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

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Abstract

The distribution of U(VI) from aqueous media into chloroform solution of N,N'-ethylenebis (4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H₂BuEtP) a Schiff base has been studied to determine the effect of buffer media, mineral acids, auxiliary complexing agents and 4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP) on the distribution behaviour. A 1:1 interaction was observed between U(VI) and the ligand during the extraction process and one mole of hydrogen ion was found to have been displaced in the reaction process. The study shows that pH¹/₂ of the extraction of U(VI) shifted from 4.88 ± 0.10 to 2.14 ± 0.10 for CHCl₃ solutions of H₂BuEtP and H₂BuEtP-HBuP respectively. Extraction constants (Log K_{ex}) -1.68 ± 0.12 and -0.72 ± 0.13 were determined respectively from the studies, indicating that addition of HBuP made the extraction process more efficient. Species extracted were characterized as complexes with suggested formulae UO₂(HBuEtP)X and UO₂(HBuEtP)X.HBuP where X is an anion. Graphical analysis shows also that UO₂(HBuEtP)X.HBuP could be extracted as UO₂(BuP)X.(H₂BuEtP), indicating a potential synthetic method for metal complex species with position isomers by liquid-liquid extraction technique. Studies of extraction from auxiliary complexing agents support the existence of species proposed above leading to enhanced extraction of U(VI) from $X = NO_3^2$, SO_4^2 , CH₃COO⁻, SCN⁻, Cl⁻, l⁻ and F⁻ media. Percentage extraction of U(VI) from mineral acids suggests that U(VI) extraction tend to increase with decrease in acid strength.

Keywords: acids, anions, pH, N,N'-ethylenebis, solvent Extraction, Uranium(VI)

1. Introduction

Derivatives of 1-phenyl-3-methyl-4-acyl-pyrazolone-5 are well established as a class of β -diketone that form very stable metal complexes (Chen, Zhan, & Meng, 1996; Uzoukwu, Al-Juaid, Hitchcock, & Smith, 1993; Uzoukwu, Gloe, Menzel, & Rademacher, 2001). They are renowned for their wide application in solvent extraction (Uzoukwu & Mbonu, 2003; Eyal, Baniel, Hajdu, & Mizrahi, 1990; Barkat, Kameche, Tayeb, Benabdellah, & Derriche, 2004) studies and have recently attracted much attention due to their potential application in electronic (Lu et al., 2008) and spent fuel (Zhang, Wanyan, & Kumagai, 2004; Parajuli, Hirota, & Seko, 2011; Mezhov, Kuchumov, & Druzhenkov, 2002) reprocessing programmers. Beta-diketones as bidentate ligands employ the O=C-C=C-OH moiety as the principal functional group in their complication reactions with transition metals. In continuation of our work on the synthesis and characterization (Uzoukwu, Gloe, & Duddeck, 1998a) 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 transition metal extractant and recovery of radioactive metals. Schiff bases are compounds that contain the carbon-nitrogen double bond traditionally connected to an aryl or alkyl group. 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. Earlier studies have

shown that Schiff bases of 4-acylpyrazolone are capable of forming interesting metal complexes (Uzoukwu, Gloe, & Duddeck, 1998b; Amarasekara, Owereh, Lyssenko, & Timofeeva, 2009) with appealing coordination properties. Some reports on trivalent Sm, Eu and Gd complexes of tridentate salicylidene hydrazone derivatives of 4-acylpyrazolone-5 (Liu, Jia, Ji, & Yu 2003) have shown that their solid complexes have fluorescence properties and the thiosemicarbazone (Liu, Liu, Jia, & Yu, 2005) Schiff base derivatives exhibited biochemical (Yadav, Pandey, & Sengupta, 1995) photo chromic (Liu et al., 2005) and acid chromic properties due to tautomerism in their molecular structures. Reports of promising antitumor, antipyretic and anti-inflammatory activity of Schiff bases are also known (Yadav et al., 1995; Magdy, Farag, Salah, Tarek, & Nader, 2007).

As the search for efficient metal ion extractants goes on, we have studied the application of N,N'-ethylenebis(4-butanoyl-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 (Uzoukwu, et al., 1998a). The study investigated the effect of pH, acids and anions on the extraction of U(VI) from aqueous solutions using the tetra dentate ligand with a view of understanding the role played by these media in the interaction of U(VI) with Schiff base derivatives of 4-acylpyrazolone. The investigation also looked at the effect of 4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one with O=C-C=C-OH moiety as a synergist on the distribution behavior of U(VI) into a solution of predominantly N=C-C-OH bonding species.

