

Effect of Sulphate Ion Concentration on the Extraction of Uranium (VI) From Buffered Solutions of 1-Phenyl-3-Methyl-4-Trichloroacetyl Pyrazolone-5

Victoria Bennett, Bamidele Martin Amos-Tautua,
Ayasen Jermaine Kemeakegha, Nimibofa Ayawei

Abstract— Chloroform solutions of 1-Phenyl-3-Methyl-4-Trichloroacetylpyrazolone-5 (HTCP) for the extraction of Uranium (VI) from various buffered solutions containing different sulphate ion concentrations was investigated. Colorimetric method was used to determine Uranium (VI) concentrations in aqueous media. Uranium (VI) was not extracted between pH 0 – 2 and it was attributed to the formation of unextractable sulphate uranyl (UO_2) SO_4 complex. Optimum extraction of U(VI) of 88.70 % at pH 3.21 for solutions containing 0.01 M SO_4^{2-} , 76.84 % at pH 3.4 for solutions containing 0.1 M SO_4^{2-} and 41.24 % at pH 3.48 for solutions containing 1 M SO_4^{2-} was recorded. An increase in sulphate ion concentration decreased the optimum extraction of U(VI) from chloroform solutions of 1-Phenyl-3-Methyl-4-Trichloroacetylpyrazolone-5, thus sulphate ion concentration in buffered solutions had a masking effect on the extraction of U(VI). An adduct complex of the metal characterized as $\text{UO}_2(\text{TCP})$ was extracted with a metal ratio of 1:1

Index Terms— Percentage extraction, slope analysis, sulphate ion, Uranium (VI).

I. INTRODUCTION

Extraction among others includes separation, purification and concentration of substances. There are various methods of extraction; among them is solvent extraction, which is also known as liquid-liquid extraction. Liquid-liquid extraction technique involves two immiscible liquid phases that are in contact with one another [1].

The basis of liquid-liquid extraction is that, under a given condition, a solute would distribute between the two essentially immiscible solvents that are in contact with one another. Thus the solvent extraction process transfers the substance from the aqueous phase to the organic phase. The transfer is further enhanced by the fact that different chemical types are soluble in one solvent than the other. Extraction of metal through the process of solvent extraction is a key step in many

hydrometallurgical processes [2] for the concentration of metallic ores, recovery of vegetable oils and purification of penicillin and heat sensitive pharmaceutical products that can't be separated by other means [3].

The distribution of solute between two immiscible liquid phases is governed by Nerst distribution law [4]. The solute to be extracted is contained in the aqueous phase while the complexing agent (ligand) is contained in the organic phase. Both phases are agitated for a given period of time during which the solute migrates into the organic phase forming an extracted complex [4].

The aqueous phase includes water and mineral acids while the organic phase may be pure organic solvents such as ether, tetrachloromethane, trichloromethane, benzene, e.t.c. Also the organic phase may be any of the organic solvents listed above containing chelating agents. Many 1,3-diketones have found increasing use as metal extractants [5], [6] and some of their metal chelates have equally found application either as NMR shift agents or in later technology. Reference [7] studied the extraction of molybdenum (VI) complexes of 4-adipoly and 4-sebacoyl derivatives of bis(1-phenyl-3-methylpyrazolone-5) in the absence and presence of decanol (DOH). They reported an increase in the extraction of Mo (VI) into chloroform at high HCl concentration (1 M). Investigation of 1-phenyl-3-methyl-4-trifluoroacetylpyrazolone-5 as an extraction and spectrophotometric reagent for Fe (III) was carried out by [8]. Their result indicated that the extracted Fe (III) complex species exhibited a broad absorbance between 420 nm and 570 nm with a maximum absorbance at 480 nm. They further studied the effect of pH of the aqueous phase in the percentage extraction of Fe (III) into the organic phase containing one or two mixtures of TOPO, HTTA (chelating agents). Their results showed absorbance was maximal and percentage extraction quantitative over the pH range 1.5 – 4.5. Reference [9] investigated the extraction of Fe(III) and U(VI) with 1-phenyl-3-methyl-4-acylpyrazolone-5 from aqueous solutions of different acids and complexing agents. It was observed that the efficiency of the extraction of Fe(III) and U(VI) from solutions of nitric, sulphuric and hydrochloric acids and solutions of EDTA and thiosulphate ions using 4-butyryl (HBuP), 4-Pamitoyl (HPP) derivatives of 1-phenyl-3-methylpyrazolone increased in the order HPP < HBuP. Iron was quantitatively extracted as the chelate FeL_3 from 10^{-3} to 10^{-2} M HCl and HNO_3 solutions with their ligands. With HBuP, the quantitative extraction was obtained up to 1.0 M HCl concentration [10].

