EFFECT OF SO_4^{2-} CONCENTRATION ON Ni(II) EXTRACTIONS FROM AQUEOUS SOLUTION USING 1-PHENYL-3-METHYL-4-TRICHLOROACETYL PYRAZOL-5-ONE IN CHLOROFORM

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The extraction of Ni^{2+} from aqueous solutions of various concentrations of SO_4^{2-} ions in buffered media using 1-phenyl-l,3-methyl4-trichloroacetyl-pyrazolone-5 (HTCP) has been investigated. The synergistic effect of butanol on the extraction of the metal was also examined. Ni^{2+} was quantitatively extracted from solutions by HTCP only at high pH values (5 - 8) over the pH range 0 – 8 studied. However, addition of butanol resulted in a synergistic extraction of Ni^{2+} up to 97.78% over the range of pH 5.00 – 8.00 from aqueous buffer media containing 0.1M SO_4^{2-} ion concentration. Increased SO_4^{2-} ion concentration resulted in a slight decrease in the extraction of Ni^{2+} ion due to masking of the metal by the SO_4^{2-} ion. In addition, overall extraction was shifted to higher pH values for extraction into chloroform solution of the ligand for Ni^{2+} using butanol. The log K_{ex} and $pH_{1/2}$ of the various extraction systems were determined.

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Introduction

Studies have shown 4-acyl pyrazolone derivatives to be excellent metal extracting agents for various type of metals, ranging from lanthanides[1,2], actinides[3,4] and other transition metals[5,6]. These studies have shown that these ligands have the capability of extracting these metal ions at pH values lower than 2 to neutral as ion pair or adduct complexes[8]. Most of the 4-acyl pyrazolone derivatives studied have pK_a > 4 and in the quest to evaluate the performance of 4-acyl derivatives with lower pKa,

Umetani and Freiser[8] successfully studied the quantitative extraction of some lanthanides with 1-phenyl-3-methyl-4-trifluoroacetyl-pyrazolone-5 with pKa < 3 at pH values close to 1. 1-phenyl-3-methyl-4-trichloroacetyl-pyrazolone-5 (HTCP) with pK_a 3.02 shown in Figure 1 has also been reported to have been successfully used in the extraction of a range of metal ions.[7,9,10] Almost all extraction studies with ligands have shown that various concentrations of different anions in the aqueous phase containing the metal ions play an important role in the percentage extraction of these metal ions[5,7,9,10,11,12], which can either be enhancing or masking the extraction of the metal ions. The effects have been utilized in optimizing extractions and separation of metal ions[13,14].In continuation of our studies on the extractions of metal ions with the ligand 1-phenyl-3-methyl-4-trichloroacetyl-pyrazolone-5 (HTCP), we report the effect of various concentrations of sulphate ions on the extraction of Ni(II) ion in different buffered aqueous media.

Materials and Methods

Reagents and Apparatus

1-Phenyl-3-methyl-4-trichloroacetyl-pyrazolone-5 (HTCP) was synthesized by methods reported earlier.[15] 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 was performed at the Institute for Inorganic Chemistry Technology, University of Dresden, Germany.

Stock solutions of 0.05 M HTCP were prepared by dissolving appropriate amount of the ligand in $CHCl_3$. Stock solutions of 1.704 x 10^{-2} M (1,000 mg/L) of Ni(II) were prepared by dissolving appropriate mass of ammonium nickel(II) tetraoxosulphate(VI) hexahydrate ($NiSO_4.(NH_4)_2SO_4.6H_2O$) 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 containing 0.01M, 0.1M and 1.0M SO_4^{2-} ions with 0.1M HCl/0.1 M NaCl (pH 0.1-2.9), 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 KH_2PO_4/0.1 M NaOH (pH 5.7-8.0). pH of the buffered solutions were determined with a Labtech Digital pH meter. All experiments were performed at ionic strength of 0.1 M ($NaClO_4$).

Extraction Procedure

2 mL aliquot of a buffer solution containing 8.52×10^{-4} M (50 mg/L) of Ni(II) ions and the desired pH and concentration of SO_4^{2-} ions was prepared in a 10 ml extraction container. An equal volume (2 mL) of 0.05 M HTCP in $CHCl_3$ solution or 1.9 ml of 0.05 M HTCP in $CHCl_3$ solution made up to 2 ml by addition of 0.1 ml butanol and the mixture shaken mechanically for 30 minutes at room temperature of about 32°C. A shaking time of 30 minutes was found suitable enough for attaining the equilibration. For HTCP variation, the organic phase contained HTCP in $CHCl_3$ ranging from 1.25×10^{-2} M – 4.375×10^{-2} M, while for Ni^{2+} variation, the aqueous phase contained Ni^{2+} concentration in the range 12.5 mg/L – 37.5

mg/L. The phases were allowed to settle and separated. Concentration of Ni(II) ion in aqueous phase was determined with a Buck Scientific Atomic Absorption Spectrophotometer (AAS) 205. Ni(II) ion concentration extracted into the organic phase was determined by the difference between the concentration of Ni(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.

