The Role of Some Commom Anions in the Multi-Metal Extraction Using 4,4´-(1*E*,1*E*´)-1,1´-(Ethane-1,2-Diylbis(Azan-1-YL-1Ylidene))Bis(5-Methyl-2-Phenyl-2,3-Dihydro-1*H*-Pyrazol-3-OL) (H_2BuEtP)

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Abstract. The roles of CH_3COO^-, PO_4^{3-}, and SO_4^{2-} 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 were studied using ligand H_2BuEtP alone and in the presence of another ligand 4-butanoyl-2-4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-one (HBuP) in chloroform organic phases using solvent-solvent extraction methods using 2 batches of extractions based on theoretically number of batches needed to achieve 99.9% extractions of the four metals from single metal extractions studies with same organic phases. 50 mgL^{-1} each of the four metal in 2 mL aqueous solutions containing 0.001 M – 0.1 M of the anions CH_3COO^-, PO_4^{3-} and SO_4^{2-} and buffered to pH 4.75 and 7.5 containing either 2 mL 0.05 M H_2BuEtP or 2 mL 0.05 M H_2BuEtP/0.05 M HBuP in a 9:1 volume ratio was agitated mechanically for an hour, allowed to settle and organic extractants removed and fresh organic extractants added and process repeated. Aqueous raffinates are then analysed for the four metals by comparing with standards using Atomic Absorption Spectrometry for Cadmium, Lead and Nickel and colorimetry for Iron using 1,10-phenanthroline. The results show that CH_3COO^-, PO_4^{3-} and SO_4^{2-} can be used for the multi-metal extraction of the four metals and single digit batches (5-8) of extraction were the least needed to get 99.9% extraction of Cadmium (II), Iron (II), Lead (II) and Nickel (II) simultaneously from aqueous solutions buffered to either pH 4.75 or 7.5 using either H_2BuEtP alone or H_2BuEtP/HBuP. 0.1 M CH_3COO^- and buffered to pH 4.75 using chloroform solutions of ligand H_2BuEtP alone and 0.05 M PO_4^{3-} with aqueous solution buffered to pH 7.5 using H_2BuEtP/HBuP organic phase with 99.9% extraction of the four metal theoretically extractable after 5 batches of extractions gave the best result. pH 7.5 was slightly better for the multi-metal extraction of Cadmium (II), Iron (II), Lead (II) and Nickel (II) from aqueous solutions. CH_3COO^- and SO_4^{2-} effects were significantly different for Cadmium and iron extractions at both pH 4.75 and 7.5 for H_2BuEtP alone but not significantly different in H_2BuEtP/HBuP organic phases. PO_4^{3-} and SO_4^{2-} effects were significantly different for Iron extractions alone at both pHs for H_2BuEtP alone and significantly different for Cadmium and Iron at pH 4.75 for H_2BuEtP/HBuP organic phases. Changes in permittivities/dielectric contants of the solvents leading to favourable energetics in the transfer of formed complexes or adducts from aqueous media to the organic phases was attributed to the simultaneous extractions of the four metals.

Key words: multi-metal, extraction.

Introduction

Heavy metals pose a serious threat to the environment, attributed to their toxic effects on both flora and fauna (Gbaruku and Uhegbu, 2007: 197-201; Tchounwou et al., 2012: 133-164; Jaishankar et al., 2014: 60-72). Many methods have been designed and studied for their applicability and efficacy for different types of heavy metals in various types of environmental samples such as soils (Chibuike and Obiora, 2014: 1-13), wastewater samples (Hala, 2013: 276-282; Belete, 2017: 72-75) and industrial effluents (Mohamed, 2011: 361-377; Gunatilake, 2015). Solvent-solvent extraction employing ligands leading to the formation of metal complexes that are usually more soluble in the organic phases, hence, extraction of metals from the aqueous phases to the organic phases, have shown from studies to have great potentials in heavy metal extraction from our environment (Karapinar et al., 2013: 1-7; Houariet al., 2019: 5040-5048; Selvi et al., 2019: 66).

These studies with ligands have shown that polydentate ligands have done better than the common ligands due to formation of chelates complexes, which are very stable because of their ring structures and high hydrophobicity (Sartore and Dey, 2019: 1-11; Tsantis et al., 2020). Thus, there has been a gradual shift in these studies from simple ligands to chelating agents. A class of chelating agents that have shown very promising results in heavy metal extractions, from studies, are the Schiff bases, which are chelating agents with a carbon – nitrogen double bond (N=C) (Bottino et al., 1988: 341-345; Uzoukwu et al., 1998: 1180-1183). Most of these studies have centered on the optimal conditions for the extraction of a single metal. pH, equilibration time, solvents, synergists, acids, anions and auxiliary complexing agents are factors that affect these extractions (Uzoukwu, 2009: 166-196). These factors have been utilized in optimizing the extractions of many heavy metals and also in the separation of one metal from another in aqueous solutions using a particular ligand or Schiff base (Okafor and Uzoukw, 1990: 167-172; Godwin et al., 2020: 865-869). The Schiff base 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) has been studied using solvent-solvent extraction for Pb^{2+}, UO_2^{2+}, Ni^{2+}, Fe^{2+} and Cd^{2+}, since its synsthesis by Uzoukwu, et al. (1998: 1180-1183). The results from these studies also show that > 90% extraction of all studied metals was achieved with ligand H_2BuEtP alone or in the presence of a second ligand HBuP at a particular pH or in the presence of different concentrations of common acids, anions and auxiliary complexing agents in the aqueous phase. The pH range in which the optimal extractions occurred for these metals was reported as 4.75 – 7.5 (Godwin and Uzoukwu, 2012a: 14-21; Godwin and Uzoukwu, 2012b: 105-116; Godwin et al., 2012: 269-273; Godwin et al., 2013: 1581-1589; Godwin et al., 2014: 59-72; Godwin and Tella, 2017: 1329-1342; Godwin et al., 2019).

Research in the removal of heavy metals is gradually shifting into methods that are very efficient, less time consuming, cost effective and applicable in both acid and alkaline pH ranges (Selvi et al., 2019). The Schiff base 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) H_2BuEtP) in extraction studies with Pb^{2+}, UO_2^{2+}, Ni^{2+}, Fe^{2+} and Cd^{2+} has shown that common acids (CH_3COOH, HCl, HNO_3, H_3PO_4, and H_2SO_4), anions (F^-, Br^-, Cl^-, I^-, CH_3COO^-, NO_3^-, PO_4^{3-} and SO_4^{2-})and auxiliary complexing agents (thiocyanate SCN^-, oxalate $C_2O_4^{2-}$, tartrate $C_2H_4O_6^{2-}$ and $EDTA^{4-}$) have varying effects at different pHs and in the ligand H_2BuEtP alone and in the presence of another Schiff base 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one HBuP (Godwin and Uzoukwu, 2012a: 14-21; Godwin and Uzoukwu, 2012b: 105-116; Godwin et al., 2012: 269-273; Godwin et al., 2014: 59-72; Godwin et al., 2019). This effects have been utilized in separating Fe (III) from U (VI) (Okafor and Uzoukwu, 1990: 167-172) and in designing the separation of uranium and lead that have a parent/daughter relationship and thus can be used for dating (Godwin and Uzoukwu, 2013: 1581-1589). However, related recent studies have shown that, changes in relative permittivities or dielectric constants for both aqueous and organic phases as a result of the presence of a second metal may increase distribution ratio D of an otherwise masked metal at a particular condition (Godwin et al., 2020). This has been shown to lead to improved bimetal extraction with significantly reduced separation factors β_{XY} of the two metals that could be separated from theoretical separation factors β_{XY} close to 10^4 (Godwin et al., 2020: 865-869). The results from these study indicated that this Schiff base 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) has potentials for multi-metal extraction from buffered aqueous phase using the acids, anions and complexing agents. Hence, the first in a series, we have evaluated the effects of some common anions CH_3COO^-, PO_4^{3-} and SO_4^{2-} in the simultaneous extraction of Cd^{2+}, Fe^{2+}, Ni^{2+} and Pb^{2+} from aqueous media buffered to pH 4.75 and 7.5 using chloroform solutions of the 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) alone and in the presence of another Schiff base 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) as a synergist. The objectives is to; determine the effects of the concentration of the anions on the extractions, compare results for pH 4.75 and 7.5, the two organic phases, determine the possibility of multi-metal extractions and optimal conditions for these extractions.

Material and Methods

Schiff bases 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) and 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) were synthesized and characterized by methods outlined by Uzoukwu et al. (1998: 1180-1183). Other reagents were of analytical grades.

