

HALIDE IONS EFFECTS IN MULTI-METAL EXTRACTIONS USING 4,4'-(1E,1E')-1,1'-(ETHANE-1,2-DIYLBIS(AZAN-1-YL-1YLBIDENE))BIS(5-METHYL-2-PHENYL-2,3-DIHYDRO-1H-PYRAZOL-3-OL) (H₂BuEtP)

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Abstract

The effects of halide ions Br⁻, Cl⁻, F⁻ and I⁻ in the multimetal extractions of Cadmium, Lead, Nickel and Iron from aqueous media buffered to either pH 4.75 or 7.5 using chloroform solutions of the Schiff base ligand 4,4'-(1E,1E')-1,1'-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-ol) (H₂BuEtP) alone or in the presence of a second ligand 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) as extractants was studied. 2 mL aqueous solutions containing 50 mg l⁻¹ each of the four metal ions, 0.0001 M – 0.1 M of each halide ion and buffered to either pH 4.75 or pH 7.5 were mixed with either a 2 mL chloroform solutions of 0.05 M H₂BuEtP or 2 mL chloroform solutions of 0.05 M H₂BuEtP/0.05 M HBuP in a 9:1 ratio by volume. The mixtures were mechanically agitated using an equilibration time of 60 minutes and allowed to settle. The aqueous raffinate was analysed for the metals using atomic absorption spectrophotometer for Cadmium, Lead and Nickel and Iron colorimetrically using 1,10-Phenanthroline and compared with standards. Distribution ratios (D) and percentage extraction (%E) and number of batches (n) needed to extract 99.9% of the metals were calculated, tabulated, plotted and statistically compared. Aqueous solutions buffered to pH 7.5 and containing either 0.05 M Cl⁻ or F⁻ using chloroform solutions of the ligand H₂BuEtP alone gave the best results with 99.9% extraction of Cadmium, Lead, Nickel and Iron theoretically possible after 2 batches of extractions. With Mixed ligands H₂BuEtP/HBuP as extractant, at least 4 batches were theoretically required to extract 99.9% of the four metals from aqueous solutions buffered to pH 7.5 and containing either 0.05 M Br⁻ or 0.001 M Cl⁻, or 0.01 M F⁻. pH 7.5 was a better buffer medium for the multimetal extractions of the four metals than pH 4.75 and there were significant differences in the multimetal extractions of all the metals except Iron in the two buffers in both organic extractants. The organic extractants H₂BuEtP and H₂BuEtP/HBuP were not significantly different in the multimetal extractions of the four metals in both buffers. The efficiencies of the halide ions in the multimetal extractions of Cadmium, Lead, Nickel and Iron was in the order Cl⁻ = F⁻ > I⁻ > Br⁻. The extraction of the metals from the aqueous phases to the organic phases was attributed to favourable energetics in the transfer of the metal complexes in the ligand H₂BuEtP alone or adducts in mixed ligands H₂BuEtP/HBuP organic phases as a result of changes in permittivities/dielectric constants of the two phases.

Keywords: Halide Ions, Ligands, Multimetal Extractions and Permittivities/Dielectric Constants

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I. Introduction

The removal of heavy metals from our environment has become very necessary and important as result of their many reported health effects on both plants and animals (Singh and Kalamdhad, 2011; Chibuike and Obiora, 2012). Older methods like precipitation, distillation and crystallization were time consuming, required expensive instrumentations, reagents and not very efficient. There is an urgent need to get more efficient methods and lots of research works have been reported and ongoing on new and efficient methods for heavy metals extractions (Lone et al., 2008; Zhitong et al., 2012; Selvi et al., 2019). Solvent-solvent extraction employing ligands in the organic phases to complex the metals in the aqueous phases with the resultant metal complexes being more soluble in the organic phases and thus, the metals extracted to the organic phases (Halil et al., 2015; Rajab and Sami, 2017) have shown lots of promises in heavy metal extraction studies. The metals can be stripped from the organic phases with appropriate reagents, purified and reused (Szyzewski et al., 2009; Ekebafe et al., 2012). The metal complexes formed have been reported to have antibacterial and antifungal properties and have led to studies such as the synthesis of varieties of metal complexes of heavy

metals with a range of different ligands, characterization and biochemical activities (Ekennia *et al.*, 2015; Abu-Dief and Mohamed, 2015).

The tetradentate ligand 4,4'-(1E,1E')-1,1'-(ethane-1,2-diylbis(azan-1-yl-1-ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-3-ol) (H₂BuEtP) a Schiff base which was first synthesized by Uzoukwu *et al.*, 1998 have been used in extraction studies for Pb²⁺, UO₂²⁺, Ni²⁺, Fe²⁺ and Cd²⁺ with very encouraging results (Godwin and Uzoukwu, 2012a; Godwin and Uzoukwu, 2012b; Godwin *et al.*, 2012; Godwin *et al.*, 2013; Godwin and Tella, 2017). The halide ions F⁻, Cl⁻, Br⁻ and I⁻ effects in these studies were also comprehensively reported alongside those of common acids, other anions and some auxiliary complexing agents (Godwin and Uzoukwu, 2012a : Godwin and Uzoukwu, 2012b : Godwin *et al.*, 2012 : Godwin *et al.*, 2014 : Godwin *et al.*, 2019). In Pb²⁺ extraction, the halide ions had varying trends but the mixed ligands H₂BuEtP/HBuP organic phase was a far better extractant with > 90% extractions with all the halogen ions than the ligand H₂BuEtPalone organic phase with < 88% for Cl⁻, Br⁻ and I⁻ and complete masking of UO₂²⁺ at above 0.05 M Cl⁻ and 1.0 M I⁻ (Godwin and Uzoukwu, 2012a). Godwin and Uzoukwu, 2012b in extraction of UO₂²⁺ with H₂BuEtP studies reported similar effects of the halide ions as those observed for Pb²⁺, with mixed ligands H₂BuEtP/HBuP organic phase better as extractant than the ligand H₂BuEtPalone organic phase. However, quantitative masking was observed only above 0.05 M Br⁻ for both H₂BuEtPalone and mixed ligands H₂BuEtP/HBuP organic phase. The trend of the effects of halide ions in the extraction of Ni²⁺ with same H₂BuEtP organic phases was similar with those reported for Pb²⁺ and UO₂²⁺ even though they results were slightly poorer as only F⁻ and I⁻ gave > 90% extraction of Ni²⁺ with mixed ligands H₂BuEtP/HBuP whilst with H₂BuEtPalone, percentage extraction of Ni²⁺ was < 60% for all halide ions (Godwin *et al.*, 2012). Halide ions greatly enhanced the extraction of Fe²⁺ with > 95% extraction achieved in both H₂BuEtPalone and mixed ligands H₂BuEtP/HBuP organic phases. However, unlike Pb²⁺, UO₂²⁺ and Ni²⁺ extractions, H₂BuEtPalone organic phase was a better extractant for Fe²⁺ than the mixed ligands H₂BuEtP/HBuP organic phase (Godwin *et al.*, 2014). In the extraction of Cd²⁺, both ligand alone H₂BuEtP and mixed ligands H₂BuEtP/HBuP organic phases gave > 75% extraction of Cd²⁺ at 0.001 M of all the halide ions even though the mixed ligands H₂BuEtP/HBuP organic phase was statistically slightly better with > 97% extraction of Cd²⁺. As also observed with UO₂²⁺, Pb²⁺ and Ni²⁺, the percentage extraction of Cd²⁺ decreased with increase in halide ions concentration (Godwin *et al.*, 2019).

Since acids, anions and auxiliary complexing agents can have both releasing and masking effects depending on the metal, type of organic phase and pH of aqueous solution. This has been utilized in separating metals in which a particular reagent at a particular pH is functioning as a releasing agent for a metal and as masking agent for the other metal for that ligand organic phase at a given equilibration time with separation factors $\beta_{XY} \approx 10^{14}$ (Uzoukwu, 2009; Okafor and Uzoukwu, 2009; Li *et al.*, 2018). However, recent bimetal extraction studies have also shown that conditions can exist in which a reagent can function as releasing agent for more than one metal and thus, this can be used for bimetal or multi-metal extraction. It was reported that, this was possible as result of changes in permittivities/dielectric constants of both aqueous and organic phases leading to reductions in separation factors β_{XY} (Godwin *et al.*, 2020). Thus, the need arises to study the effect of all reagents used in studies of the extraction of some heavy metals with the Schiff base H₂BuEtP in multi-metal extractions. In the first of these studies, the effect of CH₃COO⁻, PO₄³⁻, and SO₄²⁻ in the multi-metal extraction of Cadmium (II), Iron (II), Lead (II), and Nickel (II) from aqueous solutions buffered to pH 4.75 and 7.5 was studied using ligand H₂BuEtP alone and in the presence of another ligand 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) in chloroform organic phases. It was reported that an aqueous phase containing 0.1 M CH₃COO⁻ and buffered to pH 4.75 using chloroform solutions of ligand H₂BuEtP alone and 0.05 M PO₄³⁻ buffered to pH 7.5 using H₂BuEtP/HBuP organic phase can be used theoretically to extract 99.9% of the four metals after 5 batches of extractions. pH 7.5 was slightly better for the multi-metal extraction of Cadmium (II), Iron (II), Lead (II) and Nickel (II) from aqueous solutions with formation of metal complexes and adducts with favourable energetics in their transfer from the aqueous phases to the organic phases (Godwin and Young, 2020).