Victoria Bennett, Department of Chemical Sciences, Faculty of Basic and Applied Sciences, University of Africa, Toru-Orua, Sagbama, Nigeria
Bamidele Martin Amos-Tautua, Department of Chemical sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Amassoma, Nigeria
Ayasen Jermaine Kemeakegha, Department of Chemical sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Amassoma, Nigeria
Nimibofa Ayawei, Department of Chemical sciences, Faculty of Science, Niger Delta University, Wilberforce Island, Amassoma, Nigeria

[11] studied the extraction of U(VI) and V(V) with 4-adipoyl and 4-sebaroyl derivative of Bis(1-phenyl-3-methylpyrazolone-5) on the effect of decanol (synergist) on the distribution behavior of these metal ions. Their results showed that addition of decanol to the organic phase resulted in the enhancement of the extraction of V(V) at high HCl concentrations [11].

1-Phenyl-3-methyl-4-acetylpyrazolone-5 (HPMAP) is an interesting ligand. Apart from being a β -diketone, it possesses heterocyclic pyrazolone moiety. The molecule in addition to having four potential coordination (donor) sites, can exhibit tautomerism and each tautomer may function as a uni or bidentate ligand, coordinate to the metal atom through mono ionic or neutral form or form a bridge between two metal atoms. HPMAP and its derivatives have proved to be good chelating agents. They complex with various metals forming chelates. Hence, they are good metal extractants from solutions with low pH values [1]. 1-Phenyl-3-methyl-4-trichloroacetylpyrazolone-5 (HTCP) is a derivative of HPMAP. UO_2 is an insoluble crystalline radioactive substance that has become today's nuclear fuel of choice [12]. This study is on the Effect of sulphate ion concentration on the extraction of Uranium (VI) from buffered solutions of HTCP

II. EXPERIMENTAL

Materials

All reagents and chemicals used were of analytical grade from BDH, Acros Organics, Aeser and Aldrich.

III. SYNTHESIS OF

1-PHENYL-3-METHYLPYRAZOLONE-5 (HPMP)

1-Phenyl-3-methylpyrazolone-5 (HPMP) was synthesized according to method reported by [13]. 49 mL (50 g, 0.384 mol) of redistilled ethylacetoacetate was mixed with 36.5 mL (40 g, 0.37 mol) of phenyl hydrazine in a 50 mL beaker. In a fume cupboard, the mixture was heated and stirred on a boiling water bath for 2 hrs. The resultant reddish syrup was cooled and 100 mL of diethylether was added and stirred vigorously. The complex precipitate was filtered and washed with more of the ether to remove colour impurities. The product was recrystallized from hot water to give white crystals. It had a molecular weight of 173.21 g, melting point of 126 °C and molecular formula $C_9H_{10}ON_2$.

IV. SYNTHESIS OF

1-PHENYL-3-METHYL-4-ACETILPYRAZOLONE-5 (HPMAP)

1-Phenyl-3-Methyl-4-acetylpyrazolone-5 (HPMAP) was synthesized according to method reported by [14]. 7 g of HPMP was dissolved in 80 mL of dioxane and warmed in a 500 mL flat-bottomed flask fitted with a dropping funnel and a reflux condenser. The resultant solution was cooled to room temperature. 8 g of calcium hydroxide was added and stirred using a magnetic stirrer. 3.5 mL of acetyl chloride was added to the mixture from the dropping funnel within 3 minutes. The reaction was refluxed below 50 °C for 1 hr. The orange coloured mixture was poured into a beaker containing 300 mL of chilled 3 M HCl and stirred vigorously. The reaction mixture was stored in a refrigerator until brown crystals appeared. The crystals were filtered and washed with water and recrystallized

from hot ethanol to give yellow crystals which were dried in air and a desiccator. It had a molecular weight of 200.41 g, melting point of 66 °C and molecular formula $C_{12}H_{12}O_2N_2$.

