

Solvent Extraction Studies of Uranium (VI) from Aqueous Media into Chloroform Solution of *N,N'*-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine)

U. J. Chukwu^{1*} and J. Godwin²

¹*Department of Pure and Industrial Chemistry, University of Port Harcourt, PMB, 5323, Port Harcourt, Rivers State, Nigeria.*

²*Department of Chemical Sciences, Niger Delta University Wilberforce Island Bayelsa State, Nigeria.*

Authors' contributions

This work was carried out in collaboration between all authors. Author UJC designed the study, performed the statistical analysis, wrote the protocol, and wrote the first draft of the manuscript. Author JG managed the analyses of the study and the literature searches. All authors read and approved the final manuscript.

Research Article

Received 28th March 2013
Accepted 18th June 2013
Published 10th August 2013

ABSTRACT

The extraction of Uranium (VI) from aqueous media of varying pH values (0.3 – 9.0) was studied using chloroform solution of 0.05M *N,N'*-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H_2PrEtP) Schiff base. The effect of 4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HPrP) as a mixed ligand in these extractions was also studied. The ligand H_2PrEtP was shown to behave in solution as a very weak acid with potentiometrically determined acid dissociation constants pK_a of 6.1 ± 0.1 and 7.6 ± 0.1 . Colorimetric method was used to determine the Uranium(VI) concentrations in aqueous media after extraction processes. Slope analysis showed that the extracted uranyl complexes were $UO_2(HPrEtP).X$ in the absence of the mixed ligand ($H_2PrEtP/HPrP$) and $UO_2(HPrEtP)HPrP.X$ in the presence of HPrP as a mixed ligand, with the excess anion X^- coming from the buffers. The $pH_{1/2}$ shifted from 6.9 ± 0.10 for H_2PrEtP to 4.4 ± 0.10 for $H_2PrEtP/HPrP$ organic mixture. Though, $\log K_{ex}$ values (-5.84

*Corresponding author: Email: lydiuche@yahoo.com;

$\pm 0.18 \log K_{ex} H_2PrEtP > -8.71 \pm 0.50 \log K_{ex} H_2PrEtP/HPrP$) indicated that the formation constant for $UO_2(HPrEtP)_2$ was higher than that for $UO_2(HPrEtP)HPrP$. Thus, the mixed ligand organic phase was shown to be a better extractant for Uranium(VI) with a wide extraction pH range of 4.0–6.5, a higher partition coefficient (K_D) of 2.49 and quantitative extraction of 99.9% compared to extraction pH range of 7.75 – 8.75 and K_D of 1.49 when H_2PrEtP was used alone.

Keywords: Aqueous media; buffered; extraction; *N,N'*-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine); mixed ligand; uranium (VI).

1. INTRODUCTION

The extraction of metal ions from aqueous media into chloroform solutions of 1-phenyl-3-methyl-4-acyl pyrazolone and its derivatives have been extensively studied and reported [1-3]. The use of new *Schiff* bases in liquid-liquid extraction of metals is one area which has generated lots of interesting and positive research results in the past couple of years [4-6]. New *Schiff* bases and their derivatives have been synthesized, characterized and tested successfully in liquid-liquid extraction of many metals [7-9]. One of such new *Schiff* base is *N,N'*-ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) and its derivatives *N,N'*-(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H_2BuEtP), *N,N'*-Bis(1-phenyl-3-methyl-4-acetylpyrazoloneimine)-1,2-propane (H_2ADPP) and *N,N'*-ethylenebis(1-phenyl-3-methyl-4-propionylpyrazoloneimine) (H_2PrEtP) have been successfully synthesized and characterized using ultraviolet, infrared, 1H and ^{13}C NMR [9]. The 4-acylbispyrazoloneimines possess heterocyclic pyrazolone moiety and functions as tetradentate β -hydroxyimines. The *Schiff* base *N,N'*-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) has equally been used in the metal extraction studies of Uranium (VI) into chloroform solutions from aqueous media of varying pH values in the presence and absence of synergists [10]. Interestingly, this *Schiff* base has a pK_a value of 6.6 ± 0.1 which is not very acidic as most other common ligands. As the search for more efficient metal ion extractants goes on and in continuation of our studies on metal extraction with acyl bis(1-phenyl-3-methylpyrazol-5-oneimine) derivatives, we have studied the application of *N,N'*-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) which has received little or no attention as a potential metal ion extractant long after its synthesis was reported [9], in the extraction of Uranium (VI) from aqueous media of varying pH values of 0.3 to 9.0 in the presence and absence of ($HPrP$) as a mixed ligand.