In continuation of the series on multi-metal extraction, the effect of the halide ions on the multi-metal extraction of Pb²⁺, Ni²⁺, Fe²⁺ and Cd²⁺ from aqueous solutions buffered to pH 4.75 and 7.5 using H₂BuEtP alone and in the presence of HBuP as organic extractants have been studied.

The objectives were; to evaluate the effect of the halogen ions concentrations on the distribution ratios of the metals, compare results for the halogen ions for pH 4.5 and 7.5, compare ligand H₂BuEtP alone with those of mixed ligands H₂BuEtP/HBuP organic phase and ascertain optimal conditions for the multi-metal extraction of the four metals with the ligand H₂BuEtP.

II. Experimental

The Schiff bases H₂BuEtP and H₂BuEtP were synthesized using methods outlined by Uzoukwu *et al.*, 1998, purified and characterized as previously reported (Godwin *et al.*, 2020). Sodium or ammonium halide salts were used and all reagents used were of analytical grade.

Eighty 10 mL extraction bottles with lids were divided into 4 sets of the halide ions F⁻, Cl⁻, Br⁻ and I⁻ ions labelled; ligand H₂BuEtP alone at pH 4.75, ligand H₂BuEtP alone at pH 7.5, mixed ligands H₂BuEtP/HBuP at pH 4.75 and mixed ligands H₂BuEtP/HBuP at pH 7.5. 1000 mgL⁻¹ stock solutions of Pb²⁺, Ni²⁺, Fe²⁺ and Cd²⁺ ions were prepared using equivalent weight of their salts in distilled water with addition of 2 mL of 2M HNO₃ to prevent hydrolysis. Each bottle contained 2 mL aqueous phases containing 50 mgL⁻¹ each of four metal ions from taken 0.1 mL of 1000 mgL⁻¹ stock solutions of the metal ions, 0.001 – 0.1 M of each halide ion from appropriate volume of stock solutions of the different halide ions and made up the 2 mL mark with buffer of 4.75 or 7.5. 2 mL of either 0.05 M H₂BuEtP in chloroform or 9:1 volume ratio chloroform solutions of 0.05 M H₂BuEtP and 0.05 M HBuP were added to get 2 sets of ligand H₂BuEtP alone and mixed ligands H₂BuEtP/HBuP organic phases. The bottles with both phases were agitated mechanically for an hour. One hour has been reported to be suitable for equilibration to occur (Godwin and Uzoukwu, 2012a; Godwin and Uzoukwu, 2012b; Godwin *et al.*, 2012; Godwin *et al.*, 2013; Godwin and Tella, 2017). The phases were allowed to separate out and 0.1 mL for Cadmium, lead and Nickel and 0.4 mL for Iron was taken from each aqueous raffinate, analysed by comparing absorbances with standards of each metal and equation 1 and 2 used to calculate Distribution Ratios (D) and Percentage Extraction (%E). Cadmium (228.8 nm), Lead (217 nm) and Nickel (232 nm) was analysed with an Atomic Absorption Spectrophotometer while Iron was analysed colorimetrically with a UV Spectrophotometer at 520 nm with 0.1 mL of 0.01% 1,10-phenanthroline after addition of 0.1 mL each of 10% CH₃COONa and 10% NH₂OH solutions (Saywell and Cunningham, 1937).

$$\text{Distribution Ratio } D = \frac{\text{Standard Absorbance} - \text{Raffinate Absorbance}}{\text{Raffinate Absorbance}} \quad (1)$$

$$\text{Percentage Extraction } \%E = \frac{\text{Standard Absorbance} - \text{Raffinate Absorbance}}{\text{Standard Absorbance}} \quad (2)$$

Distribution ratios data for pH 4.75 and 7.5 and ligand H₂BuEtP alone and in the presence of HBuP for each Halide ion was compared with others statistically using the R software package [R Development Core Team 2008]. The *p* test statistics [Sprinthall, 2011] was used to test the hypothesis, if the two groups were significantly different in these extractions or not. The null hypothesis (*H*₀), that the two groups of interest are not significantly different is rejected if the value of the test statistics is less than the significant level $\alpha = 0.05$, and the alternative hypothesis (*H*_a), the two groups of interest are significantly different is accepted. If the *p* value is greater than the significant level $\alpha = 0.05$, the null hypothesis is accepted and we conclude that there is no significant difference between the groups of interest.

Equation 3 was used to calculate *n* batches of extractions needed theoretically to achieve 99.9% extraction of metal ions, where *C*_{aq} is the amount of metal ions originally present in the aqueous phases and *C* is the amount of metal ions that remains in an aqueous phase after extractions.

$$C/C_{aq} = \left[\frac{1}{D + 1} \right]^n \quad (3)$$

III. Results and Discussion

The results obtained and the extraction parameters are as stated in the Table that follow while the percentage extraction of the various metals are as expressed in the Figures that follow.

Table 1a: Extraction parameters for the four metals in Br⁻ at pH 4.75 for Ligand H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
Br ⁻ (M)	Raffinate Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0954	0.0282	0.0025	0.158	0.0011	0.0390	0.6400	2.9684	6283	181	14	5
0.005	0.0954	0.0033	0.0027	0.026	0.0011	7.8788	0.5185	23.1154	6283	3	17	2
0.01	0.0954	0.0292	0.0025	0.033	0.0011	0.0343	0.6400	18.0000	6283	205	14	2
0.05	0.0954	0.0292	0.0033	0.066	0.0011	0.0343	0.2424	8.5000	6283	205	32	3
0.1	0.0954	0.0292	0.0040	0.074	0.0011	0.0343	0.0250	7.4730	6283	205	280	3

Table 1b: Extraction parameters for the four metals in Br⁻ at pH 7.5 for Ligand H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
Br ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0272	0.0001	0.0001	0.136	2.5120	292	40	3.6103	6	1	2	5
0.005	0.0312	0.0004	0.0001	0.012	2.0609	72.25	40	51.25	6	2	2	2
0.01	0.0405	0.0001	0.0001	0.013	1.3580	292	40	47.3076	8	1	2	2
0.05	0.0587	0.0001	0.0001	0.016	0.6269	292	40	38.1875	14	1	2	2
0.1	0.0688	0.0001	0.0001	0.115	0.3881	292	40	4.4522	21	1	2	4