2. Experimental

2.1 Reagents and Apparatus

The bone white N,N'-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) (H₂BuEtP) shown in scheme 1a was synthesized by methods described elsewhere (Uzoukwu, et al., 1998a). The ligand's purity after recrystallization from aqueous ethanol was established by elemental analysis for C, H and N; analysis of IR and NMR spectral data at the Institute for Inorganic Chemistry Technology, University of Dresden, Germany.



N,N'-ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) Scheme 1a

Stock solutions of 0.05 M H₂BuEtP were prepared by dissolving appropriate mass of the ligand in CHCl₃. Stock solutions 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 8.4 x 10^{-3} M (2,000 mg/L) of U(VI) were prepared by dissolving appropriate mass of the metal acetate (UO₂(CH₃COO)₂.2H₂O) in 0.1 mL of 10 M HCl and making up to mark in a 50 ml volumetric flask 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). pH of the buffered solutions were determined with a

Labtech Digital pH meter. Solutions of 0.001-2 M mineral acid or complexing agent concentrations were prepared by diluting appropriate volumes of stock solutions of mineral acid or sodium salt of complexing agent. All experiments were performed at ionic strength of 0.1 M (NaClO₄).

Modelling of H_2BuEtP was carried out using ChemBio3D Ultra 11.0 molecular modeling package. The pK_a of the Schiff base was determined potentiometrically as reported elsewhere (Uzoukwu, Gloe, & Duddeck, 1998c).

2.2 Extraction Procedure

2 mL aliquot of a buffer solution containing 8.4×10^{-4} M (200 mg/L) of U(VI) ions and the desired pH of solution was prepared in a 10 ml extraction container. For extraction studies involving mineral acid or complexing agents, 2 ml aliquot of solution containing 8.4×10^{-4} M of U(VI) ions and the desired mineral acid or complexing agent concentration was prepared in a 10 ml extraction container. An equal volume (2 mL) of chloroform solution of 0.05 M concentration of H₂BuEtP or 0.05M H₂BuEtP :0.05 M HBuP (9:1 ratio by volume) was added and the mixture shaken mechanically for 30 minutes at room temperature of about 30 °C. A shaking time of 30 minutes was found suitable enough for equilibration. The phases were allowed to settle and separated. Analysis of the U(VI) ion in aqueous raffinate was determined calorimetrically as follows: 1 ml aliquot of the aqueous raffinate was neutralised with 10 % sodium carbonate and 10 % sodium hydroxide. The yellow colored solution was developed with 10 % hydrogen peroxide solution and absorbance against a reagent blank obtained at 370 nm with a UV-visible spectrophotometer. U(VI) ion concentration extracted into the organic phase was determined from the difference between the concentration of U(VI) 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 .

3. Results and Discussion

Result from modelling calculation of H_2BuEtP is presented as scheme 1b. It shows no substantial difference between the structural schemes 1a and 1b. Although both C=N groups of ethylenediamine appeared in the same structural plain the two C-OH groups are however slightly orientated out of plane with respect to each other (Scheme 1b).



Molecular modeling of *N*,*N*'-Ethylenebis(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-oneimine) Scheme 1b

From graphical result presented in Figure 1 the pK_a of the ligand was determined as 6.6 ± 0.1 . This has been ascribed to first ionization of one of the –OH groups of the ligand. It is also an indication that the ligand is a very weak acid. A second pK_a value of 6.9 ± 0.1 was also determined from the graph.



Figure 1. Graphical presentation of potentiometric titration between 20 ml 2.5 x 10-3 M H2BuEtP and 5 x 10-3 M NaOH, both prepared in 80 % aqueous 1,4-dioxane solution (a) pH-volume plot (b) ΔpH/Δvolume-volume plot

3.1 Effect of Buffer Solution

Extraction of U(VI) from aqueous media into an organic solvent '(o)' containing a tetra dentate ligand H₂BuEtP can be represented by the following equations:

$$UO_2^{2+} + H_2 BuEtP_{(o)} \Longrightarrow UO_2 (BuEtP)_{(o)} + 2H^+$$
(1)

where H_2BuEtP is the tetra dentate Schiff base with the assumption that the metal: ligand interaction is in the 1:1 mole ratio.