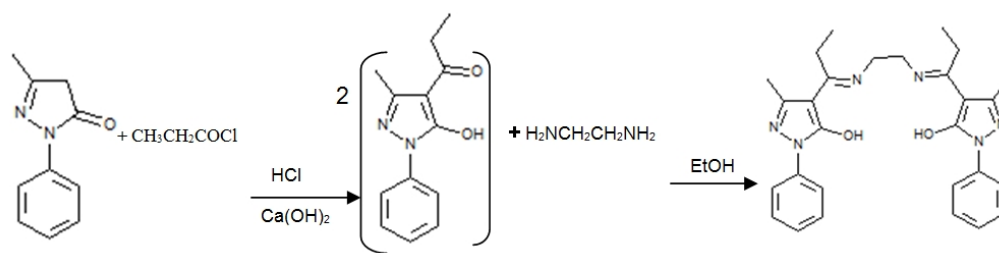
2. MATERIALS AND METHODS

All reagents and chemicals used were of analytical grade from BDH and Aldrich. The *Schiff* base *N,N'*-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H_2PrEtP) was synthesized according to method reported by Uzoukwu et al. [9] as shown in Scheme 1. The ligand's purity after recrystallization from aqueous ethanol was established by elemental analysis for C, H and N; analysis of IR, UV and NMR spectral were carried out at the Institute for Inorganic Chemistry Technology, University of Dresden, Germany and has been reported [9,10]. The *Schiff* base was slightly soluble in ethanol, soluble in methanol, $CHCl_3$, acetone, CH_2Cl_2 and benzene. It had a melting point of $215^\circ C$ and molecular formula $C_{28}H_{32}O_2N_6$. Stock solution of H_2PrEtP

(0.05M) was prepared by dissolving the appropriate mass of the Schiff base (2.4331g) in 100ml chloroform solution. This constituted the organic phase. Additionally, 0.05M stock solution of 4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HPrP) in chloroform was used as a mixed ligand. Metal stock solution of 2000mg/L was prepared by dissolving 0.3564g of $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 100ml volumetric flask using deionized water. Buffer solutions of pH 0.3 to 9.0, containing 0.05M, Cl^- ions, were prepared by combining appropriate mixtures of acids and their conjugate salts as previously reported by Chukwu and Uzoukwu 2010 [12]. Determination of the pH was done using a Consort C531 pH/conductivity meter. The aqueous phase comprises 2ml aliquot of the buffer solution containing 200mg/l of the metal ion for each pH value. While 2ml stock solution of the Schiff base H_2PrEtP in chloroform made up the organic phase. In the presence of the mixed ligand, a mixture of the Schiff base H_2PrEtP and the ligand HPrP in the ratio of 9:1 made up the organic phase for extraction in the presence of mixed ligand. The pK_a of the Schiff base was determined potentiometrically as reported elsewhere [8,10,11].