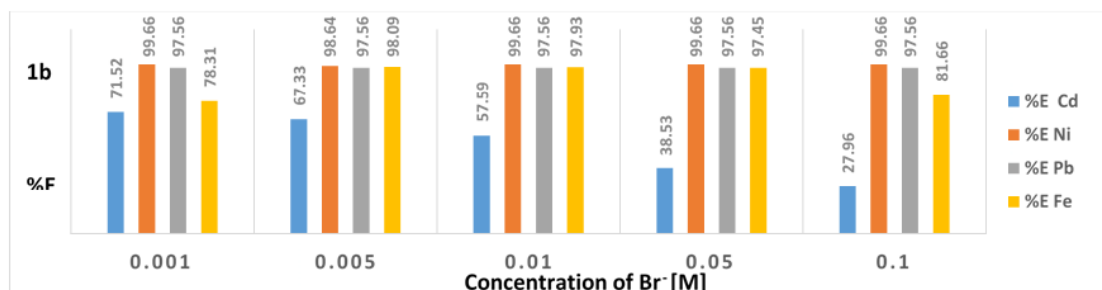
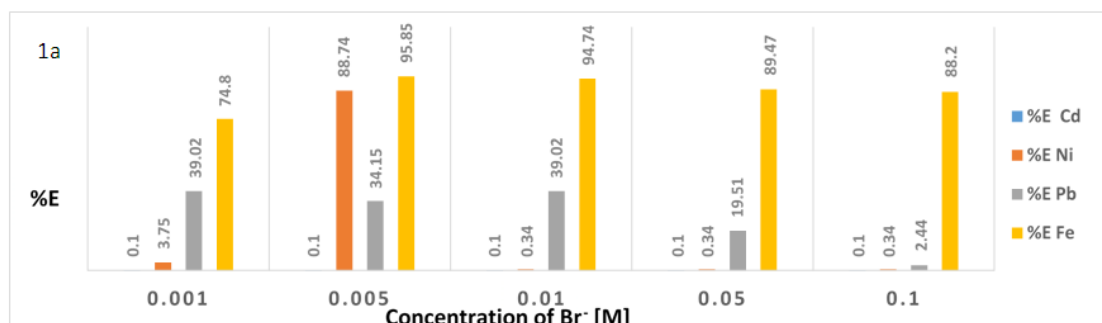
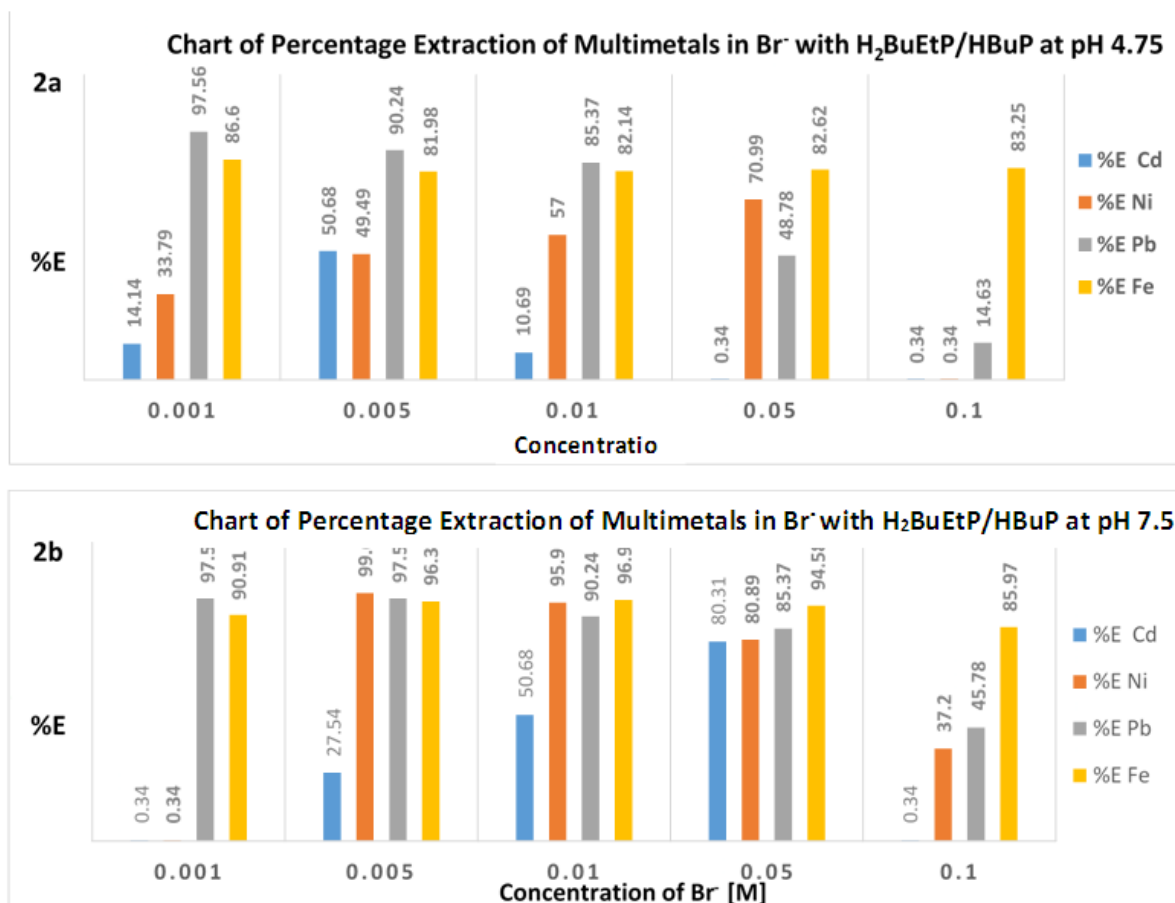


Table 2a: Extraction parameters for the four metals in Br⁻ at pH 4.75 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627						
Br ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction				
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	%E _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0820	0.0194	0.0001	0.084	0.1646	0.5103	40	6.4643	86.60	45	17	2	2
0.005	0.0471	0.0148	0.0004	0.113	1.0276	0.9797	9.25	4.5487	81.98	10	10	3	4
0.01	0.0767	0.0126	0.0006	0.112	0.2451	1.3254	5.8333	4.5982	82.14	32	8	4	4
0.05	0.0954	0.0085	0.0021	0.109	0.0034	2.4471	0.9524	4.7523	82.62	2035	6	10	4
0.1	0.0954	0.0292	0.0035	0.105	0.0034	0.0034	0.1714	4.9714	83.25	2035	2035	44	4

Table 2b: Extraction parameters for the four metals in Br⁻ at pH 7.5 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
Br ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0954	0.0292	0.0001	0.057	0.0034	0.0034	40	10	2035	2035	2	3
0.005	0.0692	0.0001	0.0001	0.023	0.3801	292	40	26.2609	22	1	2	2
0.01	0.0471	0.0012	0.0004	0.019	1.0276	23.4167	9.25	32	10	2	3	2
0.05	0.0188	0.0056	0.0006	0.034	4.0798	4.2321	5.8333	17.4412	4	4	4	2
0.1	0.0954	0.0184	0.0021	0.088	0.0034	0.5924	0.9524	6.1250	2035	10	10	4



The results from Table 1a indicate that at all concentrations of Br⁻ at pH 4.75 with H₂BuEtP alone, Cadmium was completely masked with 0.1% extraction as indicated in Fig. 1a. Apart from Iron that %E was >74% at all concentrations with 0.005 M – 0.01 M Br⁻ giving the best extraction of 95.85% and 94.75% and Nickel extraction of 88.74% at 0.005 M Br⁻, all other extractions were less than 40% and clearly showed that Br⁻ at pH 4.75 with H₂BuEtP alone was not suitable for the multi-metal extraction of the four metals. However, Br⁻ at pH 7.5 with H₂BuEtP alone showed from Fig. 1b that > 57% extraction of the four metals can be achieved from 0.001 M – 0.01 M Br⁻. Concentrations above 0.01 M Br⁻ results in increased masking of Cadmium resulting in 27.96% extraction at 0.1 M Br⁻ even though > 81% extractions were recorded for the other three metals at these concentrations of Br⁻. Calculated number of batches, *n*, needed to achieve 99.9% extraction of the four metals from Table 1b is 8 at 0.01 M Br⁻ and 6 at 0.001 M – 0.005 M Br⁻. Table 1b also clearly showed that 0.005 M – 0.05 M Br⁻ can be used for the multi-metal extraction of Lead, Nickel and Iron with 2 batches of extractions as Fig. 1b showed that at these concentrations of Br⁻, > 97% extractions of the three metals was recorded.

The favourable extractions can be attributed to changes in permittivities/dielectric constants of both phases resulting in favourable energetics in the transfer of the formed complexes Cd(HBuEtP)Br (Godwin *et al.*, 2019), Pb(BuEtP)(BuEtP)₂·4H⁺ (Godwin and Uzoukwu, 2012a), Ni(HBuEtP)₂ (Godwin *et al.*, 2012) and Fe(BuEtP) (Godwin *et al.*, 2014) from the aqueous phases to the organic phase (Housecroft, and Sharpe, 2001). pH 7.5 gave better results than pH 4.75 and statistically there was significant differences between them in the extractions of Cadmium (*p* = 0.009), Lead (*p* = 0.000) and Nickel (*p* = 0.0005) with only Iron (*p* = 0.1631) showing no significant difference in its extractions in the two buffers with Br⁻ (Sprinthall, 2011).

In the extraction using mixed ligands H₂BuEtP/HBuP with Br⁻ at pH 4.75, masking was also observed for Cadmium as was with H₂BuEtP alone but as shown in Fig. 2a, this was only at a maximum at above 0.01 M Br⁻ with 0.005 M Br⁻ giving 50.68% as the highest percent extraction of Cadmium. Nickel extractions was only completely masked at 0.1 M Br⁻ with lower concentrations of Br⁻ showing good extraction ranging from 33.79% at 0.001 M to 70.99% at 0.05 M of Br⁻. While Lead had percent extractions ranging from 97.56% at 0.001 M to 48.76% at 0.05 M with masking more pronounced at 0.1 M, the extraction percentages for Iron were all > 81%. Generally, Table 2a shows that 0.005 M Br⁻ with 10 batches of extractions theoretically needed to get 99.9% extraction of the four metal was the best with Br⁻ at pH 4.75 using mixed ligands H₂BuEtP/HBuP. At pH 7.5, Fig. 2b shows Cadmium was completely masked at 0.001 M thereafter, the extractions increased gradually and

peaked at 0.5 M with 80.31% and completely masked again at 0.1 M Br⁻. Nickel was also masked at 0.001 M but had percent extractions between 80.98% at 0.05 M to 99.66% at 0.005 M. Lead percent extraction of 45.78% at 0.1 M Br⁻ was the least as the rest concentrations of Br⁻ gave > 85% extraction of Lead.Iron extractions even though were higher but were not much different from those gotten at pH 4.75 with all > 85% extractions. Table 2b shows that at pH 7.5 with 0.05 M Br⁻ with mixed ligands H₂BuEtP/HBuP can be used theoretically to simultaneously extract 99.9% of the four metals after 4 batches of extractions.