$$K_{ex} = \frac{[UO_2(BuEtP)_{(o)}][H^+]^2}{[UO_2^{2^+}][H_2BuEtP_{(o)}]}$$
(2)

The distribution ratio D is given by $D = [UO_2(BuEtP)_{(0)}]/[UO_2^{2+}])$ which on substitution into equation (2) gives,

$$LogD = log K_{ex} + log[H_2BuEtP] + 2pH$$
(3)

where K_{ex} is extraction constant. Extraction plots presented on Figures. 2 (a) and (b) show the influence of pH of solution on the distribution behavior of U(VI) into chloroform solutions of H₂BuEtP and H₂BuEtP-HBuP respectively. A slope of 1 was recorded in each of the graphs indicating that 1 mole of hydrogen ion was displaced during extraction in each of the different extraction systems. This result does not agree with equation (1) for a 1:1 interaction between U(VI) and H₂BuEtP in which 2 moles of hydrogen was expected to be displaced. Slope analysis of extraction results presented in Figure 3 shows that the metal interacted with one mole of H₂BuEtP. The probable reaction during the extraction process can therefore be represented as shown.

$$UO_2^{2^+} + H_2BuEtP_{(o)} + X = UO_2(HBuEtP)X_{(o)} + H^+$$
(4)

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

$$K_{ex1} = \frac{[UO_2(HBuEtP)X_{(o)}][H^+]}{[UO_2^{2^+}][H_2BuEtP_{(o)}]}$$
(5)

where X⁻ is an incorporated in K_{ex1}. Hence the distribution ratio $D_1 = [UO_2(HBuEtP)X_{(0)}]/[UO_2^{2+}]$ shall on substitution into equation (5) give,

$$Log D_{l} = log K_{exl} + log [H_{2}BuEtP] + pH$$
(6)

The partition coefficient (K_{D1}) of UO₂(HBuEtP) $X_{(o)}$ species is defined as K_{D1} =[UO₂(HBuEtP) $X_{(o)}$] /[UO₂(HBuEtP)X] for which a value of 0.56 ± 0.11 was determined. Data of all the extraction processes are contained on Table 1. To be in conformity with equation (4) the structure suggested for the extracted uranyl complex species is shown in scheme 2.



 $UO_2(HBuEtP)X_{(0)}, X^- = Cl^-, CH_3COO^-, etc$ Scheme 2

3.2 Influence of Hbup on the Distribution of U(VI) into H2buetp

Plots of the distribution of U(VI) into chloroform solutions of a mixture of H_2BuEtP and HBuP are presented in Figures 4(a) and (b). The plots show that one mole of U(VI) interacted with one mole of H_2BuEtP in the presence of a fixed concentration of HBuP and also with one mole of HBuP in the presence of a fixed concentration of H_2BuEtP. Involvement of one mole of U(VI) in all the extraction processes (Uzoukwu, Gloe, & Duddeck, 1998c) was determined by plots presented in Figures 5(a) and (b). In each of the plots a slope of zero was obtained. In view of these experimental results the suggested reaction between U(VI) and H_2BuEtP in a mixture with a fixed HBuP concentration is therefore,

$$UO_2^{2^+} + H_2 BuEtP_{(o)} + HBuP_{(o)} + X = UO_2(HBuEtP)X.HBuP_{(o)} + H^+$$
(7)

In which HBuP, acting as a synergist lead to an increase in extraction of U(VI) as UO₂(HBuEtP)X.HBuP species. Thus, the extraction of U(VI) was observed to increase from 78 % in the absence of HBuP to 98 % when HBuP was added. It also gave rise to a wider pH range of 4 - 7.5 from a narrow pH range of 6 - 8.5 where quantitative extraction of U(VI) could be achieved. These are reflected in the increased values recorded for both partition coefficient $K_{D2} = [UO_2(HBuEtP)X.HBuP_{(o)}]/[UO_2(HBuEtP)X.HBuP] = 1.74\pm0.20$ (K_{D2}, 1.74 ±0.20 > K_{D1}, 0.56±0.11) and extraction constant K_{ex2} = -0.72 (K_{ex2}, -0.72 ±0.13 > K_{ex1}, -1.68±0.12) (Table 1). Figures 2(a) and (b) also show that pH¹/₂ shifted from 4.88 (H₂BuEtP) to 2.14 (H₂BuEt-HBuP mixture); an indication that the ligand mixture is a better extractant for U(VI) from aqueous solutions of lower pH values.