1000 mgL^{-1} stock solutions of the four metals were prepared by dissolving appropriately weighed salts of the metals in distilled water with addition of 2 mL of 2M HNO_3 to prevent hydrolysis. Four sets of fifteen 10 mL extraction volumetric flasks with glass covers were labelled accordingly. Each set contained two sets of an anion with concentrations ranging from 0.001 M - 0.1 M, 50 mgL^{-1} of each of the four metals by pipetting 0.1 mL from stock solutions of the metals. The aqueous solutions of the metals are made up to 2 mL mark with buffer solutions of pH 4.75 and 7.5. Organic phases of 2 mL chloroform solutions of 0.05 M of 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) alone was added to one set and 0.05 M of 4,4´-(1*E*,1*E*´)-1,1´-(ethane-1,2-diylbis(azan-1-yl-1ylidene))bis(5-methyl-2-phenyl-2,3-dihydro-1*H*-pyrazol-3-ol) (H_2BuEtP) and 0.05 M of 1-(3-hydroxy-5-methyl-2-phenyl-2,3-dihydro-1H-pyrazol-4-yl) butan-1-one (HBuP) in a 9:1 volume ratio were added to the other set. The two phases were mechanically agitated for an hour for equilibration to occur. The phases were allowed to separate out in a separating funnel and organic extractants removed and replaced with fresh organic phases according to labels and agitation process repeated for another hour. The phases were allowed to separate out and 0.2 mL of aqueous raffinates taken and analysed for the four metals; Cadmium, nickel and lead using Atomic Absorption Spectrophotometer and iron using colorimetric determination using 0.2 mL of 0.1% 1,10 phenathroline after addition of 0.2 mL each of 10% CH_3COONa and 10% NH_2OH solutions. The absorbances of raffinates and standards of metal ions are used to calculate distribution ratios D and percentage extractions %E using equations 1 and 2.

$$\text{Distribution ratio D} = \text{Standard absorbance} - \text{Raffinate Absorbance}/\text{Raffinate Absorbance} \quad (1)$$

Percentage Extraction %E = Standard absorbance – Raffinate Absorbance/Standard Absorbance × 100 (2)

Distributio ratios data for pH 4.75 and 7.5 and ligand H_2BuEtP alone and in the presence of HBuP for each anion and with other anions were statistically analysed using the R software package [R Development Core Team 2008]. The t test statistics (Sprinthall, 2011: 183-213) was used to test the hypothesis,if the two organic phases were significantly different in these extractions. The null hypothesis (H_0), that the two organic phases of interest are not significantly different is rejected if the value of the test statistics is greater than the critical value and the alternative hypothesis (H_a), the two groups of interest are significantly different is accepted. The p value was also used. 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 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.

$$C/C_{aq} = [\frac{1}{D+1}]^n \tag{3}$$

Results and Discussion

Tables 1-2 showing the extraction parameters in the multi-metal extractions of Cd (II), Ni (II), Pb (II) and Fe (II) from aqueous media containing CH_3COO^- at pH 4.75 and 7.5 using ligand H_2BuEtP alone in chloroform showed increased distribution ratios D of the four metal ions as the concentration of CH_3COO^- increased apart from Cd (II) at pH 7.5 that showed decreasing distribution ratios D as the concentration of CH_3COO^- increased, which was the general trend as reported for the studies with single metal extraction under similar conditions (Godwin and Uzoukwu, 2012a: 14-21; Godwin and Uzoukwu, 2012b: 105-116; Godwin et al., 2012: 269-273; Godwin et al., 2014: 59-72; Godwin et al., 2019: 1702-1711). The results indicate that there was enhanced extractions of the four metals at CH_3COO^- concentration of 0.1M at pH 4.75 with percentage extraction %E as shown in Fig. 1 > 86%. Table 1 with calculated number of batches needed to achieve 99.9% extraction of the four metals giving 2 for Cadmium, Nickel, Iron and 4 for Lead. Since two batches was used in the study, the result is indicating that the four metals can be simultaneously extracted up to 99.9% using 0.1 M CH_3COO^- from an aqueous medium buffered to pH 4.75 using chloroform solution of the ligand H_2BuEtP after 5 batches of extractions with fresh organic extractants. The change in general trend observed with the single metal ions confirm that the presence of four metal ions have an effect on the dialectric constants of the two solvents water and chloroform leading to a favourable $\Delta_{transfer}$ G^0 of the formed complexes $[Pb(BuEtP)(BuEtP)2^{4-}.4H^+]$, $Ni(HBuEtP)_2$, Fe(BuEtP) and Cd(HBuEtP) from the aqueous media to the chloroform organic phases (Housecroft and Sharpe, 2001) as reported in the bimetal extraction using H_2BuEtP and the effect on separation factor β_{XY} (Godwin et al., 2020: 865-869). Extraction parameters values for pH 7.5 shown in Table 2 were better for Nickel, Lead and Iron than at pH 4.75 in Table 1 with percentage extraction %E in Fig. 2 for the three metals > 85% at all studied concentrations of CH_3COO^-. Calculated number of batches of extraction needed to get 99.9% extraction of the three metals as shown in Table 2 can be achieved in 3 batches of extractions using 0.1 M CH_3COO^-. With H_2BuEtP alone, the results for pH 4.75 and 7.5 statistically showed significant different in the extractions of Cadmium (0.04) and Nickel (0.00) but did not show significant difference for Lead (0.12) and Iron (0.07). With the mixed ligandsH_2BuEtP/HBuP, only Lead (0.52) showed no significant difference while there was significant difference in Cadmium (0.003), Nickel (0.004) and Iron (0.00) extraction in pH 4.75 and 7.5.

Table 1. Extraction parameters for the four metal in CH_3COO^- at pH 4.75 for Ligand H_2BuEtP alone

1.25 mgL^{-1} Metal Standards Absorbance	Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185											
CH_3COO^- (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd1}	D_{Ni1}	D_{Pb1}	D_{Fe1}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
0.001	0.1443	0.0237	0.0148	0.0015	0.31	1.56	0.15	122.33	26	8	64	2
0.005	0.0093	0.0187	0.0093	0,0024	19.31	2.25	0.77	76.08	3	6	12	2
0.01	0.0059	0.0153	0.0046	0.0014	31.02	2.97	1.80	131.14	2	5	7	2
0.05	0.0046	0.0083	0.0059	0.0012	40.04	6.31	2.59	153.17	2	4	6	2
0.1	0.0023	0.0017	0.0023	0.0004	81.13	34.71	6.17	461.50	2	2	4	2

Table 2. Extraction parameters for the four metal in CH_3COO^- at pH 7.5 for Ligand H_2BuEtP alone

1.25 mgL^{-1} Metal Standards Absorbance	Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185											
CH_3COO^- (M)	Raffinates Absorbance				Distribution Ratios D				n Batches needed to get 99.9% extraction			
	Cd	Ni	Pb	Fe	D_{Cd2}	D_{Ni2}	D_{Pb2}	D_{Fe2}	n_{Cd}	n_{Ni}	n_{Pb}	n_{Fe}
0.001	0.0934	0.0001	0.0024	0.0041	1.02	606	5.88	44.12	10	2	4	2
0.005	0.1264	0.0001	0.0023	0.0027	0.50	606	6.17	67.52	17	2	4	2
0.01	0.1567	0.0001	0.0019	0.0001	0.21	606	7.68	1849	37	2	4	1
0.05	0.1586	0.0001	0.0001	0.0001	0.19	606	165	1849	40	2	2	1
0.1	0.1680	0.0001	0.0001	0.0001	0.12	606	165	1849	59	2	2	1