V. SYNTHESIS OF

1-PHENYL-3-METHYL-TRICHLOROACETILPYRAZO LONE-5 (HTCP)

HTCP derivative of the ligand was then synthesized according to method reported by [15] with equimolar quantities of 1-phenyl-3-methyl-4-acetylpyrazolone-5 and tetrachloromethane. A 70 mL aqueous solution of tetrachloromethane containing 0.5 M (5.36 g) of tetrachloromethane was prepared and warmed. 70 mL of a hot ethanol solution (45 °C) containing 0.5 M (6.07 g) of the HPMAP was added to the solution. The complex precipitate was washed with 2:1 water ethanol solution. The resulting product was dried in air and stored in a desiccator.

The purity of 1-Phenyl-3-methyl-4-trichloroacetylpyrazolone-5 was established by elemental analysis for C, H and N, analysis of IR, UV and NMR spectral at the Chemistry laboratory, Vaal University of Technology, South Africa. It has a molecular weight of 319.58 g, melting point of 136 °C and molecular formula $C_{12}H_9O_2N_2Cl_3$ and a pink coloration. HTCP is soluble in DMSO, DMF and dioxane.

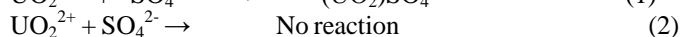
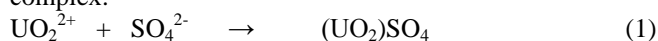
Stock solution of HTCP (0.05M) was prepared by dissolving the appropriate mass of the ligand (0.7988 g) in 50ml chloroform solution. This constituted the organic phase. Metal stock solution of 2000mg/L was prepared by dissolving 0.1782 g of $UO_2(CH_3COO)_2 \cdot 2H_2O$ salt in 50ml volumetric flask using deionized water. 0.2 mL of 10 % NaOH, 0.2 mL of 10 % Na_2CO_3 and 1 mL of 6 % H_2O_2 were added in the flask and made up to the mark. This made up the aqueous phase with a working concentration of 200mg/l in the various buffered solutions of pH 0 to 3.5. The pKa of the Schiff base was determined potentiometrically as reported by [16] [17].

VI. EXTRACTION PROCEDURE

Equal volumes (5ml) of the aqueous phase containing UO_2^{2+} and the organic phase containing chloroform of 1-phenyl-3-methyl-4-trichloroacetylpyrazolone-5 (HTCP) were agitated mechanically for 30mins at room temperature in stoppered extraction bottles. The two layers were then allowed to separate and the raffinate withdrawn. Concentration of UO_2^{2+} in the aqueous phase was determined by colorimetric technique using a Spectronic 20 Genesys UV-Vis spectrophotometer at wavelength 370nm and calculated by difference.

VII. RESULTS AND DISCUSSION

The result obtained from the study of extraction of UO_2^{2+} from 0.01 M, 0.1 M and 1 M SO_4^{2-} ion concentration respectively in the aqueous phase into 0.05 M solution of organic solvent (chloroform of 1-phenyl-3-methyl-4-trichloroacetylpyrazolone-5) showed that UO_2^{2+} was not extracted between the pH range of 0 - 2. This was attributed to the formation of unextractable sulphate-uranyl complex.



However, extraction of UO_2^{2+} occurred between pH 2-3.5. Figures 1 and 2 show the variation of Log D with pH and the percentage extraction for the extraction of UO_2^{2+} from buffered solutions containing 0.01 M SO_4^{2-} ion concentration. A slope of 1 was obtained indicating that 1 proton was displaced during the reaction process while the percentage extraction obtained was 88.70 %.

The extraction process of UO_2^{2+} from aqueous media containing HTCP (or) which is the ligand can be represented by the following equations:



The metal: ligand interaction is in the 1:1 mole ratio.