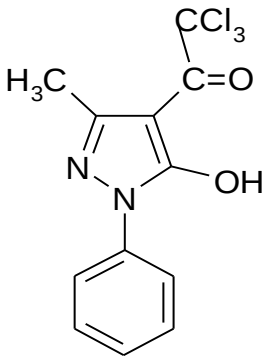

Figure 1: Structure of 1-phenyl-3-methyl-4-trichloroacetyl-pyrazol-5-one (HTCP)

Results and Discussion

Effect of sulphate ions and pH on the extraction of Ni^{2+} from buffered solutions.

The studies show that, while there was marginal extractions of Ni^{2+} from pH of 2.07 for 0.01M SO_4^{2-}, extractions at higher concentrations of SO_4^{2-} started at higher pH values (4.53 for 0.1M and 5.53 for 1.0M). Figure 2 show that the percentage extraction of 97.96% achieved for 0.01M SO_4^{2-} on the extraction of Ni^{2+} at pH 6.34 – 7.30 dropped gradually to 96.28% at pH 7.31 – 7.65 for 0.1 M SO_4^{2-} to 94.47% at pH 7.38 – 7.78 for 1.0 M SO_4^{2-}.

Extraction data from Table 1 also show that the $pH_{1/2}$ shifted to higher pH values (5.20 ± 0.1)[0.01M] < 6.20 ± 0.1[0.1M] < 6.75 ± 0.1[1.0M] and log K_{ex} decreased -9.37 ± 0.83)[0.01M] > -10.95 ± 0.48[0.1M] > -11.3 ± 0.56. [1.0M] as the concentration of SO_4^{2-} increased. These findings are similar to results reported in other studies.[7,9,16]

Figure 2a -2c showed that a slope of 2 was obtained for all the three (SO_4^{2-}) concentrations 0.01M, 0.1M, 1.0M studied, indicating that 2 moles of protons were displaced during the extraction process by the interaction of Ni^{2+} with HTCP and combining these results with those from Figure 4 and 5, we can write the equation of reaction for the extraction process as follows;

$$Ni^{2+} + 2HTCP \longrightarrow Ni(TCP)_2 + 2H^+ \qquad (1)$$

The complex specie $Ni(TCP)_2$ extracted, shown in equation 1, is similar to what was reported earlier. [7,17,19]

The results imply that masking of Nickel II ion is enhanced as the sulphate (SO_4^{2-}) ion concentration of the solution increased. For 0.1M sulphate ion concentration, Ni^{2+} was not extracted at pH range (0-4.22). Similarly, for 1M sulphate ion concentration Ni^{2+} was unextractable up to pH 5.04. The implication is that Nickel may have formed stable and unextractable sulphato-Nickel complexes[18] in solution as shown in equation 2:

$$Ni^{2+} + 2SO_4^{2-} \rightarrow [Ni(SO_4)_2]^{2-} \qquad (2)$$

Thus, the results indicated that the extraction of Ni^{2+} is more favourable at higher pHvalues with decrease in sulphate ion concentration in the buffered solution.