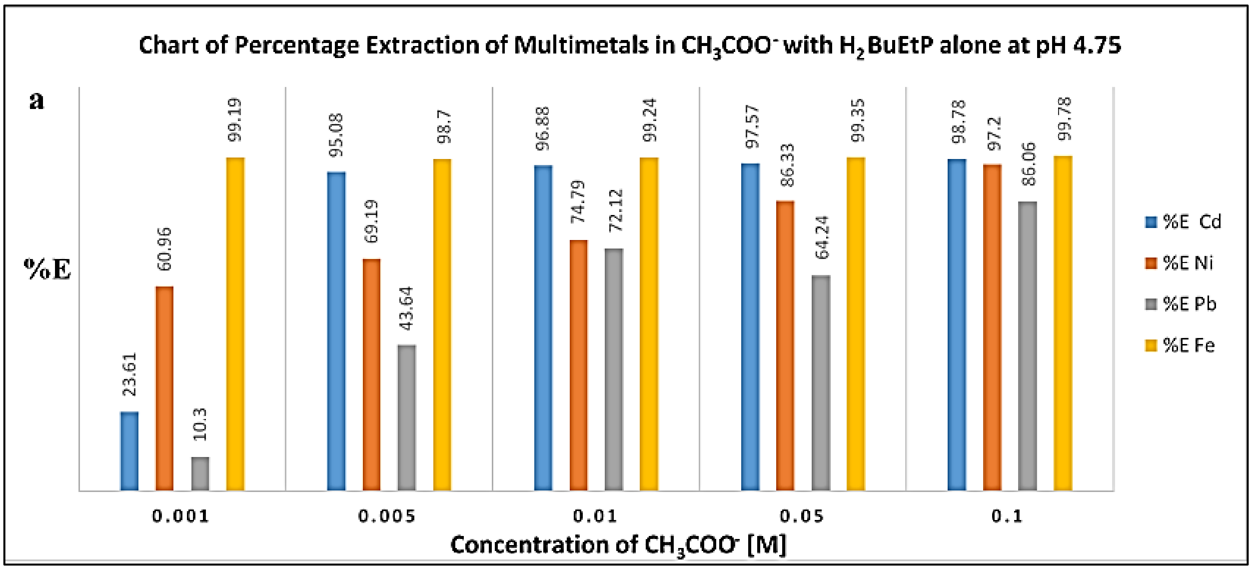

Fig. 1. Chart of %E of the Four Metals in CH_3COO^- with ligand H_2BuEtP alone at pH 4,75

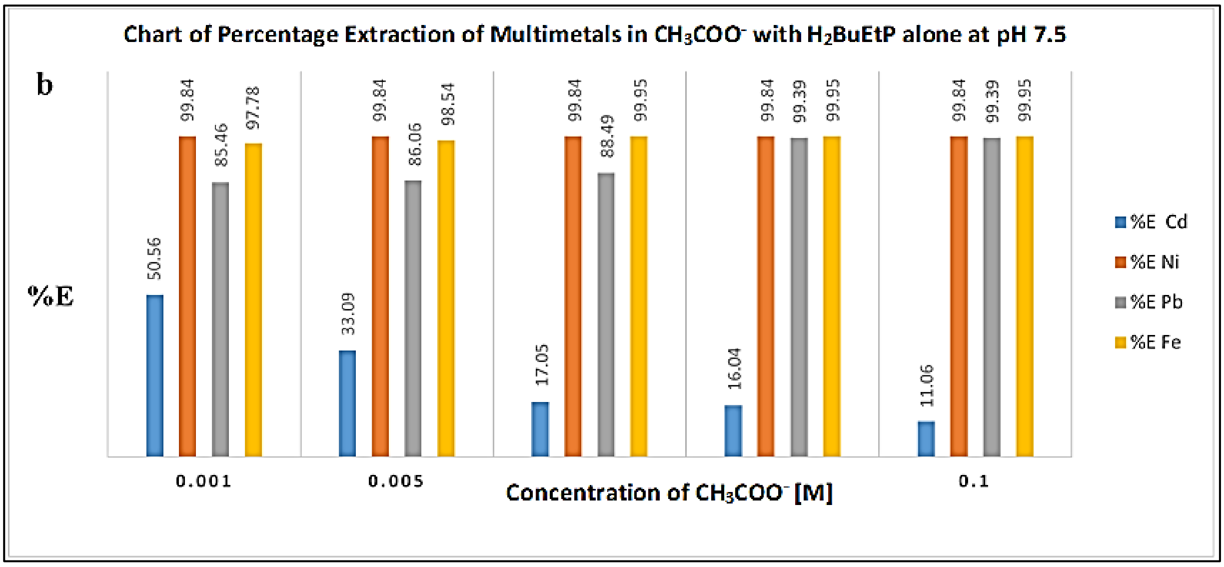

Fig. 2. Chart of %E of the Four Metals in CH_3COO^- with ligand H_2BuEtP alone at pH 7,5

In the presence of a second ligand HBuP, the extraction parameters shown in Tables 3-4 and percentage extractions %E in Figs. 3-4 were a slightly different from those with ligand H_2BuEtP alone. While Nickel and Iron showed similar trend of increasing percentage extraction %E with increasing concentration of CH_3COO^- at pH 4.75, Cadmium and Lead showed increasing percentage extraction %E with increase in concentration of CH_3COO^- and peaked at different concentrations of CH_3COO^-. Cadmium peaked at 0.05 M CH_3COO^- with 50.66% and Lead at 0.01 M CH_3COO^- with 60.09% at pH 4.75 and 38.06% Cadmium at 0.01 M CH_3COO^- and 79.39% Lead at 0.05 M CH_3COO^- for pH 7.5. Fig. 3 also showed that 99.95% extraction of Iron was gotten at all studied concentrations of CH_3COO^- with the mixed ligands H_2BuEtP/HBuP at pH 7.5. With the mixed ligands H_2BuEtP/HBuP, 11 batches of extractions are theoretically needed to obtain 99.9% extraction of the four metals with 0.05M CH_3COO^- at pH 4.75 and 16 batches at pH 7.5 with 0.01 M CH_3COO^-. The results of ligand H_2BuEtP alone are slightly better than those for mixed ligands $H_2BuEtP/HBuP$ as the adduct [Cd(HBuEtP).BuP] had unfavourable $\Delta_{transfer}$ G^0 from the aqueous media to the chloroform solution at all concentration of CH_3COO^-. Statistically with CH_3COO^-, there was no significant difference between the two organic phases (H_2BuEtP alone and $H_2BuEtP/HBuP$ at pH 7.5 as all p-values where all > 0.05 and had values Cadmium (0.63), Nickel (0.35), Lead (0.12) and Iron (0.14). However, at pH 4.75, Nickel (0.66) and Lead (0.37) show no significant difference but Cadmium and Iron with p-values of 0.04 show significant difference between the two organic phases.

Table 3. Extraction parameters for the four metal in CH_3COO^- at pH 4.75 for Mixed Ligands $H_2BuEtP/HBuP$

2.5 mgL^{-1} Metal Standards Absorbance					Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185							
CH_3COO^- (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	0.1000	0.0140	0.0115	0.024	0.89	3.34	0.44	6.71	11	5	19	4
0.005	0.1224	0.0110	0.0134	0.013	0.54	4.52	0.23	13.23	16	4	33	3
0.01	0.1112	0.0075	0.0051	0.012	0.70	7.09	2.24	14.42	13	4	5	3
0.05	0.0932	0.0070	0.0053	0.011	1.03	7.67	2.11	15.82	10	4	6	3
0.1	0.0970	0.0053	0.0080	0.004	0.95	10.45	1.06	45.25	11	3	10	2

Table 4. Extraction parameters for the four metal in CH_3COO^- at pH 7.5 for Mixed Ligands $H_2BuEtP/HBuP$

1.25 mgL^{-1} Metal Standards Absorbance					Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185							
CH_3COO^- (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	0.1492	0.0048	0.0164	0.0001	0.27	11.65	0.01	1849	30	3	1136	1
0.005	0.1291	0.0001	0.0075	0.0001	0.32	606	1.20	1849	25	2	9	1
0.01	0.1170	0.0001	0.0050	0.0001	0.62	606	2.30	1849	15	2	6	1
0.05	0.1592	0.0001	0.0034	0.0001	0.19	606	3.85	1849	41	2	5	1
0.1	0.1613	0.0001	0.0072	0.0001	0.17	606	1.29	1849	44	2	9	1

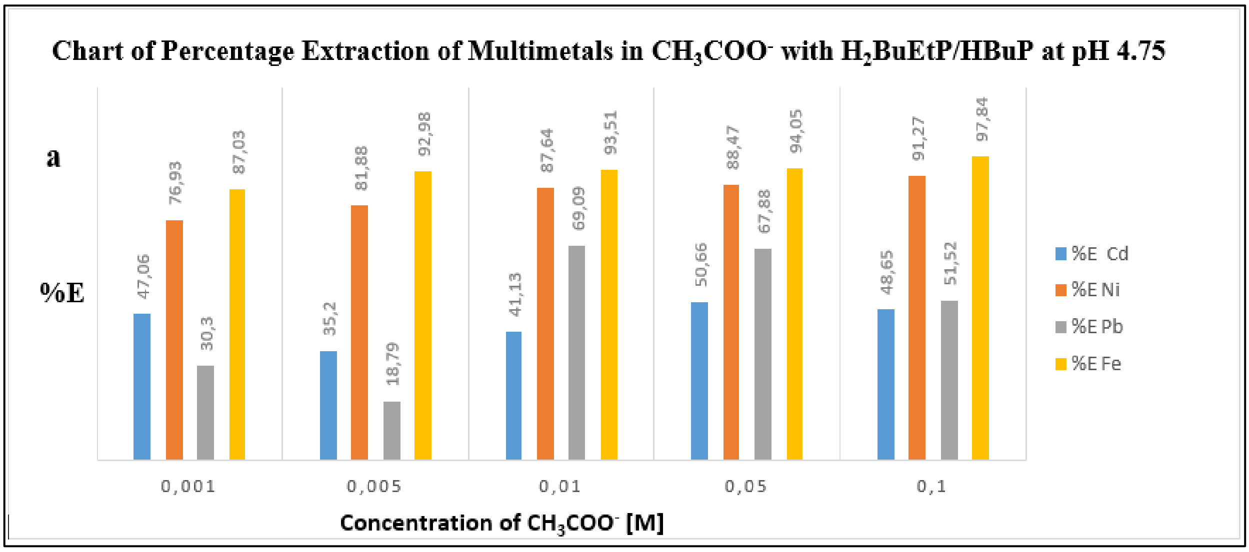

Fig. 3. Chart of %E of the Four Metals in CH_3COO^- with ligands H_2BuEtP/HBuP at pH 4.75