The extraction constant (Kex) is given by the equation

$$K_{ex} = \frac{[UO_2(HTCP)(or)][H^+(aq)]}{[UO_2(aq)][HTCP(or)]} \quad (4)$$

The distribution ratio D is given by

$$D = \frac{UO_2(HTCP)(or)}{UO_2^{2+}} \quad (5)$$

Substituting equation 5 into equation 4, gives equation 6.

$$\log D = \log K_{ex} + \log[HTCP] + pH \quad (6)$$

Extraction of UO_2^{2+} occurred between pH 2-3.5. Figures 3 and 4 show the variation of Log D with pH and the percentage extraction for the extraction of UO_2^{2+} from buffered solutions containing 0.1 M SO_4^{2-} ion concentration. A slope of 1 was also obtained indicating that 1 proton was displaced during the reaction process while the percentage extraction obtained was 76.84 %.

Figs. 5 and 6 also gave a result similar to those of Figs 2 and 4, but a lower percentage extraction of 55.49 % for UO_2^{2+} from buffered solutions containing 1 M SO_4^{2-} ion concentration. Figs. 2, 4 and 6 showed that optimal percentage extraction decreased from 88.70 % to 76.84 % to 55.49 % as the SO_4^{2-} ion concentration in the buffered phase increased from 0.01 M to 0.1 M and 1 M respectively. The results thus indicated that the extraction of UO_2^{2+} is more favorable between pH 2 and 3.5, although maximum extraction of UO_2^{2+} ion decreased with increase in SO_4^{2-} ion concentration in the buffered phase. Similar results have been reported by [9] in their extraction study on the extraction of Fe(II) with chloroform of 1-Phenyl-3-methyl-4-trichloroacetylpyrazolone-5 from aqueous solutions of different acids and complexing agents. Furthermore, the result showed that a slope of 1 was obtained for all the three SO_4^{2-} ion concentrations, indicating that the interaction between UO_2^{2+} and the ligand (HTCP) resulted in the release of one mole of H^+ . The result further indicates that distribution (D) depends on the pH of the solution (aqueous phase) and the concentration of the ligand in the organic phase. Method of slope analysis of the extraction of UO_2^{2+} is as discussed by previous authors [16] [17]. The slope gives the number of molecules, n, of the ligand (HTCP) that reacted with the molecules of the metal (UO_2^{2+}) ion during the extraction process and can be represented by the following equations:

$$n = \frac{d[\log D]}{d[\log HA]} \quad (7)$$

$$n = \frac{[d \log D]}{[d pH]} \quad (8)$$

$$n = \frac{d[\log D]}{d[\log M^{2+}]} \quad (9)$$

From equation 8, n is equal to 1, which confirmed that in each case, 1 mole of proton was displaced. Plot of variation of log D with log [HTCP] for the extraction of UO_2^{2+} into chloroform solutions containing 0.01 M SO_4^{2-} buffered media at a pH value of 3 is presented in Fig. 7.

A slope of Zero was obtained. This was an indication that the interaction involved 1 mole of the metal at the pH value studied after solving equation 7. Earlier results showed that 1 mole of proton was released during the interaction. The results also showed that, at all levels of interaction studied, the interaction involved 1 mole of the ligand and 1 mole of the metal.

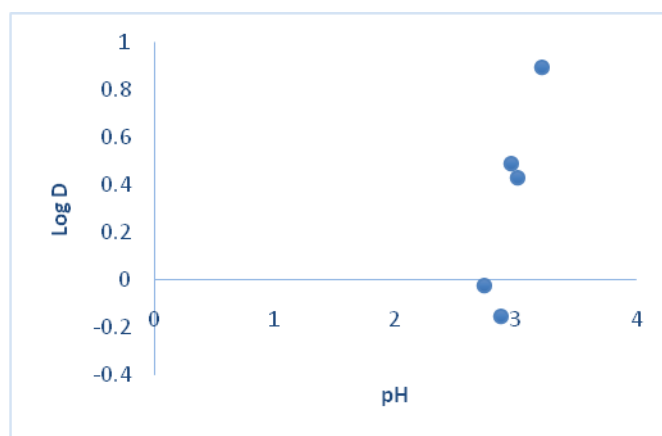


Fig. 1: Extraction plot of 200 mg/l U(VI) ion with solutions of 0.05 M HTCP in chloroform from buffered solutions containing 0.01 M SO_4^{2-} at 25 °C

