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Research Paper

Investigation on the Extraction and Separation of Ba(II), Sr(II) and Se(IV) from Aqueous Phase

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Abstract

The ionic liquid thenoyltrifluoroacetone (TTA) and tri-iso-butyl phosphate (TBP) was used to extracted of Ba(II), Sr(II) and Se(IV). The effect of the variables that mostly affect the metal extraction process, namely extracting concentration, pH, shaking time and temperature was studied. As extraction measurement parameter, the metal extraction percentage (E%) and the metal distribution coefficient (D) were used. The equilibrium slope method was used in estimating the stoichiometry of the resulting organic complexes. The obtained plots are straight lines whose slopes are close to 2, which might be attributed to the extraction of a species of 2:1 (extractant /metal) stoichiometry. The free energy ΔG^*, enthalpy ΔH^* and entropy ΔS^* were identified proving exothermic and spontaneous reaction of the present extraction process.

Keywords: Ionic Liquid, Solvent Extraction, Thenoyltrifluoroacetone, Tri-iso-butyl phosphate, Separation.

Introduction

The separation procedure of a chemical species from a matrix is essentially based on the transportation of the solute between the two involved phases, generally an organic and an inorganic one. Specifically, solvent extraction uses the concept of unique solute distribution ratios between two immiscible solvents. However, there are several situations where solutes have been observed to completely move from the inorganic to the organic phase [1]

Although solvent extraction as a method of separation has long been known to the chemists, only in recent years it has achieved recognition among analysts as a powerful separation technique. Liquid-liquid extraction, mostly used in analysis, is a technique in which a solution is brought into contact with a second solvent, essentially immiscible with the first, in order to bring the transfer of one or more solutes into the second solvent. The separations that can be achieved by this method are simple, convenient and rapid to perform, they are clean as much as the small interfacial area certainly precludes any phenomena analogous to the undesirable co-precipitation encountered in precipitation separations [1]**.** Solvent extraction is widely applied to processes of metal ions recovery, ranging from aqueous solutions in hydrometallurgical treatment to environmental applications. It is also considered a useful technique to increase the initial concentration of the solute, commonly used in the separation processes of analytical applications [2]. Organic solvent extraction is the transport of solutes, e.g. metal ions, from an inorganic (or aqueous) phase to an organic phase.

Solvents used comprise of an extractant + diluent combination. The roles of each are as follows: 1) the extractant, as a specific metal ion extractant, 2) the diluent,as a solvent condition controller, i.e. hydrophobicity, which can affect the molecules extractability[3].

The uptake of very large amounts of barium that are water-soluble may cause paralyses and in some cases even death. Small amounts of water-soluble barium may cause a person to experience breathing difficulties, increased blood pressures, heart rhythm changes, stomach irritation, muscle weakness, changes in nerve reflexes, swelling of brains and liver, kidney and heart damage [4]**.**

Selenium salts are toxic in large amounts, but trace amounts are necessary for cellular function in many organisms, including all animals. Selenium is a mineral found in the soil. Selenium naturally appears in water and some foods. While people only need a very small amount, selenium plays a key role in the metabolism. Selenium has attracted attention because of its antioxidant properties. Antioxidants protect cells from damage. Evidence that selenium supplements may reduce the odds of prostate cancer has been mixed, but most studies suggest there is no real benefit. The safe upper limit for selenium is 400 micrograms a day in adults. Anything above that is considered an overdose [4]**.** This study aims to contribute to knowledge on the extraction Ba(II), Sr(II) and Se(IV)from aqueous solution by means of solvent extraction technique using thenoyltrifluoroacetone (TTA) and tri-iso-butyl phosphate (TBP).

Materials and Methods

Apparatus

The metal ion concentration in the initial solution and the metal ions left in the bulk solution were determined by A flame atomic absorption spectrometer (FAAS) model Analyst 100 (PerkinElmer) was used for the determination of metal concentration using an air–acetylene flame. pH measurements for all solutions were measured using pH meter model OP-02/2 (Germany) with a combined electrode reading to +0.05 pH value, that was calibrated with pH 4.00, 7.00 and 10.00 buffer standards. A mechanical shaker model SA-31 (Yamato shaker) was used.

All reagents and solvents were of standard analytical grade and used without further purification and were obtained from Merck (Germany).The reagents used in this study as extractant were thenoyltrifluoroacetone (TTA) and tri-iso-butyl phosphate (TBP).

To study the effect of extractants (TTA) and (TBP) concentration on extraction of Ba(II), Sr(II) and Se(IV) the concentration of extractants were varied in the range 0.01 to 1.5 M. In all these experiments and the initial metal ion concentration was the same at a constant value of 5 mg/l at constant pH.