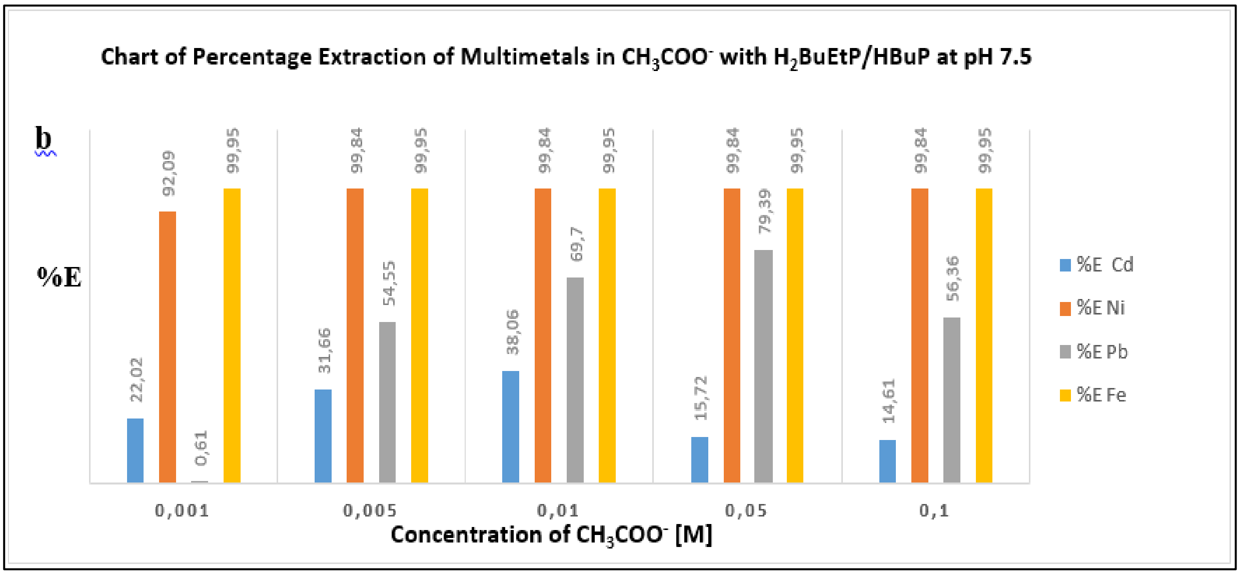

Fig. 4. Chart of %E of the Four Metals in CH_3COO^- with ligands H_2BuEtP/HBuP at pH 7.5

In the presence of PO_4^{3-}, ligand H_2BuEtP alone and in the presence of HBuP at both pH 4.75 and 7.5 show a trend in most cases of decreasing percentage extraction %E of the four metals with increasing PO_4^{3-}concentration with a few exceptions as shown in Figs. 5-8. The few exceptions were with ligand H_2BuEtP alone; at pH 4.75, where Nickel extraction of 86.49% at 0.005 M PO_4^{3-} was slightly higher than that at 0.001 M PO_4^{3-} with 85.5% and Iron with percentage extractions of between 97.03% - 97.78%. At pH 7.5, Lead increased from 87.27% extraction at both 0.001 M and 0.005 M PO_4^{3-} to 99.39% extraction at 0.01 M PO_4^{3-} and there after extraction of Lead was masked as percentage extraction of Lead dropped drastically to 3.03% and 1.21% at 0.05 M and 0.1 M PO_4^{3-} respectively. Iron had > 99% extraction at all concentrations of PO_4^{3-}. Nickel also dropped slightly from 99.84% extraction from 0.001 M – 0.01 M PO_4^{3-} to 91.27% at 0.05 M and 92.7% at 0.1 M PO_4^{3-}. With H_2BuEtP alone, Cadmium (0.06) and Lead (0.32) showed no significant difference while Nickel (0.04) and Iron (0.008) showed significant difference between pH 4.75 and 7.5. With mixed ligands $H_2BuEtP/HBuP$, at pH 4.75 there was a small increase in the extraction of Nickel from 85.67% at 0.001 M $PO_4^{3-}$to 86.49% at 0.005 M PO_4^{3-} while at pH 7.5, the trend for Cadmium and Lead started at 0.005 M PO_4^{3-} with 81.1% for Cadmium and 87.27% for Lead as extraction was masked at 0.001 M PO_4^{3-} with %E of 7.46% for Cadmium and 0.61% for Lead respectively. Masking has been attributed to formation of compounds with strong ionic bonds between that metal ion and the anion of interest resulting in formation of compounds that are very soluble in the aqueous media and thus formation of a metal complex or adduct with the ligand H_2BuEtP or mixed ligands $H_2BuEtP/HBuP$ is greatly reduced (Uzoukwu, 2009: 166-196). The ionic compounds formed have unfavourable $\Delta_{transfer}$ G^0 from aqueous to organic phase while the formed metal complex or adduct will have favourable $\Delta_{transfer}$ G^0 from aqueous to organic phase leading to the small %E recorded at these concentrations of anions (Housecroft and Sharpe, 2001). Nickel and Iron had > 99% extraction at all concentrations of PO_4^{3-} at pH 7.5 and these very high percentage extractions %E might be due to the anions functioning as releasing agents leading to the easy formation of metal complexes or adducts which have very favourable $\Delta_{transfer}$ G^0 from aqueous to organic phase as they are hyprophobic (Housecroft and Sharpe, 2001: Godwin and Uzoukwu, 2012a: 14-21: Godwin and Uzoukwu, 2012b: 105-116; Godwin et al., 2012: 269-273; Godwin et al., 2014: 59-72; Godwin et al., 2019). Tables 5-8 also show that 6 batches of extractions are needed to achieve 99.9% extraction of the four metal with 0.001 M – 0.01 M PO_4^{3-} at pH 7.5 with ligand H_2BuEtP alone since 2 batches of extractions were used for the study. Statistically, $H_2BuEtP/HBuP$ for pH 4.75 and 7.5 show significant difference for Cadmium (0.06) and Lead (0.32) while there was no significant for Nickel and Iron with p value 0.00. However, in the presence of HBuP, 5 batches of extractions are theoretically required with 0.005 M PO_4^{3-} and 6 batches of extractions are also needed with 0.01 M – 0.05 M PO_4^{3-}. pH 7.5 was generally better than pH 4.75 with PO_4^{3-} unlike CH_3COO^- as the best multi-metal extraction at pH 4.75 from Tables 5-8 with 12 batches needed to achieve 99.9% extractions of all four metals with 0.001 M PO_4^{3-} for both organic phases. Statistically, apart from Iron (0.00) that showed significant difference at pH 4.75, there was no significant difference between H_2BuEtP alone and $H_2BuEtP/HBuP$ for the other three metals. Comparing distribution ratios between PO_4^{3-} (Tables 5-8) and CH_3COO^- (Tables 1-4) with H_2BuEtP alone and with $H_2BuEtP/HBuP$ at both pH 4.75 and 7.5, statistically indicated that for H_2BuEtP alone, apart from pH 4.75 for Cadmium (0.035) that showed significant difference, there was no significant difference in their effects on the multi-metal extractions of the four metal. For $H_2BuEtP/HBuP$, Cadmium (0.03) and Iron (0.04) were the only extractions that showed significance difference between PO_4^{3-} and CH_3COO^-.