2.1 Extraction Procedure

Equal volumes (2ml) of the aqueous phase containing UO_2^{2+} and the organic phase containing the Schiff base H_2PrEtP only were agitated mechanically (using a griffin flask mechanical shaker) for 40mins at room temperature in stoppered extraction bottles (extraction time reported to be adequate for equilibration [11]). While a mixture of the Schiff base H_2PrEtP and the ligand HPrP in the ratio of 9:1 made up the organic phase for extraction in the presence of mixed ligand. Both layers were equally agitated as described above. Thereafter, both layers were allowed to separate. Concentration of UO_2^{2+} in the aqueous phase was thereafter determined by colorimetric technique [10] using a UV-Vis spectrophotometer (Spectronic 20 Genesys) at wavelength 370nm and the value of D calculated by difference. The color development for determination of Uranium was by addition of 0.2ml each of 10% NaOH, 10% Na_2CO_3 and 1ml 6% H_2O_2 solutions.



Scheme 1. Reactions for the Synthesis of N,N'-ethylenebis(4-Propionyl-2,4-Dihydro-5-Methyl-2-Phenyl-3H-Pyrazol-3-oneimine)

3. RESULTS AND DISCUSSION

Results for the determination of the ion dissociation constant (pK_a) values are as presented in Fig. 1. The results showed that the Schiff base has a pK_{a1} value of 6.1 ± 0.1 . This has been ascribed to first ionization of one of the $-\text{OH}$ groups of the ligand. It is an indication that the ligand is a very weak acid. A second pK_{a2} value of 7.6 ± 0.1 was also determined from the graph.

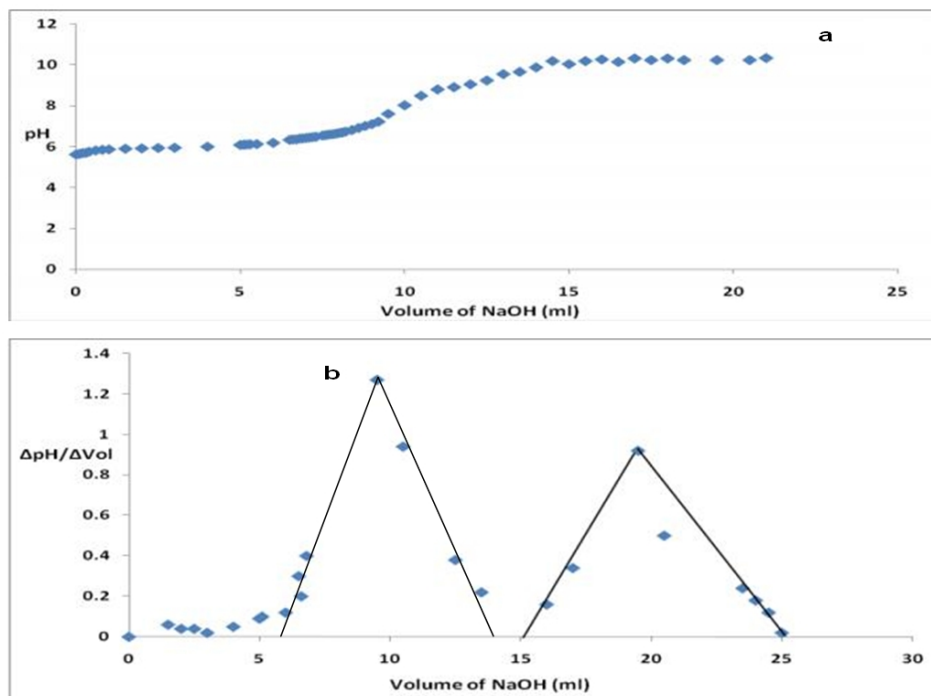


Fig. 1. Graphical presentation of potentiometric titration between 20 ml 2.5×10^{-3} M H_2PrEtP and 5×10^{-3} M NaOH, both prepared in 80 % aqueous 1,4-dioxane solution (a) pH-volume of base plot (b) $\Delta\text{pH}/\Delta\text{volume}$ of base vs. volume of base plot