Just like observed with H₂BuEtP alone, 99.9% of Lead, Nickel and Iron can be extracted after 2 batches of extractions using 0.005 M Br⁻. In the extraction using mixed ligands H₂BuEtP/HBuP with Br⁻ at pH 4.75, masking was also observed for Cadmium as was with H₂BuEtP alone but as shown in Fig. 2a, this was only at a maximum at above 0.01 M Br⁻ with 0.005 M Br⁻ giving 50.68% as the highest percent extraction of Cadmium. Nickel extractions was only completely masked at 0.1 M Br⁻ with lower concentrations of Br⁻ showing good extraction ranging from 33.79% at 0.001 M to 70.99% at 0.05 M of Br⁻. While Lead had percent extractions ranging from 97.56% at 0.001 M to 48.76% at 0.05 M with masking more pronounced at 0.1 M, the extraction percentages for Iron were all > 81%.

Generally, Table 2a shows that 0.005 M Br⁻ with 10 batches of extractions needed to get 99.9% extraction of the four metal was the best with Br⁻ at pH 4.75 using mixed ligands H₂BuEtP/HBuP. At pH 7.5, Fig. 2b shows Cadmium was completely masked at 0.001 M thereafter, the extractions increased gradually and peaked at 0.5 M with 80.31% and completely masked again at 0.1 M Br⁻. Nickel was also masked at 0.001 M but had percent extractions between 80.98% at 0.05 M to 99.66% at 0.005 M. Lead percent extraction of 45.78% at 0.1 M Br⁻ was the least as the rest concentrations of Br⁻ gave > 85% extraction of Lead.Iron extractions even though were higher but were not much different from those gotten at pH 4.75 with all > 85% extractions. Table 2b show pH 7.5 with 0.05 M Br⁻ with mixed ligands H₂BuEtP/HBuP can be used to simultaneously extract 99.9% of the four metals after 4 batches of extractions. Just like observed with H₂BuEtP alone, 99.9% of Lead, Nickel and Iron can be extracted after 2 batches of extractions using 0.005 M Br⁻. Though H₂BuEtP/HBuP appear better as an extractant at pH 7.5 than pH 4.75, statistically there was no significant differences in the extractions of the four metals in the two buffers as the p values were all > 0.05 for all the four metals (Sprinthall, 2011). At pH 4.75, there was no significant difference between the H₂BuEtP alone organic and the mixed ligands H₂BuEtP/HBuP organic phase in the extractions of the four metals with p values all > 0.05. However, at pH 7.5 there was significant difference between the two organic phases in the extraction of Nickel and Lead with p values < 0.05 with H₂BuEtP alone results slightly better.

Table 3a: Extraction parameters for the four metal in Cl⁻ at pH 4.75 for Ligand H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
Cl ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0954	0.0292	0.0001	0.145	0.0011	0.0034	40	3.3241	6283	2035	2	5
0.005	0.0954	0.0292	0.0015	0.130	0.0011	0.0034	1.73	3.8231	6283	2035	7	5
0.01	0.0954	0.0292	0.0015	0.188	0.0011	0.0034	1.73	2.3351	6283	2035	7	6
0.05	0.0954	0.0290	0.0034	0.109	0.0011	0.0100	0.206	4.7523	6283	694	37	4
0.1	0.0954	0.0292	0.0040	0.060	0.0011	0.0034	0.025	9.45	6283	2035	280	3

Table 3b: Extraction parameters for the four metal in Cl⁻ at pH 7.5 for Ligands H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
Cl ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0320	0.0001	0.0001	0.005	1.9844	292	40.	124.4	6	1	2	1
0.005	0.0310	0.0001	0.0019	0.004	2.0156	292	1.1579	155.75	6	1	9	1
0.01	0.0065	0.0001	0.0001	0.002	13.6923	292	40	312.5	3	1	2	1
0.05	0.0054	0.0001	0.0001	0.001	16.6852	292	40	626	2	1	2	1
0.1	0.0046	0.0001	0.0034	0.002	19.7609	292	0.2059	312.5	2	1	37	1

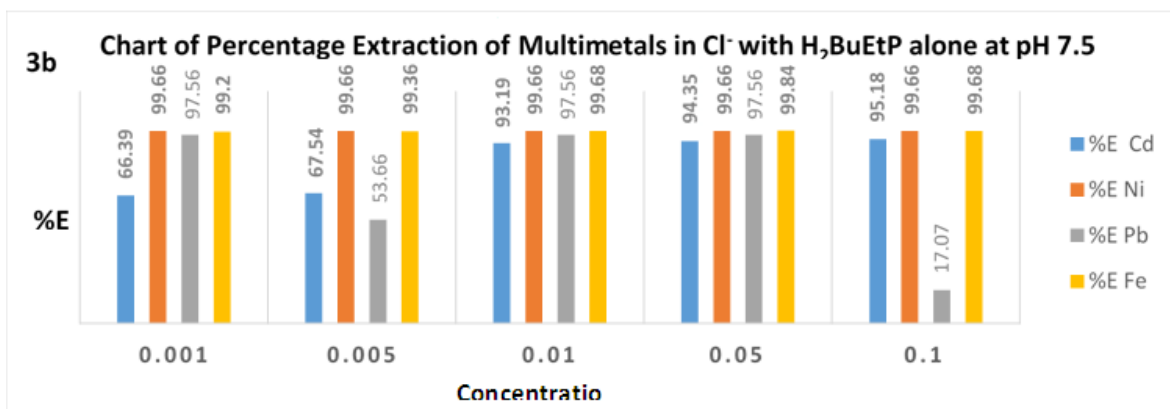
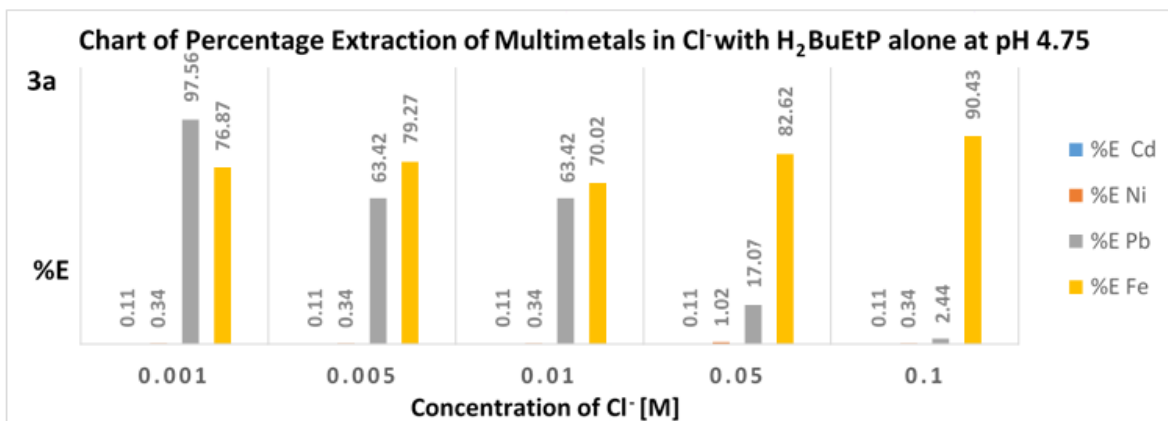


Table 4a: Extraction parameters for the four metal in Cl⁻ at pH 4.75 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
Cl ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0954	0.0292	0.0020	0.195	0.0034	0.0034	1.05	2.2154	2035	2035	10	6
0.005	0.0145	0.0292	0.0009	0.114	5.5862	0.0034	3.5	4.5	4	2035	5	4
0.01	0.0954	0.0292	0.0024	0.127	0.0034	0.0034	0.7083	3.9370	2035	2035	13	4
0.05	0.0954	0.0292	0.0026	0.191	0.0034	0.0034	0.5769	2.2827	2035	2035	15	6
0.1	0.0954	0.0292	0.0027	0.222	0.0034	0.0034	0.5180	1.8243	2035	2035	17	7