Table 5. Extraction parameters for the four metal in PO_4^{3-}at pH 4.75 for Ligand H_2BuEtP alone

<table>
<tr><td colspan="4">1.25 mgL⁻¹ Metal Standards Absorbance</td><td colspan="9">Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185</td></tr>
<tr><td colspan="4"></td><td colspan="9"></td></tr>
<tr><td rowspan="2">CH3COO- (M)</td><td colspan="4">Raffinates Absorbance</td><td colspan="4">Distribution Ratios D</td><td colspan="4">n Batches needed to get 99.9% extraction</td></tr>
<tr><td>Cd</td><td>Ni</td><td>Pb</td><td>Fe</td><td>DCd</td><td>DNi</td><td>DPb</td><td>DFe</td><td>nCd</td><td>nNi</td><td>nPb</td><td>nFe</td></tr>
<tr><td>0.001</td><td>0.0972</td><td>0.0087</td><td>0.0045</td><td>0.0055</td><td>0.94</td><td>5.98</td><td>2.67</td><td>32.64</td><td>11</td><td>4</td><td>6</td><td>2</td></tr>
<tr><td>0.005</td><td>0.1417</td><td>0.0082</td><td>0.0049</td><td>0.0055</td><td>0.33</td><td>6.40</td><td>2.37</td><td>32.64</td><td>24</td><td>4</td><td>6</td><td>2</td></tr>
</table>

0.01	0.1500	0.0435	0.0067	0.0041	0.26	0.40	1.46	44.12	30	21	8	2
0.05	0.1662	0.0527	0.0103	0.0044	0.14	0.15	0.60	41.05	54	49	15	2
0.1	0.1887	0.0560	0.0147	0.0053	0.001	0.08	0.12	33.91	6284	86	60	2

Table 6. Extraction parameters for the four metal in PO_4^{3-}at pH 7.5 for Ligand H_2BuEtP alone

1.25 mgL^{-1} Metal Standards Absorbance					Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185							
CH_3COO^- (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	0.0357	0.0001	0.0021	0.0001	4.29	606	6.86	1849	5	1	4	1
0.005	0.0381	0.0001	0.0021	0.0001	3.96	606	6.86	1849	5	1	4	1
0.01	0.0461	0.0001	0.0001	0.0001	3.10	606	164	1849	5	1	2	1
0.05	0.1521	0.0053	0.0160	0.0002	0.24	11.45	0.04	924	32	3	171	1
0.1	0.1748	0.0105	0.0163	0.0034	0.08	4.78	0.012	53.41	89	4	565	2

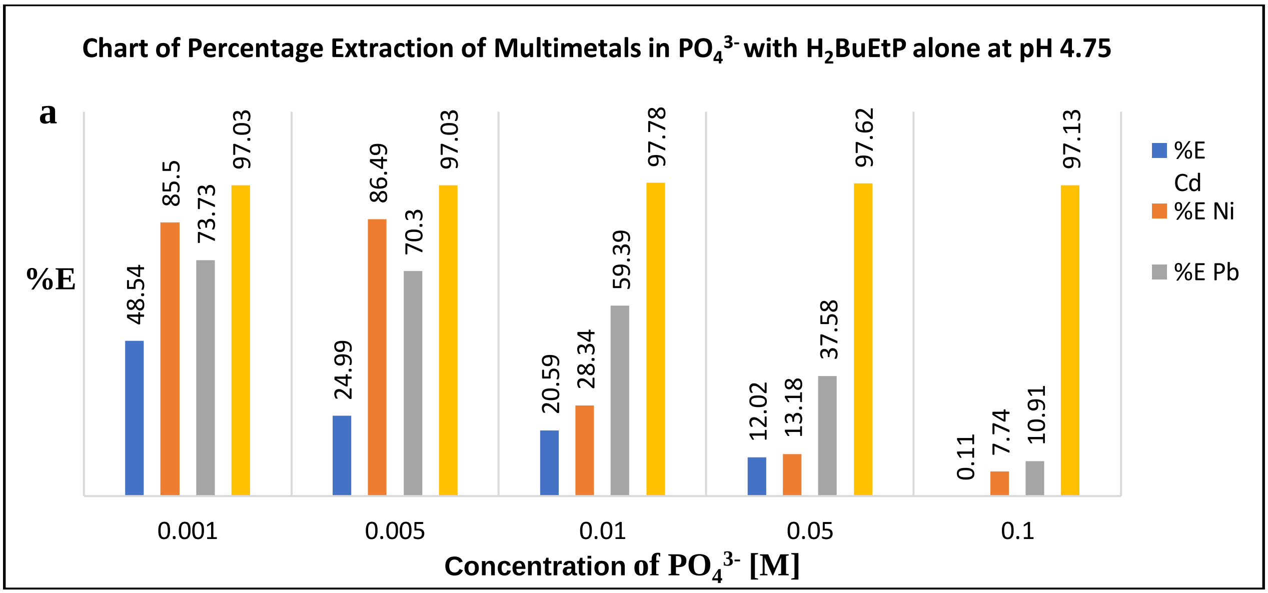

Fig. 5. Chart of %E of the Four Metals in PO_4^{3-} with ligand H_2BuEtP alone at pH 4.75

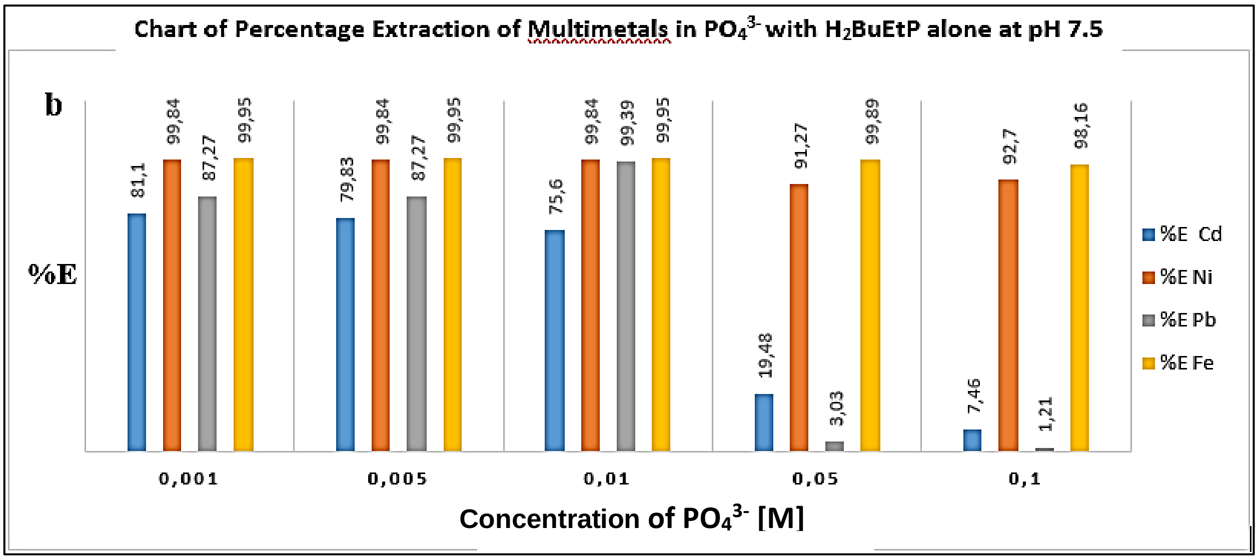

Fig. 6. Chart of %E of the Four Metals in PO_4^{3-} with ligand H_2BuEtP alone at pH 7.5

Table 7. Extraction parameters for the four metal in PO_4^{3-}at pH 4.75 for Mixed Ligands H_2BuEtP/HBuP

1.25 mgL^{-1} Metal Standards Absorbance					Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185							
PO_4^{3-} (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	0.0972	0.0087	0.0045	0.041	0.94	5.98	2.67	3.51	11	4	6	5
0.005	0.1417	0.0082	0.0049	0.044	0.33	6.40	2.37	3.21	24	4	6	5
0.01	0.1500	0.043	0.013	0.053	0.26	0.41	0.27	2.49	30	20	29	6
0.05	0.1662	0.052	0.014	0.055	0.14	0.17	0.18	2.36	54	45	42	6
0.1	0.1888	0.056	0.0162	0.055	0.0005	0.08	0.02	2.36	13819	86	377	6

Table 8. Extraction parameters for the four metal in PO_4^{3-}at pH 7.5 for Mixed Ligands H_2BuEtP/HBuP

1.25 mgL^{-1} Metal Standards Absorbance					Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185							
PO_4^{3-} (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	0.1748	0.0001	0.0164	0.0001	0.08	606	0.006	1849	89	1	1136	1
0.005	0.0357	0.0001	0.0021	0.0001	4.29	606	6.86	1849	4	1	4	1
0.01	0.0381	0.0001	0.0021	0.0001	3.96	606	6.86	1849	5	1	4	1
0.05	0.0461	0.0001	0.0001	0.0001	3.10	606	164	1849	5	1	2	1
0.1	0.1521	0.0001	0.0164	0.0001	0.24	606	0.006	1849	289	1	1136	1