The extraction of 8.4×10^{-4} M Uranium (VI) ions from aqueous media of buffered solutions (pH 0.3 -9.0) using 0.05M concentration of the Schiff base (H_2PrEtP) in chloroform and 0.05M (HPrP) as a mixed ligand in chloroform, is presented in Fig. 2 as plots of $\log D$ against pH values. The plots show the influence of pH on the distribution of U(VI) into chloroform solutions of H_2PrEtP and H_2PrEtP -HPrP respectively. Quantitative extraction was observed to occur between pH 7.75 and 8.75 in the absence of the mixed ligand (HPrP) and between pH 4.0 and 6.5 in the presence of HPrP as a mixed ligand. Optimal percentage extraction of 96.90% was obtained at pH 8.50 to 8.75 for extractions in the absence of the mixed ligand (HPrP) whereas optimal percentage extraction of 99.9% was obtained for extraction of UO_2 in the presence of HPrP as a mixed ligand between pH 6.00 to 6.50.

This is an indication of enhanced extraction in the presence of HPrP, a trend which has been reported by several authors [10,12] in extraction studies using several ligands and Schiff bases, and attributed to the formation of adducts that are more hydrophobic. The $\text{pH}_{1/2}$ is defined as the pH where 50% extraction of the metal occurs [14]. From plots of Fig. 2, the $\text{pH}_{1/2}$ of the extraction process in the absence and presence of the mixed ligand was 6.90 ± 0.10 and 4.40 ± 0.10 respectively, indicating that extraction was better and higher at relatively lower pH in the presence of the HPrP as a mixed ligand.

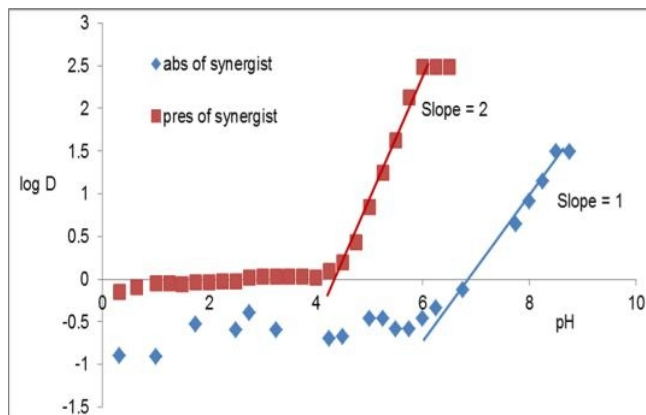
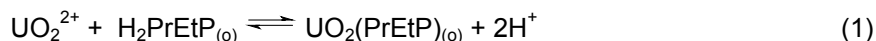


Fig. 2. Extraction plots of 8.4×10^{-4} M U(VI) using 0.05M N,N'-ethylenebis(4-propionyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H_2PrEtP) in chloroform in the absence and presence of HPrP as a mixed ligand at various pH values

Extraction of U(VI) from aqueous media into an organic solvent '(o)' containing a tetradentate ligand H_2PrEtP can be represented by the following equations:



Here, H_2PrEtP is a tetradentate Schiff base with the assumption that the metal: ligand interaction is in 1:1 mole ratio.

$$K_{ex} = \frac{[UO_2(PrEtP)_{(o)}][H^+]^2}{[UO_2^{2+}][H_2PrEtP_{(o)}]} \quad (2)$$

The distribution ratio D is given by $D = [UO_2(PrEtP)_{(o)}]/[UO_2^{2+}]$

Substituting D in equation 2 and taking logarithm of both sides we get equation 3

$$\text{Log } D = \log K_{ex} + \log[H_2PrEtP] + 2pH \quad (3)$$

From the equation K_{ex} is extraction constant. The higher the K_{ex} the better the ligand is an extractant for a particular metal ion [14].

A slope of 1 was obtained when the Schiff base H_2PrEtP was used in the absence of the synergist as shown in plots of Fig. 2. Thus, indicating that 1 mole of hydrogen ion was displaced during the extraction process. This result does not agree with equation (1) for a 1:1 interaction between UO_2^{2+} and H_2PrEtP in which 2 moles of hydrogen ions were expected to be displaced. Thus, the probable reaction during the extraction process can therefore be represented as shown in equation (4).