Table 4b: Extraction parameters for the four metal in Cl⁻ at pH 7.5 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
Cl ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0057	0.0001	0.0001	0.087	15.7544	292	40	6.2069	3	1	2	4
0.005	0.0954	0.0218	0.0001	0.032	0.0034	0.344	40	18.5938	2035	24	2	2
0.01	0.0852	0.0218	0.0001	0.035	0.1209	0.344	40	16.9143	61	24	2	3
0.05	0.0228	0.0218	0.0001	0.035	3.1886	0.344	40	16.9143	5	24	2	3
0.1	0.0788	0.0218	0.0006	0.050	0.2119	0.344	5.83	11.54	36	24	4	4

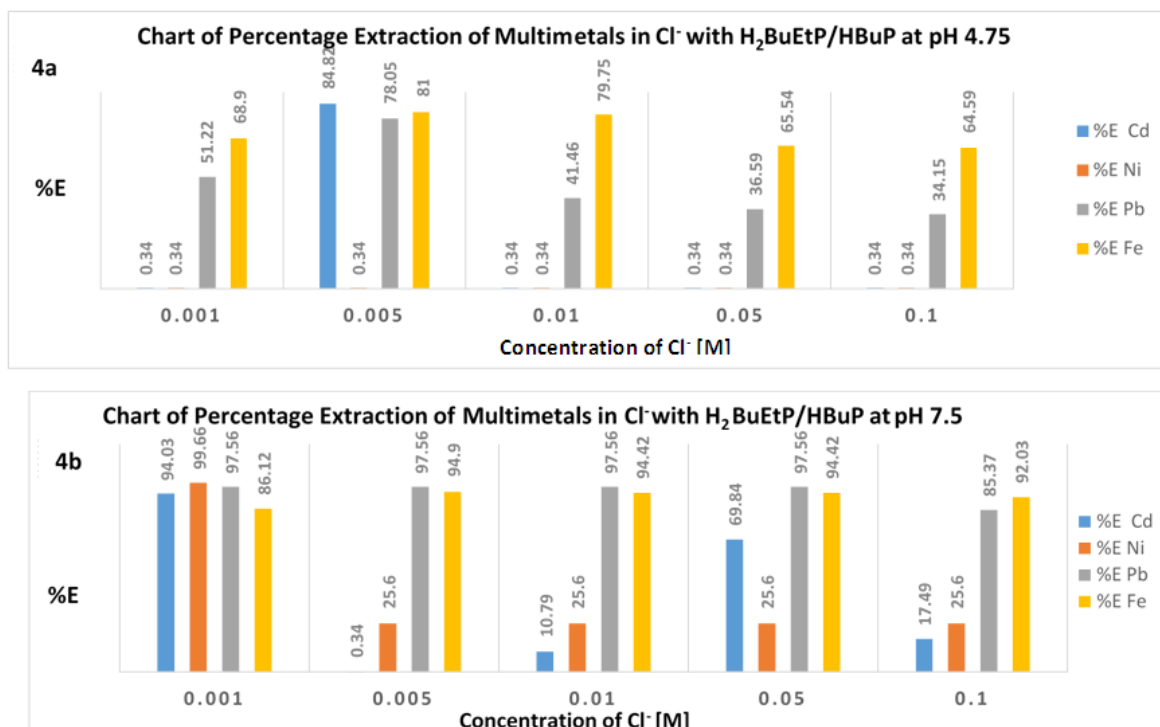


Figure 4: Chart of Percentage Extraction of Multimetals in Cl⁻ with H₂BuEtP/HBuP at (a) at pH 4.75 and (b) at pH 7.5

At pH 4.75 with H₂BuEtP alone, Cadmium and Nickel were masked at all concentrations of Cl⁻ giving < 1.02% extraction of the two metals as shown in Fig. 3a. 0.001 M Cl⁻ gave the best extraction of 97.56% for Lead and thereafter there was steady decrease in Lead extractions and above 0.01 M Cl⁻ masking of Lead became more pronounced with < 20% extraction. Iron extractions were > 70% at all concentrations of Cl⁻. Table 3a indicated that calculated batches of extraction *n* needed to extract 99.9% extraction of the four metals was 6283 and thus shows pH 4.75 with Cl⁻ using H₂BuEtP alone as extractant was not suitable for the multi-metal extraction of the four metals.

Results for Cl⁻ for pH 7.5 with H₂BuEtP alone was far better as > 50% extraction of the four metals was gotten for all concentrations of Cl⁻ except Lead that gave < 28% extraction with 0.1 M Cl⁻ as shown in Fig. 3b. Table 3b showed that chloroform solution of H₂BuEtP alone can be used as an extractant to simultaneously extract Cadmium, Lead, Nickel and Iron from an aqueous solution buffered to pH 7.5 with 99.9% extraction of the four metals theoretically achievable after 2 batches of extraction with 0.05 M Cl⁻ and 3 batches of extraction with 0.01M Cl⁻ being the least batches and best results.

Statically, there was differences between the extractions of the metals except with Lead ($p = 0.246$) in the two buffers in Cl⁻ using H₂BuEtP alone (Sprintall, 2011). With mixed ligands H₂BuEtP/HBuP as shown in Fig. 4a, pH 4.75 showed total masking of Nickel at all concentrations of Cl⁻. Cadmium was also masked at all concentrations of Cl⁻ except at 0.005 M Cl⁻ that had good extraction of 84.82%. Lead had percent extractions ranging from 34.15% - 78.05% while Iron extractions ranged between 64.59% - 81%. Calculated number of batches needed to theoretically achieve 99.9% extractions of the four metals from Table 4a, showed mixed ligands H₂BuEtP/HBuP in aqueous media containing Cl⁻ buffered to pH 4.75 was also not suitable for the multi-metal extractions of the four metals. However, it can be used for the multi-metal of Cadmium. Lead and Iron and 5 batches of extractions can be used to theoretically achieve 99.9% extractions of the three metals. This can be due to the formed Nickel adduct Ni(HBuEtP)(BuP) transfer to the organic phase not energetically favourable as against adducts of the other metal ions (Housecroft, and Sharpe, 2001).

Mixed ligands H₂BuEtP/HBuP with pH 7.5 buffer in 0.001 M Cl⁻ gave > 86% extraction of the four metals while higher concentrations showed masking of either Cadmium or Nickel or both as shown in Fig. 4b. Table 4b showed with 4 batches of extractions, the four metals can be simultaneously extracted from an aqueous medium buffered to pH 7.5 containing 0.001 M Cl⁻ using mixed ligands H₂BuEtP/HBuP in chloroform as organic extractant. That is, in this condition the formed adducts Pb(HBuEtP)(BuP), Ni(HBuEtP)(BuP), Fe(HBuEtP)(BuP) and Cd(HBuEtP).BuP have favourable energetics in their transfer from the aqueous phase to the organic phase resulting from changes in the permittivities/dielectric constants of the two phases (Housecroft, and Sharpe, 2001). Statistically with mixed ligands H₂BuEtP/HBuP, while there was no significant difference in

the extractions of Cadmium_(p = 0.422) and Nickel_(p = 0.3439), there was significant difference in the extraction of Lead_(p = 0.0016) and Iron_(p = 0.0015)between the buffers in Cl⁻.

There was also no significant difference between the two organic phases with p value all > 0.05 for pH 4.5 while there was significant differences between the two organic phases in the extractions of Nickel and Iron with p values < 0.05 at pH 7.5. Ligand H₂BuEtP alone results were also slightly better than the mixed ligands H₂BuEtP/HBuP results for Nickel and Iron.