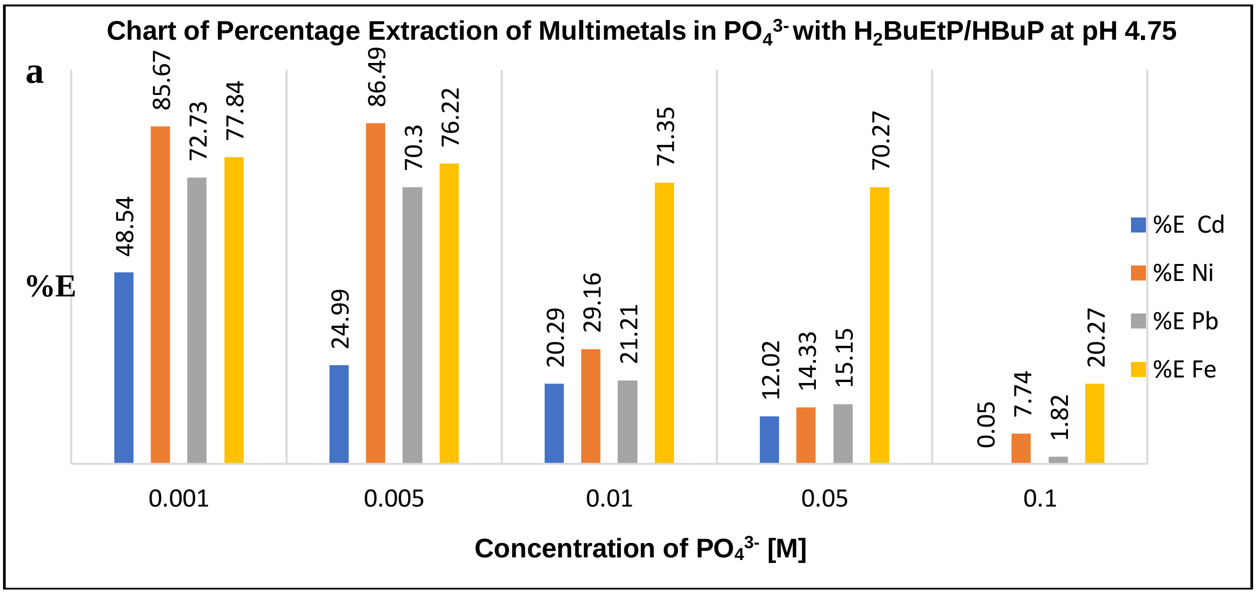

Fig. 7. Chart of %E of the Four Metals in PO_4^{3-} with ligand H_2BuEtP/HBuP at pH 4.75

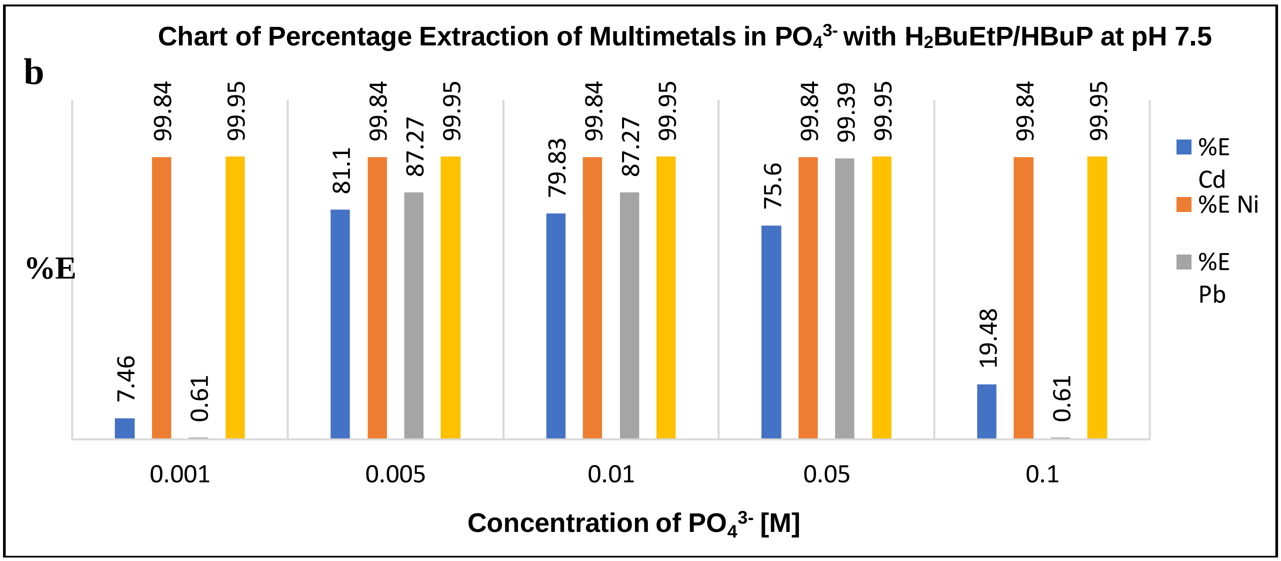

Fig. 8. Chart of %E of the Four Metals in PO_4^{3-} with ligand H_2BuEtP/HBuP at pH 7.5

Figs. 9-12 showing the effect of SO_4^{2-} on the percentage extractions in the multi-metal extractions of the four studied metals at pH 4.75 and 7.5 in both ligand H_2BuEtP alone and in the presence of HBuP had in almost all cases increasing percentage extraction of the metals with increasing concentration of SO_4^{2-} and peaks at a particular concentration of SO_4^{2-} after which the percentage extraction %E of the metals starts decreasing as masking of metals by the SO_4^{2-} begins. This behavior has been reported in the effect of acids, anions and auxiliary complexing agents in the extraction of single metals with same organic phases (Godwin and Uzoukwu, 2012a: 14-21; Godwin and Uzoukwu, 2012b: 105-116; Godwin et al., 2012: 269-273; Godwin et al., 2014: 59-72; Godwin et al., 2019). The only two exceptions were in the mixed ligands H_2BuEtP/HBuP extractant system at pH 7.5 in which Cadmium had highest percentage extraction of 67.55% at 0.001 M SO_4^{2-} and Iron with > 97% extractions in all concentrations of SO_4^{2-}. Calculated number of batches of extractions required to obtain 99.9% extractions of the four metals in both organic extractants shown in Tables 9-12 show that pH 7.5 was better than pH 4.75 for the multi-metal extraction of the four metals as 7 batches are needed with 0.005 M and 0.01 M SO_4^{2-} with H_2BuEtP alone and 8 batches with 0.001 M and 0.005 M SO_4^{2-} with H_2BuEtP/HBuP all at pH 7.5. At pH 4.75, the lowest number of batches needed to achieve 99.9% multi-metal extraction of the four metals was 17 at 0.01 M SO_4^{2-} with H_2BuEtP alone and 12 at 0.005 M SO_4^{2-} with H_2BuEtP/HBuP organic phase. With H_2BuEtP alone, there was significant difference between pH 4.75 and 7.5 in the extraction of Cadmium (0.04), Nickel (0.04) and Iron (0.001) as only Lead extraction show no significant difference between the buffers with a p value of 0.28. However, with H_2BuEtP/HBuP there was no significant difference between the two buffers for the simultaneous extraction of Cadmium (0.44), Lead (0.08) and Iron (0.054) with only Nickel (0.00) extractions showing a significant difference. Statistically, $SO_4^{2-}$and CH_3COO^- multi-metal extractions for the four metals in H_2BuEtP alone show no significant difference for Nickel (0.27) and Lead (0.15) while there was significant difference for Cadmium (0.035) and Iron (0.028) for pH 4.75. For pH 7.5, there was significant difference for only Iron (0.038) as Cadmium (0.07), Nickel (0.14) and Lead (0.53) all showed no significant difference in their extractions between $SO_4^{2-}$and CH_3COO^-. With H_2BuEtP/HBuP organic phase, there was no significant difference between $SO_4^{2-}$and CH_3COO^-as p values were all > 0.05 for the four metals. Statistically with H_2BuEtP alone organic phase, there is no significant difference between the effects of $SO_4^{2-}$and PO_4^{3-} in the multi-metal extraction of Cadmium, Nickel and Lead with p values all > 0.05 as only Iron extractions were significantly different with p value 0.00 for pH 4.75 and 0.008 for pH 7.5. However, in H_2BuEtP/HBuP organic phases, while pH 7.5 showed no significant difference between $SO_4^{2-}$and CH_3COO^- effects in the multi-metal extractions of the four metals with p > 0.05, pH 4.75 also showed no significant difference for Nickel (0.84) and Lead (0.28) but Cadmium (0.02) and Iron (0.00) extractions were significantly different for $SO_4^{2-}$and CH_3COO^-.