For which the extraction constant K_{ex1} is given as follows:

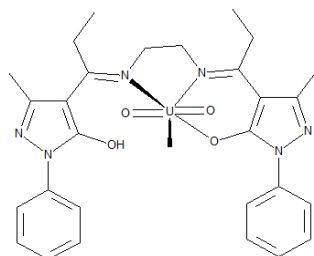
$$K_{ex1} = \frac{[UO_2(HPrEtP)X_{(o)}][H^+]}{[UO_2^{2+}][H_2PrEtP_{(o)}]} \quad (5)$$

From the equation, X^- is an anion present in excess in the solution from the high pH in which quantitative extractions occurred between pH 7.75 – 8.75 and incorporated into K_{ex1} . Hence the distribution ratio $D_1 = [UO_2(HPrEtP)X_{(o)}]/[UO_2^{2+}]$.

On substitution of D_1 into equation 5, and taking logarithm of both sides of the equation we have:

$$\text{Log } D_1 = \text{log } K_{ex1} + \text{log}[H_2PrEtP] + \text{pH} \quad (6)$$

The partition coefficient (K_{D1}) of $UO_2(HPrEtP)X_{(o)}$ species is defined as $K_{D1} = [UO_2(HPrEtP)X_{(o)}] / [UO_2(HPrEtP)X]$ for which a value of 1.49 ± 0.01 was determined. The result obtained is similar to reports by Godwin and Uzoukwu, [10], in the extraction studies of Uranium (VI) using a very similar Schiff base. Thus, the suggested uranyl complex species extracted into the organic phase is shown in Scheme 2.



Scheme 2. Proposed structure of $UO_2(HPrEtP).X$: where $X = Cl^-, CH_3COO^-$, etc. from buffers

The extraction plot for the distribution of UO_2^{2+} into chloroform solutions of a mixture of H_2PrEtP and $HPrP$ is presented in Fig. 2 and equation 7 - 9 can be proposed for the extraction process in the presence of $HPrP$ as a mixed ligand as:



The extraction constant K_{ex2} is given as follows:

$$K_{ex2} = \frac{[UO_2(HPrEtP).HPrP.X_{(o)}][H^+]}{[UO_2^{2+}][H_2PrEtP_{(o)}]} \quad (8)$$

From the equation, [HPrP] is a constant and X^- is an anion in excess and is incorporated in K_{ex2} . The distribution ratio $D_2 = [UO_2(HPrEtP).HPrP.X_{(o)}]/[UO_2^{2+}]$ which on substitution into equation (8) and taking logarithm of both sides gives equation 9:

$$\text{Log } D_2 = \text{log } K_{ex2} + \text{log}[H_2PrEtP] + 2pH \quad (9)$$

Using slope analysis as discussed by previous authors [11-13], plots of Fig. 3 gives the variation of the ligand concentration in the absence and presence of the synergist at constant pH of 8.50 and 6.25 respectively. Extraction at varying ligand concentrations of $[H_2PrEtP]$ gave a slope of 1 each at constant pH of 8.50 in the absence of synergist and pH of 6.25 in the present of HPrP as synergist. On statistical interpretation as discussed by previous authors [11-13], a slope of 1 was obtained which suggests the involvement of only one mole of the ligand in the extraction process, thus validating the suggested equation 4. Similarly, Fig. 4 presents variations of the metal ion concentration in the absence and presence of the synergist at constant pH of 8.50 and 6.25 respectively for the extraction of U(VI). In each of the plots, a slope of zero was obtained which on statistical interpretation as discussed by previous authors [11, 13] indicates the involvement of one mole of the metal ion UO_2^{2+} .