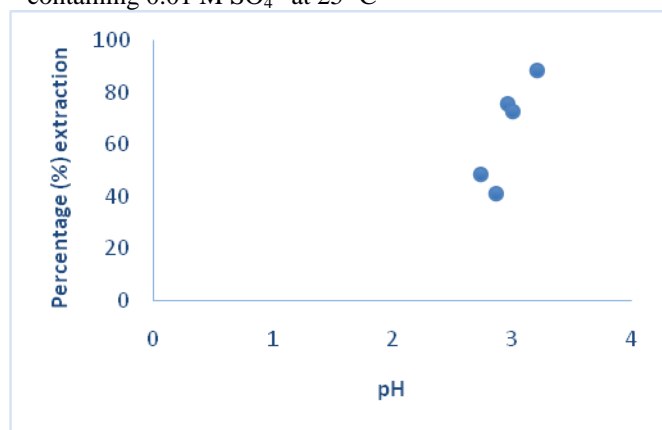


Fig. 2: Percentage (%) extraction plot of 200 mg/l U(VI) ion with solutions of 0.05 M HTCP in chloroform from buffer solutions containing 0.01 M SO_4^{2-} at 25 °C



Fig. 3: Extraction plot of 200 mg/l U(VI) ion with solutions of 0.05 M HTCP in chloroform from buffer solutions containing 0.1 M SO_4^{2-} at 25 °C

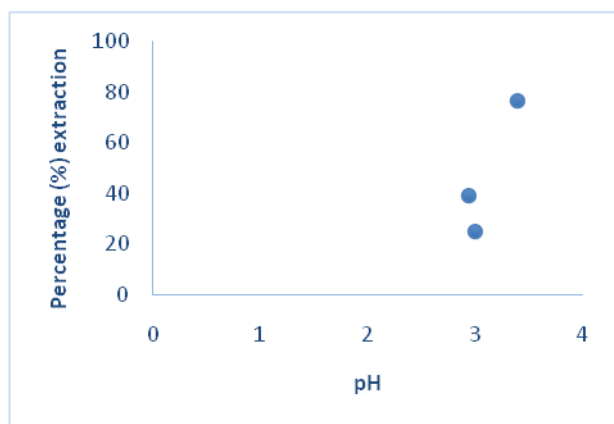


Fig. 4: Percentage (%) extraction plot of 200 mg/l U(VI) ion with solutions of 0.05 M HTCP in chloroform from buffered solutions containing 0.1 M SO_4^{2-} at 25 °C

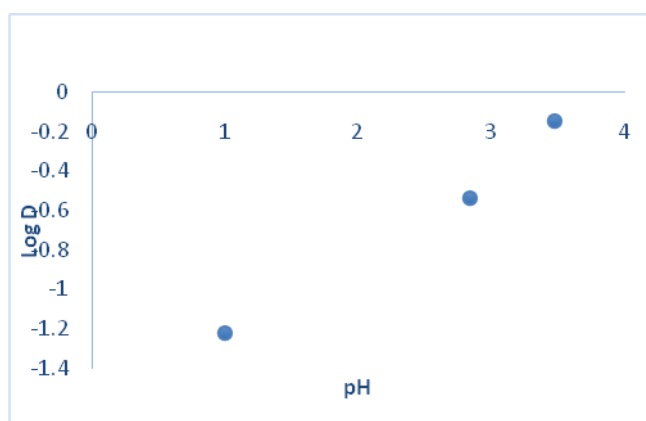


Fig. 5: Extraction plot of 200 mg/l U(VI) ion with solutions of 0.05 M HTCP in chloroform from buffered solutions containing 1 M SO_4^{2-} at 25 °C