Table 5a: Extraction parameters for the four metal in F⁻ at pH 4.75 for Ligand H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
F ⁻ (M)	Raffinates Absorbance				Distribution Ratios D			n Batches needed to get 99.9% extraction				
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0837	0.0078	0.0015	0.134	0.1410	2.7564	1.7333	3.6791	52	5	7	5
0.005	0.0621	0.0071	0.0013	0.147	0.5378	3.1268	2.1539	3.2653	16	5	6	5
0.01	0.0938	0.0292	0.0012	0.166	0.0181	0.0034	2.4167	2.7771	385	2035	8	5
0.05	0.0716	0.0218	0.0015	0.001	0.3338	0.3440	1.7333	626	24	23	7	1
0.1	0.0827	0.0094	0.0017	0.023	0.1548	2.1170	1.4118	26.2609	48	6	8	2

Table 5b: Extraction parameters for the four metal in F⁻ at pH 7.5 for Ligand H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
F ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0109	0.0047	0.0001	0.030	7.7615	5.234	40	19.9	3	4	2	2
0.005	0.0237	0.0001	0.0001	0.012	3.0295	292	40	51.25	5	1	2	2
0.01	0.0129	0.0001	0.0001	0.037	6.4031	292	40	15.946	4	1	2	3
0.05	0.0042	0.0003	0.0001	0.004	21.7381	96.6667	40	155.75	2	2	2	2
0.1	0.0151	0.0005	0.0002	0.053	5.3245	57.6	19.5	10.8302	4	2	2	2

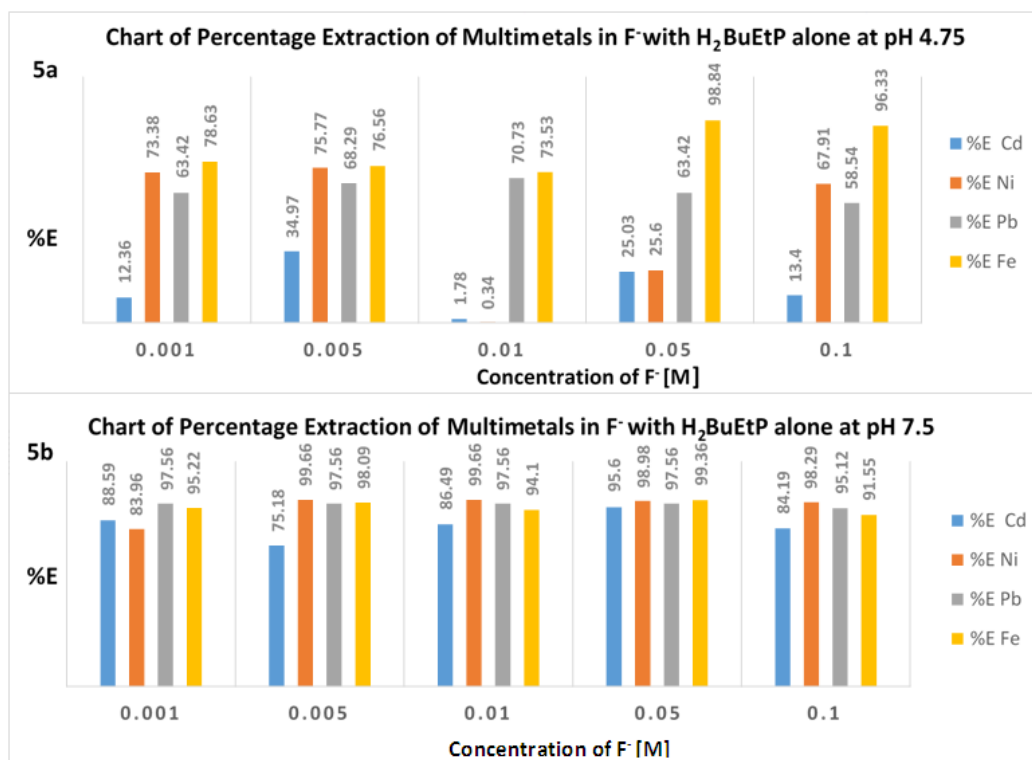


Table 6a: Extraction parameters for the four metal in F⁻ at pH 4.75 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance		Cd = 0.0955		Ni = 0.0293		Pb = 0.0041		2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627				
F ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	DCd	DNi	DPb	DFe	nCd	nNi	nPb	nFe
0.001	0.0954	0.0292	0.0001	0.111	0.0034	0.0034	40	4.6487	2035	2035	2	4
0.005	0.0954	0.0266	0.0008	0.078	0.0034	0.1015	4.125	7.0385	2035	72	4	3
0.01	0.0954	0.0292	0.0019	0.095	0.0034	0.0034	1.1579	5.6000	2035	2035	9	4
0.05	0.0954	0.0292	0.0021	0.158	0.0034	0.0034	0.9524	2.9684	2035	2035	10	5
0.1	0.0954	0.0292	0.0040	0.264	0.0034	0.0034	0.0250	1.375	2035	2035	280	8

Table 6b: Extraction parameters for the four metal in F⁻ at pH 7.5 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance		Cd = 0.0955		Ni = 0.0293		Pb = 0.0041		2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627				
F ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	DCd	DNi	DPb	DFe	nCd	nNi	nPb	nFe
0.001	0.0069	0.0001	0.0001	0.137	12.8406	292	40	3.5766	3	1	2	5
0.005	0.0063	0.0002	0.0002	0.080	14.1587	145.5	19.5	6.8375	3	2	2	4
0.01	0.0162	0.0039	0.0002	0.036	4.8951	6.5128	19.5	16.4167	4	4	2	3
0.05	0.0239	0.0146	0.0037	0.063	2.9958	1.0069	0.1081	8.9524	5	10	67	3
0.1	0.0346	0.0247	0.0040	0.264	1.7601	0.1862	0.0034	1.375	7	41	2035	8

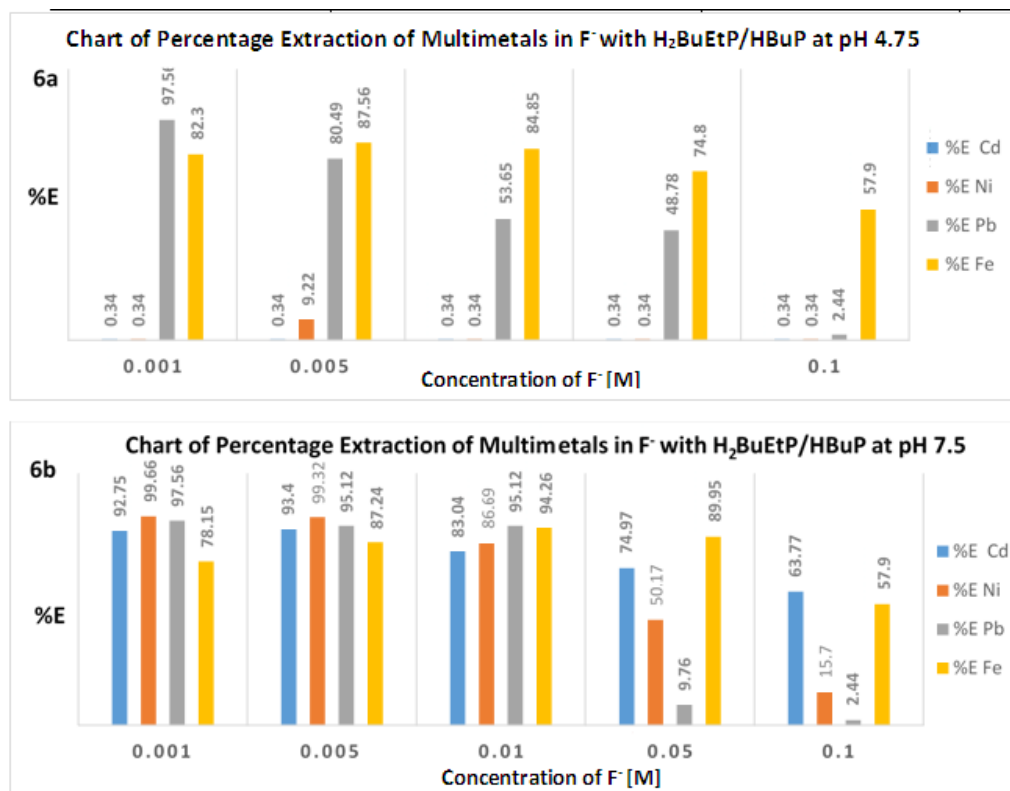


Figure 6: Chart of Percentage Extraction of Multi-metals in F⁻ with H₂BuEtP/HBuP at (a) at pH 4.75 and (b) at pH 7.5

The results of the multi-metal extraction of the four metals in aqueous media buffered to pH 4.75 containing F⁻ in H₂BuEtP alone from Fig. 5a indicated that Lead percentage extractions were in the range 58.54% - 70.73% and Iron in the range 73.53% - 98.54% at all concentrations of F⁻. However, Cadmium percentage extractions indicated masking with 34.97% as the highest percentage extraction at 0.005 M F⁻ while Nickel percentage extractions were > 67% in 0.001 M - 0.005 M and 0.1 M F⁻ with masking occurring at 0.01 M F⁻ (0.34%) and 0.05 M F⁻ (25.6%). Table 5a show that 16 batches of extraction are theoretically needed to achieve 99.9% extractions of the four metal in an aqueous solution containing 0.005 M F⁻ and buffered to pH 4.75 using chloroform solution of H₂BuEtP. This was the best results for pH 4.75 with F⁻ using H₂BuEtP alone.

The result for pH 7.5 with F⁻ using H₂BuEtP alone were far better than those of pH 4.75 as Fig. 5b show that at all concentrations of F⁻ all the four metals percentage extraction were > 75%. 0.05 M F⁻ gave the best results with all percentage extractions > 95% and Table 5b show that at this concentration, 2 batches are theoretically needed to achieve 99.9% extractions of the four metals. That is, at this concentration of F⁻, the transfer of the formed metal complexes to the organic phase is more energetically favourable resulting from changes in the permittivities/dielectric constants of the two phases (Housecroft, and Sharpe, 2001).