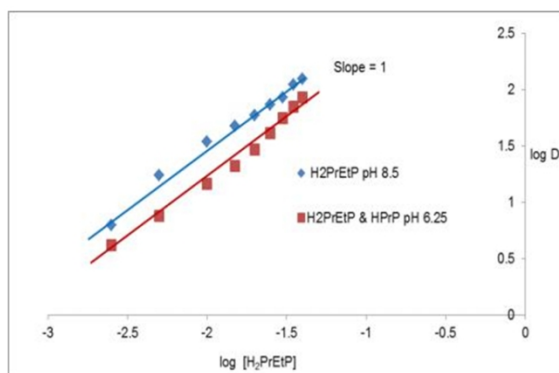


Fig. 3. Variation of ligand H_2PrEtP concentrations at constant pH values for the extraction of U(VI) in the presence and absence of a mixed ligand [HPrP] at room temperature

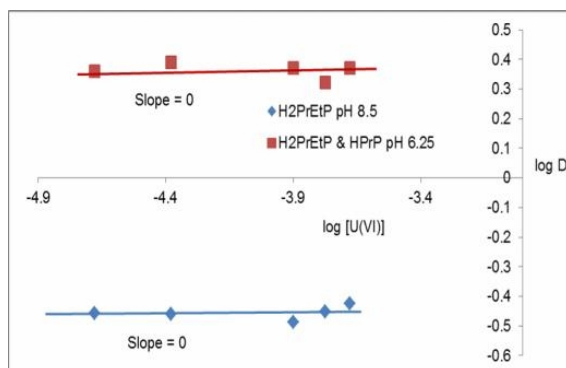
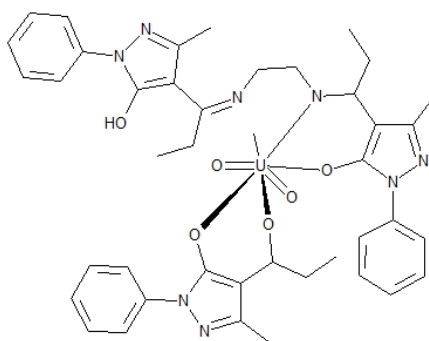


Fig. 4. Variation of metal ion concentrations at constant pH and $[H_2PrEtP]$ values for the extraction of U(VI) in the presence and absence of a mixed ligand [HPrP] at room temperature

In view of these experimental results the suggested reaction between UO_2^{2+} and H_2PrEtP in a mixture with a fixed 0.05M HPrP concentration is as given in equation 7 while the proposed structure of the metal complex is given in scheme 3. The proposed structure shown in scheme 3 is indicating that the two protons displaced in the extraction were coming from hydroxyl groups in the ligand and synergist. Thus, extracted uranyl complex species were slightly different in structure from those reported by Godwin and Uzoukwu 2012 [10], for the extraction of U(VI) using *N,N'*-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H_2BuEtP) in the presence of 4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP) as a synergist in which the protons were suggested not to be attached to the hydroxyl groups. This can be attributed to the slightly lower pK_{a1} of H_2PrEtP 6.1 in comparison to the pK_{a1} of 6.6 for H_2BuEtP , indicating that this ligand H_2PrEtP was a slightly stronger acid than H_2BuEtP and thus, ionizes better and faster [15-16].



Scheme 3. Proposed structure of $\text{UO}_2(\text{HPrEtP}).\text{PrP}.\text{X}$, where $\text{X} = \text{Cl}^-$, CH_3COO^- , etc. from buffers

Values for $\log K_{\text{ex}}$ ($-5.84 \pm 0.18 \log K_{\text{ex}} \text{H}_2\text{PrEtP}$) $> -8.71 \pm 0.50 \log K_{\text{ex}} \text{H}_2\text{PrEtP}/\text{HPrP}$ and K_{D} (Partition coefficient) ($1.49 \pm 0.01 \text{H}_2\text{PrEtP}$) $< 2.49 \pm 0.01 \text{H}_2\text{PrEtP}/\text{HPrP}$ for the extraction processes are calculated and presented in Table 1. The tabulated results suggest that uranyl complex species extracted in the absence of HPrP was $\text{UO}_2(\text{HPrEtP}).\text{X}$, and had higher formation constants. However, the higher partition coefficient (K_{D}) in the presence of HPrP as a mixed ligand show that this mixed ligand organic phase was a much better extractant for U(VI). Similar observations had been reported by previous authors [10 - 12] in the presence of mixed ligands.