Table 9. Extraction parameters for the four metal in SO_4^{2-}at pH 4.75 for Ligand H_2BuEtP alone

1.25 mgL^{-1} Metal Standards Absorbance				Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185								
SO_4^{2-} (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	0.1735	0.0228	0.0100	0.0582	0.09	1.66	0.65	2.18	81	7	14	6
0.005	0.1287	0.0203	0.0095	0.0539	0.47	1.99	0.74	2.43	18	7	13	6
0.01	0.1225	0.0181	0.0055	0.0410	0.54	2.35	2.00	3.51	16	6	7	5
0.05	0.1577	0.0137	0.0136	0.0578	0.20	3.43	0.21	2.20	39	5	36	6
0.1	0.1688	0.0386	0.0159	0.0582	0.12	0.57	0.04	2.18	62	16	187	6

Table 10. Extraction parameters for the four metal in SO_4^{2-} at pH 7.5 for Ligand H_2BuEtP alone

1.25 mgL^{-1} Metal Standards Absorbance		Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185	
SO_4^{2-} (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	0.1670	0.0253	0.0068	0.0042	0.13	1.40	1.43	43.05	56	8	8	2
0.005	0.0541	0.0001	0.0025	0.0021	2.49	606	5.60	87.10	6	2	4	2
0.01	0.0593	0.0001	0.0011	0.0054	2.19	606	14,00	33.26	6	2	3	2
0.05	0.0700	0.0001	0.0001	0.0063	1.70	606	164.00	28.37	7	2	2	3
0.1	0.1160	0.0037	0.0063	0.0147	0.63	15.41	1.62	11.59	14	3	8	3

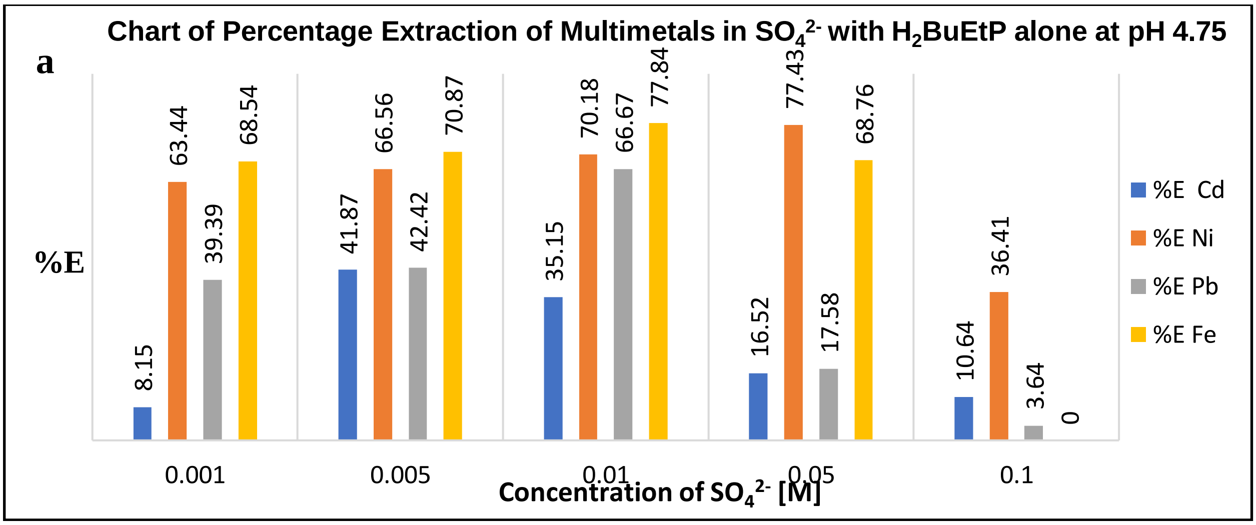

Fig. 9. Chart of %E of the Four Metals in SO_4^{2-} with ligand H_2BuEtP alone at pH 4.75

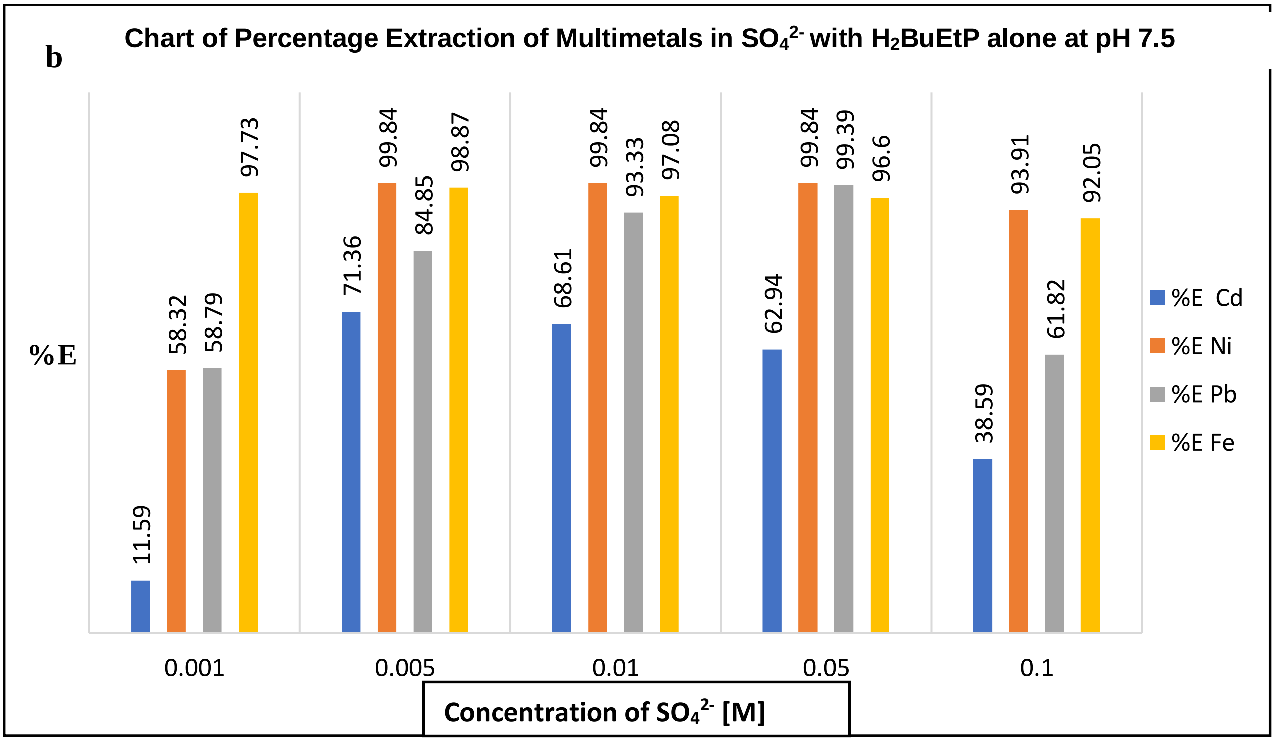

Fig. 10. Chart of %E of the Four Metals in SO_4^{2-} with ligand H_2BuEtP alone at pH 7.5

Table 11. Extraction parameters for the four metal in SO_4^{2-} at pH 4.75 for Mixed Ligands $H_2BuEtP/HBuP$

1.25 mgL^{-1} Metal Standards Absorbance					Cd = 0.1889, Ni = 0.0607, Pb = 0.0165 and Fe = 0.185							
SO_4^{2-} (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	0.1098	0.0064	0.0106	0.0057	0.72	8.48	0.56	31.46	13	3	16	2
0.005	0.0937	0.0325	0.0075	0.0054	1.02	0.87	1.20	33.26	10	11	9	2
0.01	0.0949	0.0341	0.0153	0.0054	0.99	0.78	0.08	33.26	10	12	92	2
0.05	0.1019	0.0410	0.0153	0.0056	0.85	0.48	0.08	32.04	12	12	82	2
0.1	0.1132	0.0512	0.0157	0.0058	0.67	0.19	0.05	30.90	15	41	139	2

Table 12. Extraction parameters for the four metal in SO_4^{2-} at pH 7.5 for Mixed Ligands $H_2BuEtP/HBuP$

1.25 mgL^{-1} Metal Standards Absorbance					Cd = 0.1889, , Ni = 0.0607, Pb = 0.0165 and Fe = 0.185							
SO_4^{2-} (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	0.0613	0.0001	0.0057	0.0001	2.08	606	1.90	1849	7	1	7	1
0.005	0.0652	0.0001	0.0010	0.0001	1.90	606	15.50	1849	7	1	3	1
0.01	0.0953	0.0001	0.0012	0.0002	0.98	606	12.75	924	10	1	3	1
0.05	0.1293	0.0001	0.0048	0.0030	0.46	606	2.44	60.67	19	1	6	2
0.1	0.1416	0.0001	0.0096	0.0052	0.33	606	0.72	34.58	24	1	13	2