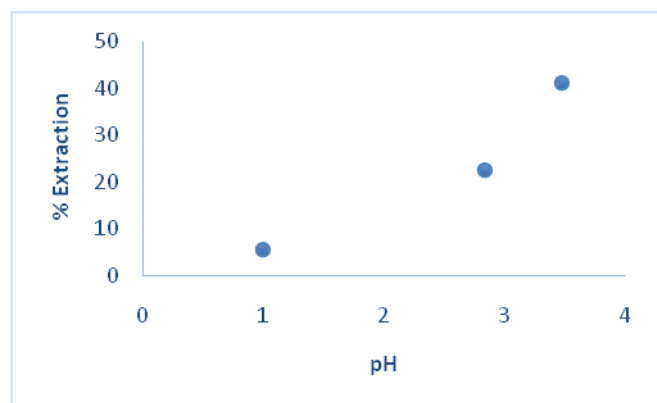


Fig. 6: Percentage (%) extraction plot of 200 mg/l U(VI) ion with solutions of 0.05 M HTCP in chloroform from buffered solutions containing 1 M SO_4^{2-} at 25 °C

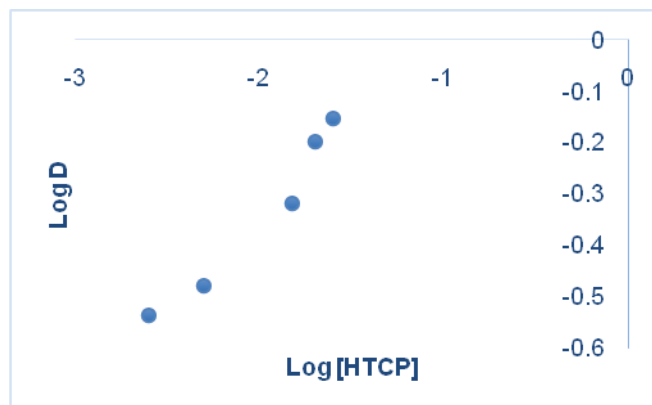


Fig. 7: Ligand (HTCP) variation at pH for extraction of 200 mg/l UO_2^{2+} into chloroform solution containing 0.01 M SO_4^{2-} at 25 °C

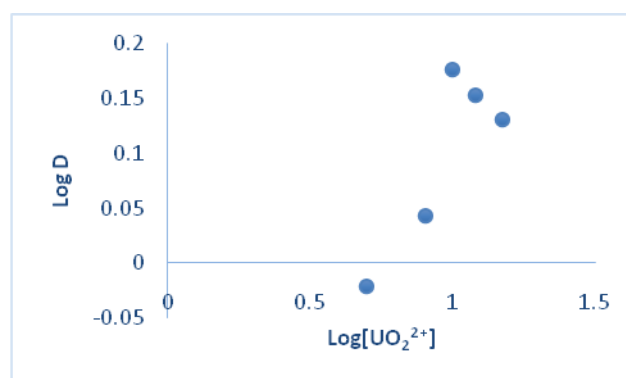


Fig. 8: Metal (UO_2^{2+}) variation at pH 3.00 for extraction of 200 mg/l UO_2^{2+} into chloroform solution containing 0.01 M SO_4^{2-} at 25 °C

The slope obtained in Fig. 8 was zero. This again is an indication that the interaction involved 1 mole of the metal at the pH value studied after solving equation 9 in which n-1 is equal to 1. Consequently, a is equal to 1 indicating that 1 mole of metal UO_2^{2+} ion was involved in the interaction statistically [16] [17]. Hence the metal ligand ratio is 1:1 and the complex formed under this condition is similar to $(\text{UO}_2)\text{TCP}$.

VIII. CONCLUSION

Solvent extraction behavior of U(VI) with HTCP from aqueous solutions was studied. From the results obtained, solutions of HTCP in chloroform did not extract U(VI) in buffered solutions containing SO_4^{2-} ions between pH 0 - 2. This was attributed to the formation of Sulphate Uranyl $(\text{UO}_2)\text{SO}_4$ complex. The results further showed that there was optimum extraction of U(VI) of 88,70 %, 76.84 % and 55.49 % between pH 2.96 - 3.21 for solutions containing 0.01 M, 0.1 M and 1 M SO_4 ion respectively, using 0.05 M HTCP in chloroform solution. An increase in SO_4^{2-} ion concentration decreased the optimum extraction of U(VI). Thus the presence of SO_4^{2-} ion in buffer solutions had a masking effect on the extraction of U(VI). However, an adduct complex of the metal characterized as $\text{UO}_2(\text{TCP})$ was extracted. Complete recovery of U(VI) will require two or three batches of extraction using the ligand within the pH range of 2 - 3.5 where U(VI) was best extracted.

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