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

$$K_{ex2} = \frac{[UO_2(HBuEtP)X.HBuP_{(o)}][H^+]}{[UO_2^{2^+}][H_2BuEtP_{(o)}]}$$
(8)

where [HBuP] and [X⁻] are constants incorporated in K_{ex2} . The distribution ratio $D_2 = [UO_2(HBuEtP)X.HBuP_{(0)}]/[UO_2^{2+}]$ which on substitution into equation (8) gives,

$$Log D_2 = log K_{ex2} + log [H_2 Bu Et P] + pH$$
(9)

Similarly the other complexation in a fixed H_2BuEtP concentration (Figure 3b) equally took place in a metal:ligand mole ratio of 1:1. The reaction can be represented as,

$$UO_2^{2^+} + HBuP_{(o)} + H_2BuEtP_{(o)} + X \implies UO_2(BuP)X.H_2BuEtP_{(o)} + H^+$$
(10)

An indication that the extracted adduct species could as well be the $UO_2(BuP)X.H_2BuEtP_{(0)}$ complex. This is because in both reactions one mole of H^+ is displaced (Figure 1b). The extraction constant K_{ex3} is given as follows:

$$K_{ex3} = \frac{[UO_2(BuP)X.H_2BuEtP_{(o)}][H^+]}{[UO_2^{2^+}][HBuP_{(o)}]}$$
(11)

where [H₂BuEtP] and [X] are constants incorporated in K_{ex3}. The distribution ratio $D_3 = [UO_2(BuP)X.H_2BuEtP_{(o)}]/[UO_2^{2^+}]$ which on substitution into equation (11) gives,

$$LogD_3 = \log K_{ex3} + \log[HBuP] + pH$$
(12)

We are suggesting that results from studies of distribution of U(VI) into organic solution of a mixture of the ligands are probably indicating extraction of complex species with structure presented in scheme 3. This satisfies the derivations of both equations 7 and 10. This is because the two protons may be very mobile within the molecule and not attached to hydroxyl groups as the formula of scheme 3 is portraying. It probably indicated a synthetic method for metal complex species with position isomers by liquid-liquid extraction technique.



 $UO_2(HBuEtP)X.HBuP_{(0)}, X^- = Cl^-, CH_3COO^-, etc.$ Scheme 3



Figure 2. Plot of extraction of 8.4 x 10⁻⁴ M U(VI) from buffer solutions into (a) chloroform solution of 0.05 M H₂BuEtP and (b) chloroform solution of 0.05 M H₂BuEtP-0.05 M HBuP in the 9:1 ratio by volume



Figure 3. LogD-log [H₂BuEtP] plot of extraction of 8.4 x 10^{-4} M of U(VI) from buffer solutions at constant pH of 5.90



Figure 4. LogD-log [Ligand] plot of extraction of 8.4 x 10^{-4} M of U(VI) from buffer solutions into chloroform solutions of ligand (a) [HBuP] was kept constant (5 x 10^{-3} M) (b) [H₂BuEtP] was kept constant (2.5 x 10^{-2} M)



Figure 5. Log D-log [U(VI)] plot of extraction of U(VI) from buffer solutions into chloroform solutions of ligand (a) 0.05 M H₂BuEtP (b) mixture of 0.05 M H₂BuEtP and 0.05 M HBuP in a 9:1 ratio

Table 1. Extraction data of the influence of pH of aqueous phase on the extraction of 8.4 x 10-4 M of U(VI) into organic solutions of 0.05 M H2BuEtP and mixture of 0.05 M H2BuEtP-0.05 M HBuP (9:1) ratio at room temprature of 30° C (ionic strength of 0.1 M NaClO4)

| | LogK _{ex} | pH ¹ / ₂ | Log K _D | Species extracted |
|---|--------------------|--------------------------------|--------------------|----------------------|
| 0.05 M H ₂ BuEtP | -1.68 ± 0.12 | 4.88 ± 0.10 | 0.56 ± 0.11 | UO2(HBuEtP)X(0) |
| $0.05 \text{ M} \text{ H}_2\text{BuEtP-}0.05 \text{ M}$ | -0.72 ± 0.13 | 2.14 ± 0.10 | 1.74 ± 0.20 | UO2(HBuEtP)X.HBuP(o) |
| HBuP (9:1) mixture | | | | |
| | | | | |