Statistically, there was significant difference in the simultaneous extractions of all the metals except Iron_(p = 0.5365) that show no significant difference between the two buffers. Mixed ligands H₂BuEtP/HBuP with buffer 4.75 show from Fig. 6a that Cadmium and Nickel was masked at all concentration of F⁻ while Lead was only completely masked at 0.1 M F⁻. Iron percentage extractions were all > 57%. Table 6a show that mixed ligands H₂BuEtP/HBuP with F⁻ at pH 4.75 was not suitable for the multi-metal extraction of the four metals. However, Fig. 6b showed that at pH 7.5 with F⁻, mixed ligands H₂BuEtP/HBuP gave > 78% extraction for all the four metals with 0.001 M – 0.01 M F⁻.

Masking of Nickel and Lead becomes very pronounced above 0.01 M F⁻. Table 6b indicated that with mixed ligands H₂BuEtP/HBuP, 4 batches of extractions are theoretically needed to achieve 99.9% extractions of the four metal with 0.005 M – 0.01 M F⁻ while 0.001 M F⁻ requires 5 batches. Thus, 0.001 M – 0.01 M F⁻ gave positive changes in permittivities/dielectric constants of the two phases, resulting in favourable energetics in the transfer of the formed metal adducts(Housecroft, and Sharpe, 2001). Mixed ligands H₂BuEtP/HBuP with F⁻ statistically show no significant differences between the two buffers in the simultaneous extractions of all the metals except Cadmium_(p = 0.0217). With pH 4.75 buffer, while there was significant differences between the two organic phases in the extractions of Cadmium and Nickel with p value < 0.05, there was no significant difference in the extractions of Lead and Iron with p value > 0.05. With buffer of pH 7.5, there was no significant differences between the two organic phases in the multi-metal extractions of all metal with p values > 0.05 except in the extraction of Lead with p value 0.04581 (Sprinthall, 2011).

Table 7a: Extraction parameters for the four metal in I at pH 4.75 for Ligand H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
I (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0954	0.0291	0.0012	0.168	0.0011	0.0069	2.4167	2.7321	6283	1005	5	5
0.005	0.0927	0.0292	0.0009	0.129	0.0302	0.0034	3.5556	3.8605	232	2035	5	5
0.01	0.0954	0.0292	0.0023	0.076	0.0011	0.0034	0.7826	7.2500	6283	2035	12	3
0.05	0.0954	0.0292	0.0040	0.143	0.0011	0.0034	0.025	3.3846	6283	2035	280	5
0.1	0.0954	0.0312	0.0040	0.149	0.0011	0.0034	0.025	3.2081	6283	2035	280	5

Table 7b: Extraction parameters for the four metal in I at pH 7.5 for Ligand H₂BuEtP alone

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
I (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0147	0.0001	0.0001	0.005	5.4966	292	40	124.4	4	1	2	2
0.005	0.0077	0.0001	0.0002	0.031	11.4026	292	19.5	19.2258	3	1	2	2
0.01	0.0058	0.0001	0.0001	0.041	15.4655	292	40	14.2927	3	1	2	3
0.05	0.0449	0.0002	0.0001	0.017	1.127	145.5	40	35.8824	9	2	2	2
0.1	0.0954	0.0289	0.0003	0.028	0.0034	0.0138	12.6667	21.3929	2035	504	3	2

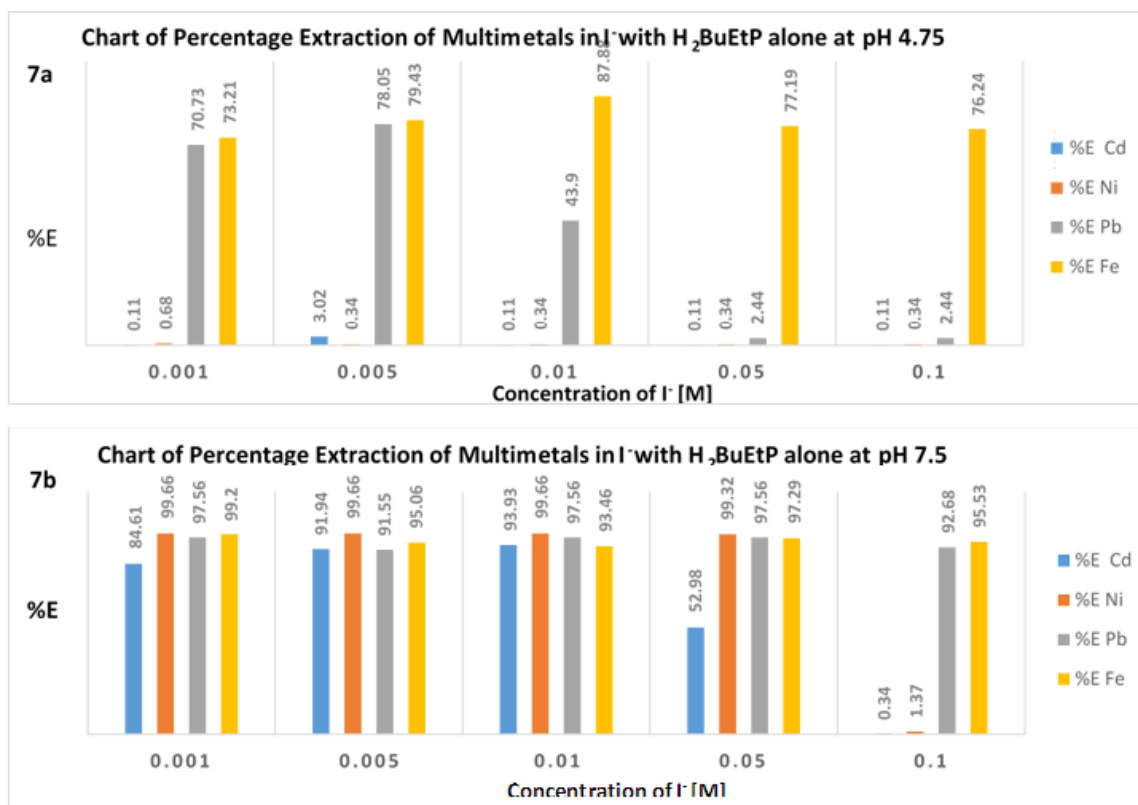


Figure 7: Chart of Percentage Extraction of Multimetals in I⁻ with H₂BuEtP alone at (a) at pH 4.75 and (b) at pH 7.5

Table 8a: Extraction parameters for the four metal in I⁻ at pH 4.75 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
I ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0954	0.0292	0.0022	0.021	0.0034	0.0034	0.8636	28.8571	2035	2035	11	2
0.005	0.0954	0.0292	0.0004	0.013	0.0034	0.0034	9.25	47.2308	2035	2035	3	2
0.01	0.0954	0.0292	0.0040	0.092	0.0034	0.0034	0.0034	5.8152	2035	2035	2035	4
0.05	0.0954	0.0292	0.0040	0.102	0.0034	0.0034	0.0034	5.1471	2035	2035	2035	4
0.1	0.0954	0.0292	0.0040	0.159	0.0034	0.0034	0.0034	2.9434	2035	2035	2035	5

Table 8b: Extraction parameters for the four metal in I⁻ at pH 7.5 for Mixed Ligands H₂BuEtP/HBuP

0.625 mgL ⁻¹ Cd, Ni and Pb Standards Absorbance				Cd = 0.0955	Ni = 0.0293	Pb = 0.0041	2.50 mgL ⁻¹ Fe Standard Absorbance = 0.627					
I ⁻ (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D _{Cd}	D _{Ni}	D _{Pb}	D _{Fe}	n _{Cd}	n _{Ni}	n _{Pb}	n _{Fe}
0.001	0.0253	0.0001	0.0001	0.046	2.7747	292	40	12.6304	5	1	2	3
0.005	0.0320	0.0001	0.0001	0.015	1.9844	292	40	40.8	6	1	2	2
0.01	0.0321	0.0001	0.0002	0.033	1.9751	292	19.5	18	6	1	2	2
0.05	0.0472	0.0001	0.0008	0.051	1.0233	292	4.125	11.2941	10	1	4	3
0.1	0.0803	0.0001	0.0012	0.057	0.1893	292	2.4167	10	40	1	6	3