Table 1. Extraction data of the influence of pH of aqueous phase on the extraction of 8.4×10^{-4} M of U(VI) into organic solutions of 0.05 M H_2PrEtP and mixture of 0.05 M H_2PrEtP -0.05 M HPrP (9:1) ratio at room temperature

Metal	Organic Phase	$\log K_{\text{ex}}$	$\text{pH}_{1/2}$	K_{D}	Species extracted
U (VI)	0.05 M H_2PrEtP	-5.84 ± 0.18	6.90 ± 0.10	1.49 ± 0.01	$\text{UO}_2(\text{HPrEtP}).\text{X}_{(\text{o})}$
	0.05 M H_2PrEtP - 0.05 M HPrP (9:1) mixture	-8.71 ± 0.50	4.40 ± 0.10	2.49 ± 0.01	$\text{UO}_2(\text{HPrEtP}).\text{HPrP}.\text{X}_{(\text{o})}$

4. CONCLUSION

The ligand H₂PrEtP is a very weak acid with pK_{a1} values of 6.1 ± 0.1 and pK_{a2} of 7.6 ± 0.1. The ligand H₂PrEtP can be used as an extractant both in the absence and presence of HPrP as a mixed ligand for U(VI) in buffered aqueous solutions. The study showed that extraction of U(VI) from aqueous media into chloroform solutions of the ligand occurred between pH 6.0 to 8.5 in the absence of HPrP and pH 4.0 to 6.5 in the presence of HPrP. Lower pH values favored extraction with chloroform solution in a mixture of the ligands. The observed enhanced extraction in the presence of HPrP resulted to an increase in optimal percentage (%) extraction of U(VI) from 96.9% to 99.9%. Although log K_{ex} values (-5.84 ± 0.18 log K_{ex} H₂PrEtP) > -8.71 ± 0.50 log K_{ex} H₂PrEtP/HPrP) is indicating higher formation constant of the complex UO₂(HPrEtP)X_(o) formed in the absence of the ligand HPrP. The very high partition coefficient K_D = 2.49, the wider range of pH 4.0 – 6.5 in which quantitative extractions occurred in the presence of HPrP, and the shift in pH_{1/2} from 6.9 ± 0.10 for H₂PrEtP to 4.4±0.10 for H₂PrEtP/HPrP, conclusively show that the complex UO₂(HPrEtP).HPrP.X_(o) distributed better in this organic phase and extraction of U(VI) is more favorable in aqueous solutions of lower pH values with this ligand mixtures. Slope analysis indicated that species characterized as adduct complexes with suggested formulae UO₂(HPrEtP)X₂ and UO₂(HPrEtP).HPrP.X, where X is an anion in excess were extracted and the mixed ligands organic phase was a better extractant for U(VI) than H₂PrEtP alone.

