff base (H_2BuEtP) which has a pKa of $6.6 + 0.1$ was found to be an efficient ligand in the distribution of UO_2^{2+} and Pb^{2+} from aqueous pH solutions into chloroform solutions as reported by Godwin and Uzoukwu [11-13]. Optimal

percentage extraction of above 98% was equally recorded for both metal ions and an efficient technique for separating both metals developed [13].

Kinetic studies on the extraction of various metal ions have been carried out with 4-acyl derivatives of 1-phenyl-3-methyl-4-acyl-pyrazolone-5 and reported [14-15]. Eigen [16] suggested that the rate of recovery of metal ions from aqueous solution is slow when the charge is large and/or the radius is small. This has been attributed to the slow substitution of the coordinated water molecules on the metal [14, 16]. The need to optimize the conditions for extraction necessitated the kinetic studies of the recovery of UO_2^{2+} and Pb^{2+} metal ions at constant pH in their distribution into chloroform solution of the schiff base (H_2BuEtP). Thus, the present study is aimed at studying the kinetics and rate of recovery of the metal ions UO_2^{2+} and Pb^{2+} from aqueous solution and to determine the mechanism that may be involved in the extraction processes.

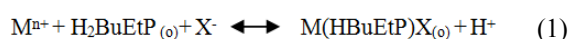## 2. Experimental

2.1. Procedure

All reagents used were of analytical grade from BDH and Aldrich. The ligand N,N'-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H$_2$BuEtP) was synthesized by methods reported elsewhere [11,12,15]. The product was purified by recrystallization from aqueous ethanol and dried in air. The purity was further established by ultraviolet, infrared, ^{1}H and ^{13}C NMR.

Stock solutions of H$_2$BuEtP (0.05M) was prepared by dissolving the appropriate mass of the schiff base (2.563g) in 100ml chloroform solution. This constituted the organic phase. Metal stock solution of 2000mg/L for UO$_2$$^{2+}$ ion was prepared by dissolving 0.3564g of UO$_2$(CH$_3$COO)$_2$.2H$_2$O in 100ml volumetric flask using deionized water, while 1000mg/L stock solution for Pb^{2+} was prepared by dissolving 0.1599g of Pb(NO$_3$)$_2$ in 100ml volumetric flask. These made up the aqueous phase with a working concentration of 200ppm for UO$_2$$^{2+}$ and 50ppm for Pb^{2+} in the various buffered solutions.

Equal volumes (2ml) of the aqueous phase containing the metal ions UO$_2$$^{2+}$ and Pb^{2+} separately and the organic phase containing the schiff base H$_2$BuEtP were agitated mechanically using a mechanical shaker at various time intervals from 0 sec to 30 minutes at room temperature in stoppered extraction bottles. Both layers were then allowed to separate. Concentration of UO$_2$$^{2+}$ in the aqueous phase was determined by colorimetric technique using a UV-Vis spectrophotometer (Spectronic 20 Genesys) at wavelength 370nm and calculated by difference. The color development for determination of Uranium was by addition of 0.2ml each of 10% NaOH, 10% NaCO$_3$ and 1ml 6% H$_2$O$_2$ solutions. While concentration of Pb^{2+} in the aqueous phase was determined using Perkin Elmer AAnalyst 200 Atomic Absorption Spectrophotometry (AAS). Distribution ratio (D = C$_o$/C) was calculated as ratio of metal ion concentration in organic phase (C$_o$) and that in the aqueous phase (C). The buffer solutions were prepared and determined using a Labtech digital pH meter.