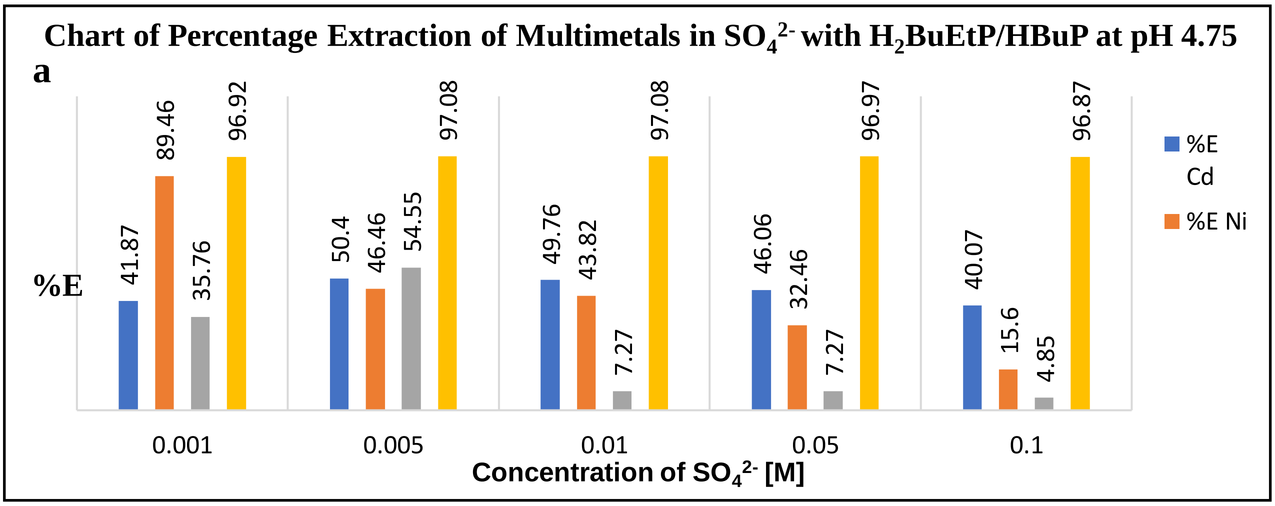

Fig. 11. Chart of %E of the Four Metals in SO_4^{2-} with ligand $H_2BuEtP/HBuP$ at pH 4.75

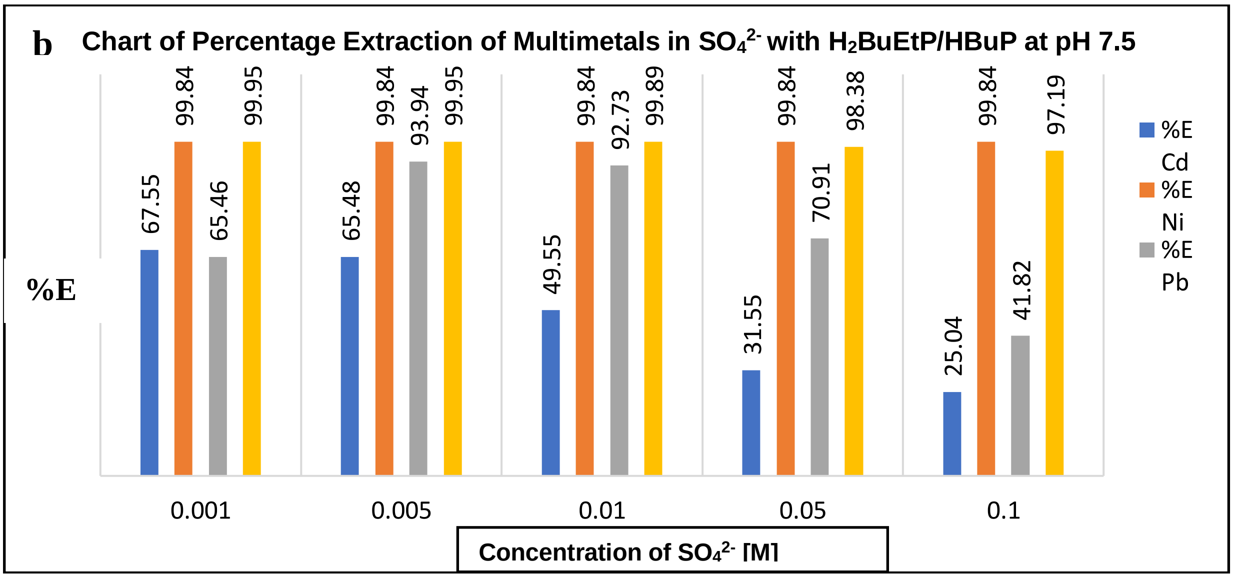

Fig. 12. Chart of %E of the Four Metals in SO_4^{2-} with ligand H_2BuEtP/HBuP at pH 7.5

Conclusion

CH_3COO^-, PO_4^{3-} and SO_4^{2-} all showed potentials for 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 using both ligand H_2BuEtP alone and H_2BuEtP/HBuP organic phases.

Cadmium (II), Iron (II), Lead (II) and Nickel (II) can be simultaneously extracted from an aqueous solution containing 0.1 M CH_3COO^- and buffered to pH 4.75 using chloroform solutions of ligand H_2BuEtP alone and 0.05 M PO_4^{3-} with aqueous solution buffered to pH 7.5 using H_2BuEtP/HBuP organic phase with 99.9% extraction of the four metal theoretically extractable after 5 batches of extractions.

6 batches of extractions are theoretically required to achieve 99.9% extraction of Cadmium (II), Iron (II), Lead (II) and Nickel (II) from aqueous solutions buffered to pH 7.5 containing 0.001 M – 0.01 M PO_4^{3-} using H_2BuEtP alone and 0.01 M – 0.5 M PO_4^{3-} using H_2BuEtP/HBuP organic phase.

0.05 M CH_3COO^- with aqueous solution buffered to pH 4.75 and 0.005 – 0.01 M SO_4^{2-} with aqueous solution buffered to pH 7.5 using H_2BuEtP alone can be used to simultaneously extract Cadmium (II), Iron (II), Lead (II) and Nickel (II) from aqueous solutions with 7 batches theoretically needed to achieve 99.9% extraction of all four metal ions.

Cadmium (II), Iron (II), Lead (II) and Nickel (II) in aqueous solutions can be simultaneously extracted from aqueous solutions buffered to pH 4.75 with 0.01 M CH_3COO^- using H_2BuEtP alone, 0.05 M SO_4^{2-} also using H_2BuEtP and 0.001 M - 0.005 M SO_4^{2-} using H_2BuEtP/HBuP with aqueous solutions buffered to pH 7.5 and 99.9% extraction of four metals theoretically achievable after 8 batches of extractions with fresh organic phases.

pH 7.5 was generally slightly better than pH 4.75 for the multi-metal extractions of Cadmium (II), Iron (II), Lead (II) and Nickel (II) from aqueous solutions but statistically CH_3COO^- and PO_4^{3-}effects were not significantly different aside Cadmium (II) extraction at pH 4.75 with both organic phases and Iron extraction for pH 4.75 with H_2BuEtP/HBuP organic phase.

CH_3COO^- and SO_4^{2-} effects were significantly different for pH 4.75 for Cadmium and iron extractions at both pH 4.75 and 7.5 for H_2BuEtP alone but not significantly different in H_2BuEtP/HBuP organic phases.

PO_4^{3-} and SO_4^{2-} effects are significantly different for Iron extractions alone at both pHs for H_2BuEtP alone and significantly different for Cadmium and Iron at pH 4.75 for H_2BuEtP/HBuP organic phases.

0.05 M – 0.1 M CH_3COO^- with H_2BuEtP alone, 0.01 M $PO_4^{3-}$and 0.05 M SO_4^{2-}both with H_2BuEtP/HBuP can be used for multi-metal extraction of Iron (II), Lead (II) and Nickel (II) from aqueous solutions buffered at pH 7.5 with 99.9% extraction of the 3 metals theoretically achievable in 3 batches.

Changes in permittivities/dielectric constants of the solvents leading to favourable energetics in the transfer of formed complexes or adducts from aqueous media to the organic phases was attributed to the simultaneous extractions of the four metals.

The current study should be extended to acids, halogen ions and auxiliary complexing agents to get comprehensive data for the multi-metal extraction of the four metals and theoretically calculated n number of batches of extraction required to simultaneously extract 99.9% of the four metals tested with specific conditions.

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