ACKNOWLEDGEMENTS

The authors wish to thank the University of Port Harcourt, Alexander von Humboldt Stiftung, Germany and Prof Karsten Gloe for research assistance to late BA Uzoukwu in the characterization of the Schiff base HPrEtP.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Kalagbor AI, Uzoukwu BA, Chukwu UJ. Extraction of Molybdenum (VI) With 4- Adipoyl And 4-Sebacoyl Derivatives of Bis(1-Phenyl-3-Methylpyrazolone-5) In Acid Media. Nature and Science. 2011;9(3):37-42.
2. Okafor EC, Uzoukwu BA. Extraction of Fe (III) and U (VI) with 1-phenyl-3-methyl-4 acylpyrazolones-5 from aqueous solutions of different acids and complexing agents. Radiochimica Acta. 1990; 51:167-172.
3. Uzoukwu BA, Mbonu JI. Effect of chloride ion in a buffer medium on the liquid-liquid extraction of Cu(II) and Ni(II) using 1-phenyl-3-methyl-4-trichloroacetyl-pyrazolone-5. Solvent Extraction and Ion Exchange. 2005;23(6):759-771.
4. Atanassova M. Synergistic solvent extraction of La(III), Eu(III) and Lu(III) with mixtures of 5,7-dibromo-8-hydroxyquinoline and crown ethers. J Uni Chem Tech Metal. 2006;41(1):81-84.
5. Oshima S, Hirayima N, Kubono K, Kokusen H, Honjo T. Structural Control of Schiff Base Ligands for Selective extraction of Copper (II). Analytical Chemistry 2002;18:1351–1355

6. Topuz B, Macit M. Solid phase extraction and preconcentration of Cu(II), Pb(II), and Ni(II) in environmental samples on chemically modified Amberlite XAD-4 with a proper Schiff base. *Environ Monit Assess.* 2011;173(1-4):709–722.
7. Zyadanogullari B, Cevizic D, Temel H, Zyadanogullari R. Synthesis, Characterization and Structure Effects on the Preconcentration and Extraction of N, N'-bis(Salicylaldehyde)-1, 4-bis(p-aminophenoxy) butane towards divalent cations. *Journal of Hazardous Materials.* 2008;150:285–289.
8. Uzoukwu BA, Gloe K, Duddeck H. '4-Acylpyrazoloneimine Schiff Bases and their Metal Complexes: Synthesis and Spectroscopic Studies', *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry.* 1998;28(5):819-831.
9. Uzoukwu BA, Gloe K, Duddeck H. N, N'-ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) derivatives: Synthesis and UV, IR, 1H and 13C NMR Spectral Studies. *Indian Journal of Chemistry.* 1998; 37B:1180–1183.
10. Godwin J, Uzoukwu BA. Distribution of U(VI) 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. *International Journal of Chemistry.* 2012;4(4):105-116.
11. Uzoukwu BA, Gloe K, Duddeck H. Extraction of Uranium(VI) and Vanadium (V) with 4-adipoyl and 4-sebacoyl derivatives of bis(1-phenyl-3-methyl-pyrazolone-5) and effect of decanol on the distribution behavior of these metal ions. *Solvent Extraction and Ion Exchange.* 1998;16(3):751-774.
12. Chukwu UJ, Uzoukwu BA. Synergistic extraction of Zn²⁺ from aqueous buffer medium of chloride ions into 1- phenyl -3- methyl -4- Trichloro Acetyl Pyrazolone - 5 in Benzene and Hexane. *Recent Patents on Materials Science.* 2010;3(2):146-150.
13. Uzoukwu BA, Adiukwu PU. Kinetic-Studies on the recovery of Lead(II) And Lanthanum(III) from aqueous-solution with Xylene solution of 1-phenyl-3-methyl-4-benzoylpyrazolone. *Indian Journal of Chemistry. Sect. A: Inorganic, Physical, Theoretical & Analytical.* 1996;35(3):230-232.
14. Uzoukwu BA. *Basic Analytical Chemistry.* Pam Unique Publishers Port Harcourt: Nigeria. 1992;38-41.
15. FA, Wilkinson G. *Advanced Inorganic Chemistry, a Comprehensive Text.* 3rd ed. Mohinder Singh Sejwal: New Delhi. 1985;893-912.
16. Lee JD, *Concise Inorganic Chemistry 5th Edition,* Published by Blackwell Science Ltd. USA. 1996;835-846.

© 2013 Chukwu and Godwin; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:

The peer review history for this paper can be accessed here:
<http://www.sciencedomain.org/review-history.php?iid=242&id=16&aid=1850>