3.3 Influence o of Acids, Anions And Auxiliary Complexing Agents on the Distribution of U(VI)

The results are presented on Table 2 as % extraction of U(VI) ions from aqueous phase of known molar concentration of species into CHCl₃ solutions of extractants. Table 2 shows that apart from phosphoric acid solutions, U(VI) is poorly extracted from mineral acid solutions into H₂BuEtP/CHCl₃. While 99 % extraction could be achieved for phosphoric acid solution (0.005 M) the maximum extraction that could be obtained for other acids was 52 % (0.5 M acetic acid). The Table also shows that when acid concentration is increased from 0.005 M to 0.5 M the % extraction of U(VI) falls gradually in many cases. This has been attributed to unextractible ion-pair uranyl anionic species which are more favorably formed at higher acid concentrations than in dilute acid solutions. Introduction of H₂BuEtP-HBuP/CHCl₃ as extractant resulted in increase in distribution of U(VI). The result is that % extraction in most cases increased to as much as 98 % even for higher acid

concentration of 0.5 M. The results show that H₂BuEtP-HBuP/CHCl₃ is a better extractant of U(VI) from acid solutions when compared with H₂BuEtP/CHCl₃. Low recovery of U(VI) from sulphuric acid solution is observed at all concentrations of the acid. To some approximation increase in % extraction of U(VI) from acid solutions could be arranged to follow the sequence: $H_2SO_4 \ll HCl \ll HNO_3$, $H_3PO_4 \ll CH_3COOH$. This seems to suggest that % extraction of U(VI) increases with decrease in acid strength.

The Table also shows that recovery of U(VI) from solutions of anions and complexing agents is tremendously improved when H₂BuEtP-HBuP/CHCl₃ was used as extractant. It shows that U(VI) extraction (H₂BuEtP/CHCl₃) increased with increase in SCN⁻, Cl⁻ and l⁻ concentrations (from 0.005 M to 0.5 M) rather than decrease as observed for the acids. This observation supports our scheme **2** where anion X plays a very important role in the structure suggested (UO₂(HBuEtP)X), and which may have lead to the slight increase in U(VI) extraction. This same view was supported by quantitative extraction of U(VI) recorded over a very wide concentration range of Cl⁻, l⁻, SO₄²⁻, NO₃⁻ and CH₃COO⁻ ions using H₂BuEtP-HBuP/CHCl₃. We had earlier concluded that H₂BuEtP-HBuP/CHCl₃ is a better extractant than H₂BuEtP/CHCl₃.

| Table 2. Extraction data of 8.4 x 1 0-4 M of U(VI) from various a | aqueous phases into chloroform solution of |
|---|--|
| ligand and 9:1 ratio of mixture of ligands at room temprature of 30°C | (ionic strength of 0.1 M NaClO4) |

| Aqueous phase | | Extraction of U(VI) ±1 | | | |
|---------------|----------------------------------|-----------------------------|---|--|--|
| | | 0.05 M H ₂ BuEtP | 0.05 M H ₂ BuEtP-0.05 M HBuP | | |
| 0.005 M | H_2SO_4 | 9 | 78 | | |
| | HC1 | 32 | 83 | | |
| | HNO ₃ | 37 | 66 | | |
| | H_3PO_4 | 99 | 97 | | |
| | CH ₃ COOH | 34 | 93 | | |
| 0.5 M | H_2SO_4 | 1 | 4 | | |
| | HC1 | 24 | 40 | | |
| | HNO ₃ | 43 | 36 | | |
| | H_3PO_4 | 34 | 36 | | |
| | CH ₃ COOH | 52 | 98 | | |
| 0.005 M | NO ₃ - | 26 | 98 | | |
| | SO_4^{2-} | 34 | 94 | | |
| | PO ₄ ³⁻ | 27 | 48 | | |
| | CH ₃ COO ⁻ | 31 | 86 | | |
| | Cl | 25 | 99 | | |
| | Br⁻ | 25 | 98 | | |
| | I- | 28 | 97 | | |
| | F- | 30 | 75 | | |
| | SCN ⁻ | 37 | 99 | | |
| | EDTA | 27 | 97 | | |
| | Oxalate | 25 | 98 | | |
| | Tartrate | 34 | 75 | | |
| 0.5 M | NO ₃ - | 31 | 88 | | |
| | SO_4^{2-} | 21 | 92 | | |
| | PO ₄ ³⁻ | 2 | 1 | | |
| | CH ₃ COO ⁻ | 34 | 94 | | |
| | Cl | 53 | 92 | | |
| | Br⁻ | 1 | 0 | | |
| | F- | 27 | 61 | | |
| | SCN ⁻ | 69 | 98 | | |
| | EDTA | 1 | 24 | | |
| | Oxalate | 22 | 49 | | |
| | Tartrate | 27 | 41 | | |