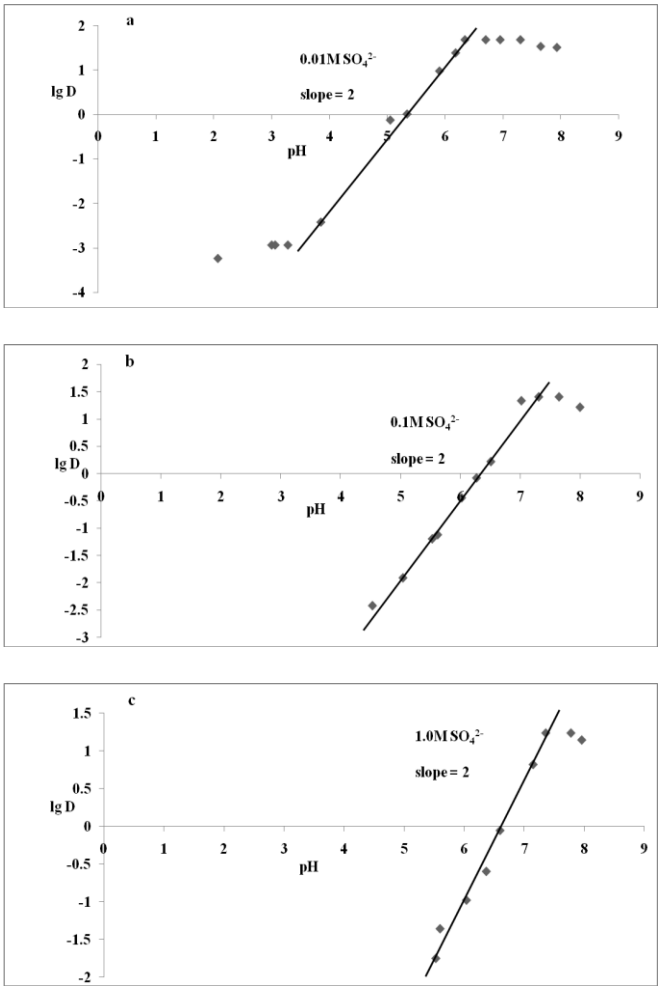

Figure 2: Extraction Plot of 50 mg/L Nickel (II) ion with Solution of 0.05M HTCP in $CHCl_3$ from Buffer Solutions containing (a) 0.01M SO_4^{2-} (b) 0.1M SO_4^{2-} (c) 1.0 M SO_4^{2-} at 32^0C

Effect of Butanol as Synergist

This was studied in buffered solution containing 0.1M SO_4^{2-} to see the effect of the synergist in the extractions.

Figure 3 shows that quantitative percentage extraction increased to 97.78% from 96.28% acheived for 0.1M SO_4^{2-} without synergist. Table 1 also shows that the extraction parameters log K_{ex} (HTCP/$CHCl_3$BuOH -7.54 ± 1.39 > HTCP/$CHCl_3$ -10.95 ± 0.48 and log D (HTCP/$CHCl_3$BuOH 1.63 ± 0.02 > HTCP/$CHCl_3$ 1.41 ± 0.01) were higher than those obtained without synergist and shift of the $pH_{1/2}$ value from 6.20 to 4.75 (a more acidic region) indicating that

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extraction of Ni^{2+} at lower pH values is more effective in chloroform solutions containing butanol as a solvating agent as the distribution of Ni^{2+} into the organic HTCP/$CHCl_3$ was better. We also noted that, while there was no extractions from pH 0 – 4.22 in the absence of butanol as synergist, there was marginal extraction of Ni^{2+} from pH 2.07. Uzoukwu and Mbonu[7] obtained similar results from their studies on the effect of chloride ion (Cl^-) concentration in the extraction of Cu (II) and Ni (II) ions using 1-phenyl-3-methyl-4-trichloroacetyl pyrazolone-5. They attributed the improved distribution of Ni^{2+} in the presence of butanol to formation of adduct and proposed the extracted metal complex to be $Ni(TCP)_2BuOH$.

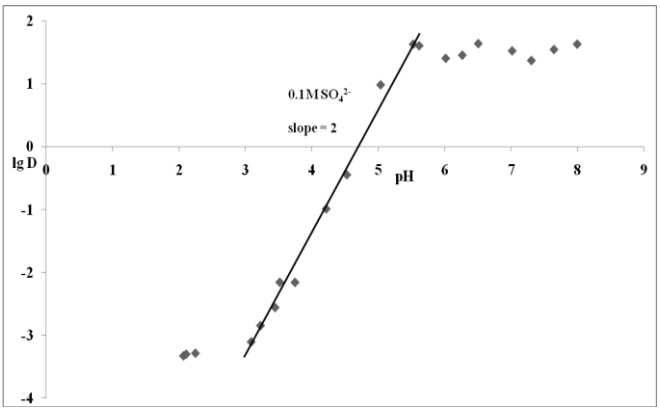

Figure 3: Extraction Plot of 50 mg/*l* Nickel (II) ion with Solution of 0.05M HTCP in $CHCl_3$/BuOH from Buffer Solutions containing 0.1M SO_4^{2-} at 32^0C