2.2. Extraction Equilibrium

The extraction of UO$_2$$^{2+}$ ion and Pb^{2+} ion from an aqueous phase using the tetra dentate ligand (H$_2$BuEtP) in the organic phase has been treated as follows as reported by Godwin and Uzoukwu [11,12]. The extraction of metal ion M^{n+} from an aqueous phase using the ligand H$_2$BuEtP in the organic phase can be treated as follows:

$$M^{n+} + H_2BuEtP_{(o)} + X^- \longleftrightarrow M(HBuEtP)X_{(o)} + H^+ \qquad (1)$$

For which the extraction constant K$_{ex1}$ is given as follows:

$$K_{ex1} = \frac{[M(HBuEtP)X_{(o)}][H^+]}{[M^{n+}][H_2BuEtP_{(o)}]} \qquad (2)$$

where X$^-$ is anion present in excess in solution and incorporated in K$_{ex1}$. Hence the distribution ratio D$_1$= [M(HBuEtP)X$_{(o)}$]/[M^{n+}] shall on substitution into equation (2) and taking logarithm of same give equation 3,

$$LogD_1 = \log K_{ex1} + \log[H_2BuEtP] + pH \qquad (3)$$

The partition coefficient (K$_{D1}$) of M(HBuEtP)X$_{(o)}$ species is defined as

$$K_{D1} = [M(HBuEtP)X_{(o)}]/[M(HBuEtP)X]$$

2.2.1. Rate of Recovery of Metal

The rate of recovery of the metal ions from the aqueous phase was followed as the rate of disappearance of the metal ion M^{n+} from the aqueous phase during the extraction process and is represented by the following equations.

$$-d[M^{n+}]/dt = K_f[M^{n+}]^a \cdot [H_2BuEtP]^b{}_{(o)} [H^+]^c \qquad (4)$$

where K$_f$ is the rate constant for the recovery process and a, b, and c are the reaction orders with respect to metal ion, ligand and hydrogen ion concentrations respectively. When [H$_2$BuEtP]$^b{}_{(o)}$ and [H$^+$]^c are present in excess equation (4) becomes:

$$-d[M^{n+}]/dt = K.[M^{n+}]^a \qquad (5)$$

if it is assumed that a=1 then, integration of equation (5) will give:

$$-\log[M^{n+}] = Kt + C \qquad (6)$$

C is a constant and

$$K = k_f[H_2BuEtP]^b{}_{(o)} + [H^+]^c \qquad (7)$$

To obtain the reaction orders b and c measurements are made with one of the quantities [H$_2$BuEtP]^b or [H$^+$]^c kept fixed while the other is varied. This means that, when [H$_2$BuEtP]$_{(o)}$ is kept constant, equation 7 becomes

$$Log K_H = \log k_f[H_2BuEtP]^b{}_{(o)} + c \log [H^+] \qquad (8)$$

From equation 8, `c` can be determined. When [H$^+$] is kept constant, equation 7 becomes

$$Log K_{H2BuEtP} = \log k_f[H^+]^c + b \log [H_2BuEtP]_{(o)} \qquad (9)$$

And from equation 9, `b` can be determined. The rate constants K$_f$ can be calculated from the intercept of plots of equations 8 and 9 when values for a, b, and c are known.

3. Results and Discussion

3.1. Equilibration and Extraction

The extraction procedure adopted for this study is same as reported in our previous work [11,12] on the extraction of Pb^{2+} and UO$_2$$^{2+}$ using the schiff base (H$_2$BuEtP), in which 2moles and 6 moles of the ligand reacted with one mole of Pb^{2+} and UO$_2$$^{2+}$ respectively during the extraction process. From the study, optimal percentage extraction of 99.714% (log K$_d$ = 1.85 ± 0.08) was recorded at pH 6.00 for extraction of Pb^{2+} at

an average equilibration time of 30 minutes. Similarly, extraction of UO_2^{2+} gave optimal percentage extraction of 98.216% (log K_d = 0.56 ± 0.01) at pH 4.30 with 20 minutes equilibration time. It was observed that a slightly more acidic medium favored the distribution of UO_2^{2+} from the aqueous phase to the organic phase.

3.2. Kinetics of Recovery

From plots of $-\log[M^{n+}]$ against time (Fig 1a and Fig 1b) for the rate of extraction of Pb^{2+} and UO_2^{2+} from aqueous media into chloroform solutions of H_2BuEtP, a linear slope was obtained showing that a=1 and thus the reaction order is first order.