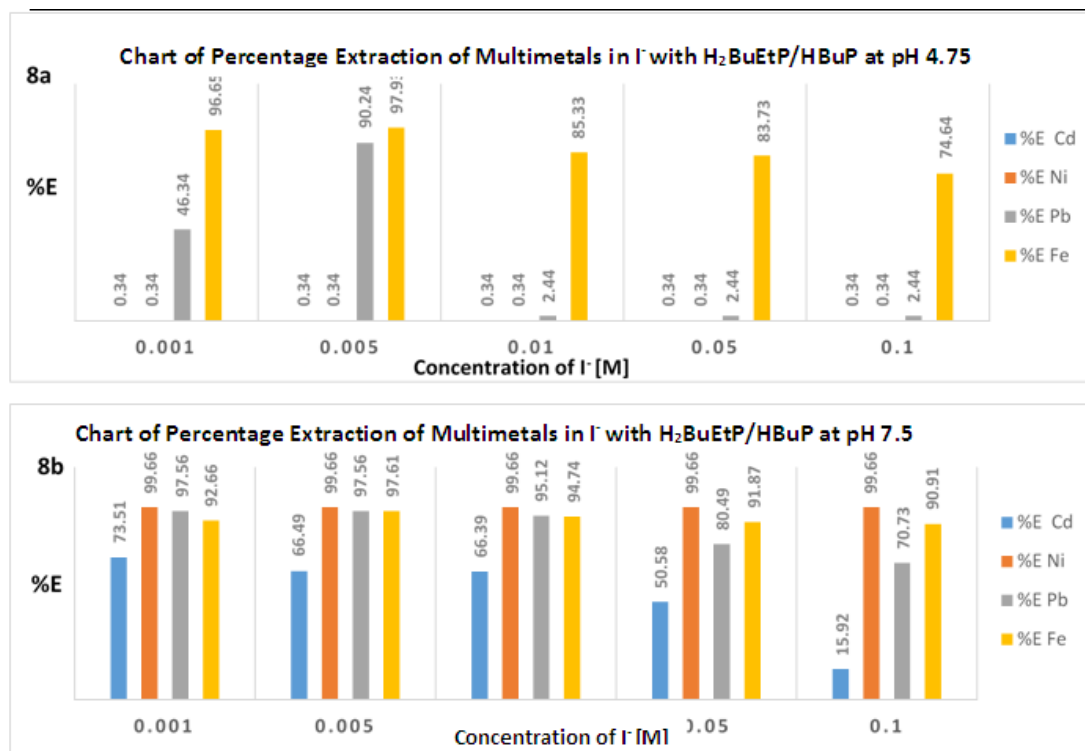


Figure 8: Chart of Percentage Extraction of Multimetals in I⁻ with H₂BuEtP/HBuP at (a) at pH 4.75 and (b) at pH 7.5

The results of the effect of I⁻ on the multi-metal extractions of the four studied metals from aqueous media buffered to pH 4.75 using chloroform solution of H₂BuEtP shown in Fig. 7a, indicated that Cadmium and Nickel extractions was masked at almost all concentrations of I⁻ with percentage extraction < 3.02% while Lead was masked at concentrations of I⁻ > 0.01 M with percentage extraction 2.44%. Iron extractions were all > 73% at all concentrations of I⁻. Number of batches needed to extract 99.9% of the four metals simultaneously from Table 7a indicated that I⁻ at pH 4.75 using H₂BuEtP was not suitable for the multi-metal extraction of the four metals. However, results with pH 7.5 were much better as complete masking for Cadmium and Nickel occurred only at I⁻ concentration of 0.1 M while Lead and Iron had percent extraction > 91% at all concentrations of I⁻ as shown in Fig. 7b. Table 7b also show that, it is theoretically possible to achieve 99.9% simultaneous extractions of the four metals after 3 batches of extraction with 0.005 M – 0.01 M I⁻ and 4 batches with 0.001 M I⁻ at pH 7.5 with H₂BuEtP alone. Table 7b also show that 2 at 0.001 M – 0.005 M, 0.05 M I⁻ and 3 at 0.01 M I⁻ batches of extractions are theoretically required to extract 99.9% of Nickel, Lead and Iron. At these conditions, the formed metal complexes transfer from the aqueous media to the organic phase are energetically favourable as a result of changes in permittivities/dielectric constants of the two phases (Housecroft and Sharpe, 2001). Statistically, pH 7.5 was significantly better than pH 4.75 for the extractions of all the metals except Iron with a p value of 0.096 (Sprinthal, 2011).

Fig. 8a showed that with the mixed ligands H₂BuEtP/HBuP, I⁻ effects for the multi-metal extractions of the four metals at pH 4.75 also had complete masking of Cadmium and Nickel at all concentrations while Lead masking was above 0.005 M I⁻. Iron had good extractions ranging from 74.64% - 96.65% with decreasing extractions as the concentration of I⁻ increased. Table 8a also showed that I⁻ at pH 4.75 with mixed ligands H₂BuEtP/HBuP was not suitable for the multi-metal extraction of the four metals. pH 7.5 results shown in Fig. 8b had percentage extractions > 50% for all the metals except Cadmium with 15.92% at 0.1 M I⁻. Nickel extractions were all 99.66% and 0.001 M – 0.01 M I⁻ gave the best extractions of the four metals with > 66% extractions. Table 8b also show that with pH 7.5 buffer using the mixed ligands H₂BuEtP/HBuP, 5 batches of extractions are theoretically needed to get 99.9% of the four metals with 0.001 M I⁻ and 6 batches are needed with 0.005 M – 0.01 M I⁻. Table 8b also show that 2 batches with 0.005 M – 0.01 M I⁻ and 3 batches with 0.001 M I⁻ are needed respectively to achieve 99.9% Nickel, Lead and Iron extractions with the mixed ligands H₂BuEtP/HBuP. Metal adducts formed with the ligands H₂BuEtP and HBuP are favourably energetically transferred from the aqueous media to the organic phase in these conditions with high percentage extractions of the metals (Housecroft, and Sharpe, 2001). As was observed with H₂BuEtP alone, mixed ligands H₂BuEtP/HBuP with I⁻ also had pH 7.5 results better and significantly different in the extractions of the metals

except Iron with p value 0.9525. There was no significant differences between the two organic phases in the extractions of the four metals as all p values were > 0.05 at both pHs with Γ (Sprinthal, 2011).

IV. Conclusion

The halide ions all showed potentials at different concentration in the multimetals extraction of Cadmium, Lead, Nickel and Iron from buffered aqueous solutions using chloroform solutions of the ligand H_2BuEtP alone or in the presence of $HBuP$. With buffer pH 4.75, at least 10 batches of extractions are theoretically needed to get 99.9% extractions of Cadmium, Lead, Nickel and Iron from an aqueous solution containing 0.005 M Br^- using chloroform solutions of the mixed $H_2BuEtP/HBuP$. 99.9% extraction of Cadmium, Lead, Nickel and Iron are theoretically possible after 2 batches of extractions from aqueous solutions buffered to pH 7.5 and containing either 0.05 M Cl^- or F^- using chloroform solutions of the ligand H_2BuEtP alone. About 99.9% extraction of Cadmium, Lead, Nickel and Iron are theoretically possible after 3 batches of extractions from aqueous solutions buffered to pH 7.5 and containing 0.005 M – 0.01 M Γ using chloroform solutions of the ligand H_2BuEtP alone.

Four (4) batches of extractions were theoretically needed to extract 99.9% of Cadmium, Lead, Nickel and Iron with Mixed ligands $H_2BuEtP/HBuP$ from aqueous solutions buffered to pH 7.5 and containing either 0.05 M Br^- or 0.001 M Cl^- , or 0.01 M F^- .

The efficiencies of the halide ions in the multimetal extractions of Cadmium, Lead, Nickel and Iron (4s in the order $Cl^- = F^- > I^- > Br^-$). Extraction of Cadmium, Lead, Nickel and Iron from the buffered aqueous solutions containing the halide ions was mainly due to favourable energetics in the transfer of the formed metal complexes with ligand H_2BuEtP alone or metal adducts with mixed ligands $H_2BuEtP/HBuP$ organic phases, resulting from changes in permittivities/dielectric constants of the two phases.

The media pH of 7.5 was better as an extraction medium than pH 4.75 in the multimetal extraction of Cadmium, Lead, Nickel and Iron with the halide ions as there was significant differences in almost all the extractions of the metals except Iron in both organic phases. There was no significant difference between ligand H_2BuEtP alone and mixed ligands $H_2BuEtP/HBuP$ in the multimetal extraction of Cadmium, Lead, Nickel and Iron with the halide ions at both pHs used for the study.

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Godwin, Jackson, et. al. "HALIDEIONS EFFECTS INMULTI-METAL EXTRACTIONS USING 4,4'-(1E,1E')-1,1'-(ETHANE-1,2-DIYLBIS(AZAN-1-YL-1YLIDENE))BIS(5-METHYL-2-PHENYL-2,3-DIHYDRO-1H-PYRAZOL-3-OL) (H2BuEtP)." *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 14(5), (2021): pp 30-44.