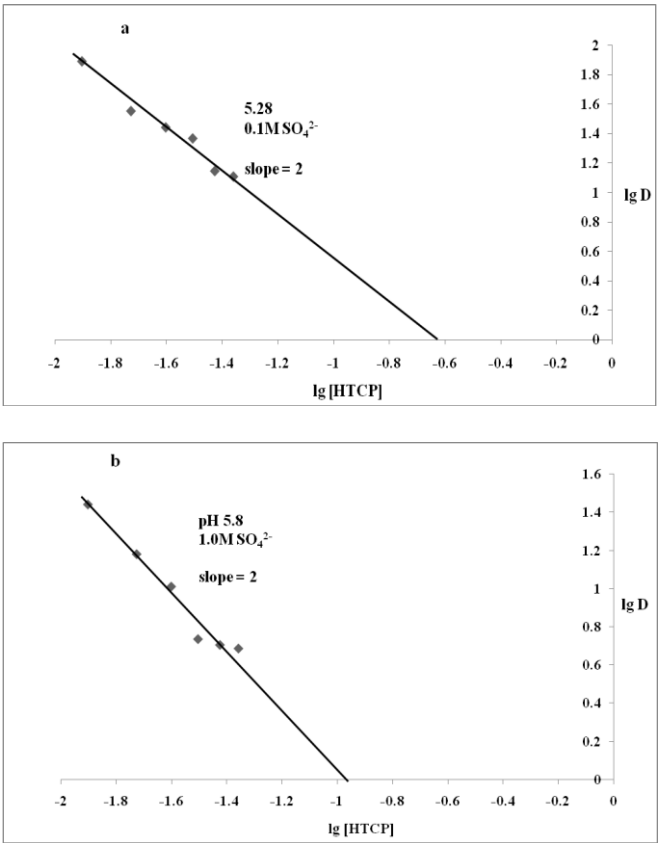

Figure 4: Ligand [HTCP] Variation at (a) pH 5.28 for solution containing 0.1M SO_4^{2+-} (b) pH 5.8 for solution containing 1.0M SO_4^{2-} for extraction of 50 mg/*l* Nickel (II) ion at 32^0C

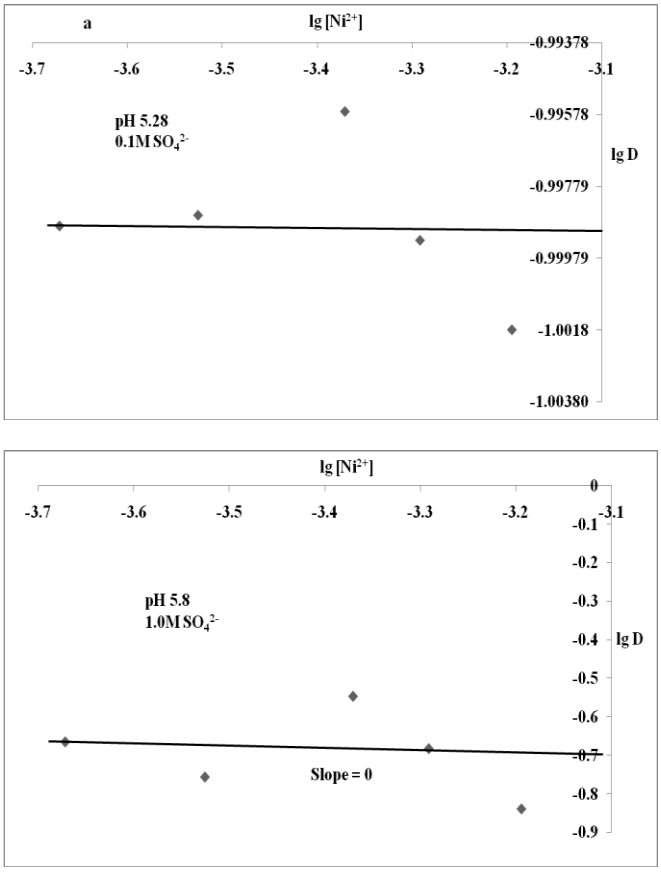

Figure 5: Metal [Ni^{2+}] Variation at (a) pH 5.28 containing 0.1M SO_4^2 (b) pH 5.8 containing 1.0M SO_4^{2-} for extraction of Nickel (II) ions into 0.05M HTCP in $CHCl_3$ containing 0.1M SO_4^{2-} at 32^0C

Table 1. Extraction data for 8.52×10^{-4} M (50 mg/L) Ni^{2+} extraction in buffered aqueous media containing various concentrations of SO_4^{2-} into organic phases containing 0.05 M HTCP/$CHCl_3$ and 0.05 M HTCP/$CHCl_3$/BuOH