This is because the extraction increased tremendously to 98 % in many cases when H_2BuEtP - $HBuP/CHCl_3$ was used. This trend probably supports scheme 3 suggested for the U(VI) adduct complex obtained. X was suggested as the ligand that completed the coordination sphere of the proposed complex that lead to increased U(VI) extraction. Perhaps coordination of X to the uranyl centre further increased the hydrophobicity of the extracted

uranyl mixed ligand complex species. This is evident in rise in extraction of the metal ion when anion concentration was raised from 0.005 M to 0.5 M. Extraction from Br⁻ and EDTA solutions were found to fall drastically when their concentrations increased from 0.005 M to 0.5 M.

4. Conclusion

The effects of buffered media on the extraction of U(VI) into H₂BuEtP a pyrazoloneimine Schiff base and its mixture with HBuP a pyrazolone have been studied. The study showed that extraction of U(VI) from aqueous solutions of low pH values is more favourable with chloroform solution of a mixture of the ligands. The observed synergism resulted to an increase in % extraction of U(VI) from 78 % to 98 % in addition to shift of the extraction process to lower pH values. Slope analysis indicated that species characterized as adduct complexes with suggested formulae UO₂(HBuEtP)X and UO₂(HBuEtP)X.HBuP, where X is an anion were extracted. Analysis shows that UO₂(HBuEtP)X.HBuP could be extracted as UO₂(BuP)X.(H₂BuEtP) species. This indicated a potential synthetic method for metal complex species with position isomers by liquid-liquid extraction technique. Studies of extraction from auxiliary complexing agents support the existence of species proposed above and this may have lead to enhanced extraction of U(VI) from Xⁿ = NO₃⁻, SO₄²⁻, CH₃COO⁻, SCN⁻, Cl⁻, I⁻ and F⁻ media. Percentage extraction of U(VI) from mineral acids shows that increase in extraction of U(VI) can be arranged in the following sequence: H₂SO₄ << HCl < HNO₃, H₃PO₄ < CH₃COOH which suggests that extraction of U(VI) tend to increase with decrease in acid strength.