The reaction order c, with respect to hydrogen ion concentration was evaluated from the plots of various $-\log K_H$ (slope from Fig.1) against the various pH ($-\log H^+$) and presented in fig. 2a and fig. 2b. This gave a straight line graph with slope of -1 for both Pb^{2+} and UO_2^{2+}. Therefore the extraction order c was 1 with respect to $[H^+]$ for both metal ions. Thus, it was deduced according to equation 8, that the rate of extraction of UO_2^{2+} and $Pb^{2+}$is dependent on the inverse of hydrogen ion concentration. A similar behavior has been reported by Uzoukwu, *et, al.* on the kinetic studies of UO_2^{2+} [15].

The reaction order b with respect to $[H_2BuEtP]$ was determined by plots of $-\log K_{(H2BuEtP)}$ against $-\log [H_2BuEtP]$ at constant pH. Slopes of +1 were obtained from plots for both UO_2^{2+} and Pb^{2+}. The extraction order, b, was therefore +1 with respect to the ligand concentration for both metals and the rate constants K_f calculated using the intercepts of the plots according to equations 8 and 9 to be 0.491min^{-1} and 0.411min^{-1} for UO_2^{2+} and Pb^{2+} respectively.
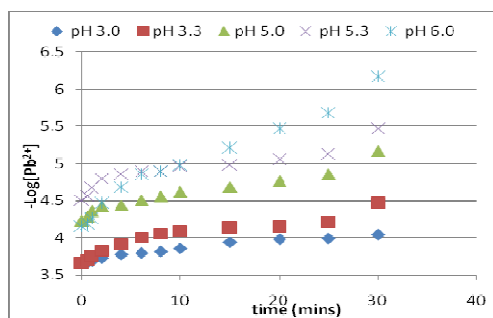

Figure 1a. *Plots of time dependence on the disappearance of Pb^{2+} metal ion concentration into ligand concentration in chloroform at constant pH.*
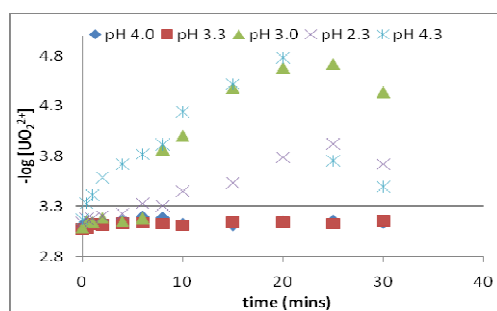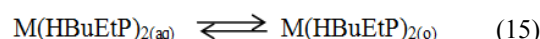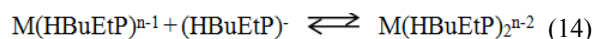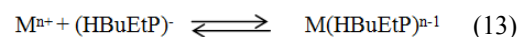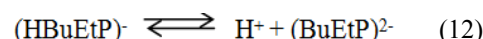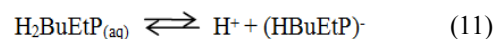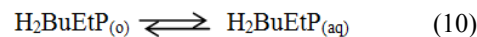

Figure 1b. *Plots of time dependence on the disappearance of UO_2^{2+} metal ion concentration into ligand concentration in chloroform at constant pH.*

3.3. Mechanism of Extraction

For the mechanism in the extraction of the metal ions from the aqueous phase into the organic phase, based on data kinetic and equilibration studies, the steps involved are as follows:

$$H_2BuEtP_{(o)} \rightleftharpoons H_2BuEtP_{(aq)} \quad (10)$$

$$H_2BuEtP_{(aq)} \rightleftharpoons H^+ + (HBuEtP)^- \quad (11)$$

$$(HBuEtP)^- \rightleftharpoons H^+ + (BuEtP)^{2-} \quad (12)$$

$$M^{n+} + (HBuEtP)^- \rightleftharpoons M(HBuEtP)^{n-1} \quad (13)$$

$$M(HBuEtP)^{n-1} + (HBuEtP)^- \rightleftharpoons M(HBuEtP)_2^{n-2} \quad (14)$$

$$M(HBuEtP)_{2(aq)} \rightleftharpoons M(HBuEtP)_{2(o)} \quad (15)$$

From the kinetics of recovery, it was deduced according to equation 8, that the rate of extraction of UO_2^{2+} and Pb^{2+} is dependent on the inverse of hydrogen ion concentration and the rate order shown to be first order.
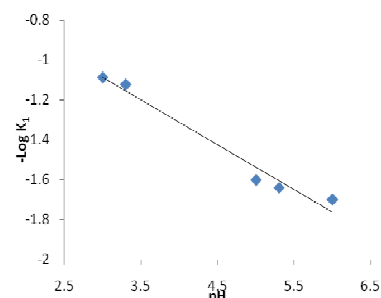

Figure 2a. *Plot for dependence of rate of extraction of Pb^{2+} metal ion on hydrogen ion concentration at constant ligand concentration.*
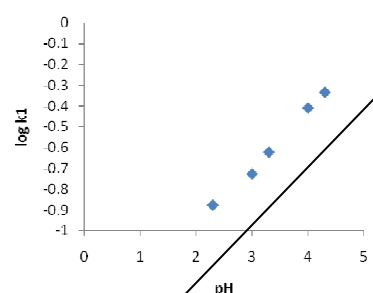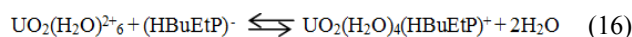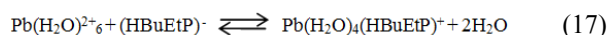

Figure 2b. *Plot for dependence of rate of extraction of UO_2^{2+} metal ion on hydrogen ion concentration at constant ligand concentration.*

Hence, equations 10 and 15 do not involve a pH dependence process and cannot be considered as rate determining steps. Also equations 11 and 12 can also be eliminated because they do not show first order dependence on the metal ions. Equation 14 shows dependence on the square or more of ligand concentration hence it is eliminated. Equation 13 which is first order in both the metal ion and ligand concentration thus represents the rate determining step of the extraction process and can be rewritten for both metal ions (UO_2^{2+} and Pb^{2+}) which are hydrated in solution as:

$$UO_2(H_2O)^{2+}_6 + (HBuEtP)^- \rightleftharpoons UO_2(H_2O)_4(HBuEtP)^+ + 2H_2O \quad (16)$$

$$Pb(H_2O)_6^{2+} + (HBuEtP)^- \rightleftharpoons Pb(H_2O)_4(HBuEtP)^+ + 2H_2O \qquad (17)$$

Therefore formation of the first chelate ring of mono-pyrazolonato metal complex is the rate determining step which involves a slow bond-weaking effect exerted by the bidentate HBuEtP on the two water molecules which are trans to each order, leading to their elimination. The other steps are expected to follow in quick succession leading to neutral bis-pyrazolonato complexes which are transferred into the organic phase.

4. Conclusion

The kinetic studies on the recovery of UO_2^{2+} and Pb^{2+} using the Schiff base H_2BuEtP has been investigated and the rate of reaction found to be first order with respect to both metal ions (UO_2^{2+} and Pb^{2+}). The rate of extraction was equally dependent on the inverse of hydrogen ion concentration for both metal ions. The rate constant K_f was equally calculated from intercepts of plots to be $0.491 min^{-1}$ for UO_2^{2+} and $0.411 min^{-1}$ for Pb^{2+} metal ions. Optimum percentage extraction of 99.714% was observed for Pb^{2+} metal ion at 30mins equilibration time and 98.216% for UO_2^{2+} metal ion at 20mins equilibration time. The study on mechanism of extraction for the metal ions from the aqueous phase into the organic phase containing $0.05M$ H_2BuEtP showed that the formation of the first chelate ring of mono-pyrazolonato metal complex is the rate determining step, which involved a slow bond-weaking effect by the bidendate H_2BuEtP on the water molecule.

Acknowledgements

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