Organic Phase HTCP/$CHCl_3$	**SO_4^{2-} Concentration in Aqueous Phase**		
	0.01M	**0.1M**	**1.0M**
$pH_{1/2}$	5.20 ± 0.1	6.20 ± 0.1	6.75 ± 0.1
Log D	1.68 ± 0.01	1.41 ± 0.01	1.23 ± 0.01
Log K_{ex}	-9.37 ± 0.83	-10.95 ± 0.48	-11.37 ± 0.56
Organic Phase HTCP/$CHCl_3$ /BuOH	**0.01M**	**0.1M**	**1.0M**
$pH_{1/2}$	-	4.75 ± 0.1	-
Log D	-	1.63 ± 0.02	-
Log K_{ex}	-	-7.54 ± 1.39	-

Conclusion

The effect of various sulphate ion (SO_4^{2-}) concentrations on the extraction of Ni^{2+} using 0.05M HTCP/$CHCl_3$ studied show that the extraction of Ni^{2+} is masked slightly by anionic sulphate-Nickel complexes formed in solution at increasing sulphate ion concentration. Slope analysis showed that Ni^{2+} was extracted as $Ni(TCP)_2$. Extraction of Ni^{2+} was enhanced by the introduction of butanol as solvating agent due to formation of adduct $Ni(TCP)_2BuOH$..

Eur. Chem. Bull. **2013**, *2*(2), 68-71 DOI: 10.17628/ECB.2013.2.68

The result also showed that the $pH_{½}$ value increased with increase in sulphate ion concentrations. This suggested that anionic sulphato complexes of Nickel II ion (Ni^{2+}) formed in solution have some effect on the extent of extraction of Nickel from the buffer media and this effect is more pronounced as the concentration of sulphate ions in solution increased.

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References

[1]Chun-Hui, H., and Freiser, H., *Solvent. Extr. Ion Exch.* **1986**, *4(1)*, 41.

[2]Umetani, S., Kawase, Y., Le, Q. T. H., and Matsui, M, *J. Chem. Soc. Dalton Trans.*, **2000,** *16***,** 2787.

[3]Yonezawa, C., and Choppin, G. R., *J. Radioanal and Nucl Chem, Articles*, **1989**,*134*, 233.

[4]Thakur, P., Chakravortty, V., and Reddy, M. L. P., *Radiochim. Acta*, **1999**, *87*, 121.

[5] Godwin, J., and Uzoukwu, B. A., *IOSR-JAC*, **2012**. *1(3)*, 14.

[6]Kalagbor A. I., Uzoukwu B. A., and Chukwu U. J. *Nat. and Sci*, **2011**, *9(9)*, 147.

[7]Uzoukwu, B. A., and Mbonu J. I., *Solvent. Extr. Ion Exch.* **2005**, *23*, 750.

[8]Umetani, S., and Freiser, H., *Inorg. Chem*., **1987**, *26*, 3179.

[9]Chukwu U. J., and Uzoukwu B. A., *Science Africa Journal*, **2008**, *7(1)*, 42.

[10]Chukwu U. J., and Uzoukwu, B. A., *Recent Pat. Mater. Sci.*

2010, *3(2)*, 146.

[11]Godwin, J and Uzoukwu, B. A. *Int. J. Chem. (Toronto, ON, Can.)*, **2012**. *4(4)*, 105

[12]Godwin, J., Nwadire, F. C., and Uzoukwu, B. A. *Eur. Chem. Bull.* **2012**, *1(7)*, 269.

[13]Okafor, E. C., and Uzoukwu, B. A., *Radiochim. Acta*. **1990**, *51*, 167.

[14]Atanassova M., and Dukov I. L., *Sep. Purif. Technol.* **2004,** *40(2)*, 171

[15]Jenson, B. S., *Acta Chem. Scand*. **1959**, *13*, 1668.

[16]Sambasiva, A. R., and Seshasayi, Y., *J. Inorg Chem.* **1978,** *60*, 1123.

[17]Uzoukwu, B. A., *Basic Analytical Chemistry, 1st edition, Pam Unique Publishing Company Ltd, Port Harcourt*, **1992**.

[18]Cotton, F. A., and Wilkinson, G., *Advances in Inorganic Chemistry, 5th edition, John Wiley and Sons Inc. USA*, **1988**.

[19]Ogwuegbu M. O. C., and Oforka, N. C., *Hydrometallurgy*, **1994**,*34*, 359.

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