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References

- Amarasekara, A. S., Owereh, O. S., Lyssenko, K. A., & Timofeeva, T. V. (2009). Structural tautomerism of 4-acylpyrazolone schiff bases and crystal structure of 5-methyl-2-phenyl-4-{1-[(pyridin-2-ylmethyl)-amino] -ethylidene}-2,4-dihydro-pyrazol-3-one. J. Struct. Chem., 50(6), 1159. http://dx.doi.org/10.1007/s10947-009-0170-4
- Barkat, D., Kameche, M., Tayeb, A., Benabdellah, T., & Derriche, Z. (2004). Ionic strength effect on the liquid-liquid extraction of zinc(II) and cadmium(II) from sulphate medium by 1-phenyl-3-methyl-4-benzoylpyrazol-5-one in chloroform. *Physics and Chemistry of Liquids, 42*(1), 53. http://dx.doi.org/10.1080/0031910031000120595
- Chen, X. Y., Zhan, S. Z., & Meng, Q. J. (1996). Synthesis and spectroscopic studies of trinuclear uranyl complexes with compartmental ligands H4L derived from 2,6-dipicolinoyl-hydrazine and 4-acyl-1-phenyl-3-methyl-pyrazolones-5 (where acyl = benzoyl, acetyl, iso-butyryl or iso-valeroyl). *Transition Met. Chem.*, *21*, 345.
- Eyal, A. M., Baniel A. M., Hajdu, K., & Mizrahi, J. (1990). New Process for Recovery of Zinc Sulfate and Sulfuric Acid from Zinc Electrowinning Bleed Solutions. *Solvent Extr. Ion Exch.*, *8*, 209.
- Liu, G., Liu, L., Jia, D., & Yu, K. (2005). Synthesis, Structure and Photochromic Properties of 1-Phenyl-3-Methyl-4-(4-Bromobenzal)-Pyrazolone-5 Thiosemicarbazone. *Structural Chemistry*, 16(2), 135. http://dx.doi.org/10.1007/s11224-005-2837-6
- Liu, L., Jia, D. Z., Ji, Y. L., & Yu, K. B. (2003). Synthesis, structure and photochromic properties of 4-acyl pyrazolone derivants. *J. Photochem. Photobiol, 154, 117.* http://dx.doi.org/10.1016/S1010-6030(02)00321-0
- Lu, J., Zhang, L., Liu, L., Liu, G., Jia, D., Wu, D., & Xu, G. (2008). Study of fluorescence properties of several 4-acyl pyrazolone derivatives and their Zn (II) complexes. *Spectrochimi. Acta.*, 71(3), 1036. http://dx.doi.org/10.1016/j.saa.2008.02.048
- Mezhov, E. A., Kuchumov, V. A., & Druzhenkov, V. V. (2002). Study of Extraction of Palladium from Nitric Acid Solutions with Nitrogen-Containing Compounds, as Applied to Recovery of Fission Palladium from Spent Nuclear Fuel of Nuclear Power Plants: 1. Extraction and Backwashing Conditions. *Radiochemistry*, 44(2), 135. http://dx.doi.org/10.1023/A:1019663027481
- Parajuli, D., Hirota, K., & Seko, N. (2011). Effective separation of palladium from simulated high level radioactive waste. J. Radioanal. Nucl. Chem., 288(1), 53. http://dx.doi.org/10.1007/s10967-010-0870-4
- Uzoukwu, B. A., Al-Juaid, S. S., Hitchcock, P. B., & Smith, J. D. (1993). The Synthesis and crystal structures of

1-phenyl-3-methyl-4-butanoylpyrazol-5-one and of two pyrazolonato complexes of iron. *Polyhedron, 12* (22), 2719. http://dx.doi.org/10.1016/S0277-5387(00)80123-0

- Uzoukwu, B. A., Gloe, K., & Duddeck, H. (1998a). N,N'-Ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) derivatives: Synthesis and UV, IR, 1H and 13C NMR spectral studies. *Indian J. Chem.*, *37B*, 1180.
- Uzoukwu, B. A., Gloe, K., & Duddeck, H. (1998b). 4-Acylpyrazoloneimine Schiff Bases and their Metal Complexes: Synthesis and Spectroscopic Studies. *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry*, 28(5), 819-831. http://dx.doi.org/10.1080/00945719809349384
- Uzoukwu, B. A., Gloe, K., & Duddeck, H. (1998c). 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. *Sol. Ext. Ion Exch.*, *16*(3), 751. http://dx.doi.org/10.1080/07366299808934551
- Uzoukwu, B. A., Gloe, K., Menzel, M., & Rademacher, O. (2001). Synthesis, Spectroscopic, and X-Ray Diffraction Studies of *cis*-Dichlorobis(4-propanoyl-2,4-dihydro-5-methyl-2-phenyl3 H-pyrazol-3-onato) Tin(IV). Z. Anorg. Allg. Chem., 627, 103.
- Uzoukwu, B. A., & Mbonu, J. I. (2005). 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 Ext. Ion-Exch.*, 23, 759.
- Yadav, S., Pandey O. P., & Sengupta, S. K. (1995). Synthesis, physico-chemical and biological studies on oxovanadium(IV) derivatives of mercaptotriazoles. *Transition Met. Chem.*, 20(2), 107. http://dx.doi.org/10.1007/BF00167006
- Zahran M. A., El-Essawy, F. A., M. Y., Salem, T. A., & Boshta, N. M. (2007). Rapid and Efficient Synthesis of 4-Substituted Pyrazol-5-one under Microwave Irradiation in Solvent-Free Conditions. Archiv der Pharmazie, 340(11), 591. http://dx.doi.org/10.1002/ardp.200700121
- Zhang, A., Wanyan, G., & Kumagai, M. (2004). Association Behavior of 4-Acylpyrazolone Derivative and Tertiary Amine of High Molecular Weight in Antagonistic Synergistic Extraction of Palladium. J. Sol. Chemistry 33(8), 1017. http://dx.doi.org/10.1023/B:JOSL.0000048052.86416.76