The effect of initial pH on the degree of extraction of metal ions was performed by varying the pH between 2 and 8, keeping the initial concentrations of the metal ions 5mg/l. In all the experimental runs the extractant concentration in the organic phase was kept constant. The effect of pH on the extraction of Ba(II), Sr(II) and Se(IV) with (TTA) and (TBP) was investigated at a phase ratio of 1:1. After shaking (5 min) the two layers for suitable time afterward separate these two layers and determine the concentrations of metal ions remainder in aqueous phase and in organic phase at each pH were performed.

The effect of shaking time (5 to 30 min) on extracted of ($1.8*10^{-5}$M) Ba(II), Sr(II) and Se(IV) in 10 ml aqueous phase by (10ml) (TTA) or (TBP) solution at ($1*10^{-3}$M) concentration was carried out, after complete shaking separate these two layers and determine the concentrations of ions in aqueous and organic phase were performed as well as distribution ratio (D) and percentage of extraction (E) were determined.

The effect of temperature on the extraction of Ba(II), Sr(II) and Se(IV) from aqueous phase by use (TTA) and (TBP) were carried out. The experiment include extracted ($1*10^{-5}$M) metal ions in (10 ml) aqueous phase at (pH=6) by (10 ml) extractant at ($1*10^{-3}$M) .Experiments were carried out by varying temperatures in the range of 22-50°C. After shaking of (5min) separate the two layers and distribution ratio (D) and percentage of extraction (E) were determined at each temperature.

The extraction efficiency of metal was represented in terms of percentage extraction (%E) as defined in Eq. (1), and distribution coefficient for extraction or the ratio of metal species in ionic liquid, presumably in the form of complex, to that in aqueous can be calculated from Eq. (2).

$\%E = [(C_i)aq – (C_f)aq / (C_i)aq] x 100$ ………….…….(1)

$D=[M]_{org}/[M]_{aq}$...(2)

where $(C_i)aq$ and $(C_f)aq$ are the concentrations of metal ion in aqueous phase before and after extraction, respectively and $[M]_{org}$ and $[M]_{aq}$ are the total metal ion concentrations in the organic and aqueous phases, respectively.

Effect of shaking time

From the kinetic side of extraction method there is effects for shaking time of the two side layers aqueous phase contain metal ions and organic phase which is immiscible in solvent extraction method. Extracted Ba(II), Sr(II) and Se(IV) at different shaking time (5-30 min) were studied. Table (1) and Figure (1) illustrates that the metal ions extraction percentage increased with the shaking time and reached the plateau within 25–30 min. The further shaking of solutions caused the slight increase of the extraction efficiency.

It was observed that, under the optimized experimental conditions, a minimum 25 min time interval was required for attaining equilibrium in the sense to extract Ba(II), Sr(II) and Se(IV) quantitatively. But with prolonged shaking over 25 min there was slight increase in the percentage extraction of each metal ions due to the dissociation of ion-pair complex. Hence, in all further studies, both the phases were equilibrated for 25 min.

Table 1: The effect of shaking time on extraction E% of Ba(II), Sr(II) and Se(IV) using extractant (TTA)

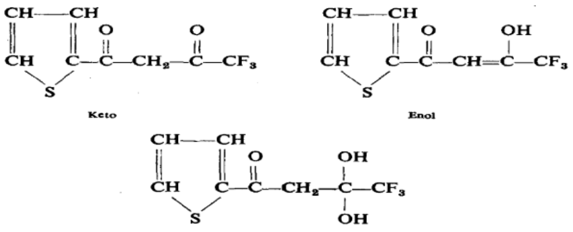
Time	Ba(II)	Sr(II)	Se(IV)
	E%	E%	E%
5	82.37	85.46	93.29
10	86.01	88.45	94.58
15	88.66	92.00	95.56
20	91.32	94.04	96.41
25	93.40	95.13	97.14
30	93.88	96.47	97.48

Effect of the Initial Concentration of the Extractant

The amount of metal ion extracted depends on the nature and type of the extractant used. The extractant should possess low water solubility, and the disengagement of its phase from the mixture should be rapid. The effect of extractant concentration between 0.01 to 1.5 M on the extraction of Ba(II), Sr(II) and Se(IV) with (TTA) and (TBP) was investigated at a phase ratio of 1:1. The experimental results show that extraction% increases with increase in extractant concentration due to the solvatant character of the extractant Table (2) and Fig (2). As can be seen with (TTA) extractant Ba(II)extraction increases from 63.67 -85.36% , Sr(II) extraction increases from 72.67 -90.94 % whereas, extraction of Se(IV) increases from 90.29- 93.83% .

Results and Discussion

The organophosphorus compounds are excellent metal ions extractants because are chelating agents, this is why they are frequently employed in the solvent extraction process [5]**.** Among the commercial phosphoric acid extractants, Tri-iso-butyl Phosphate (abbreviated as (TBP). Thenoyltrifluoroacetone (TTA) chelating agent is a 1,3-diketone and exists in the following three forms:



Thenoyltrifluoroacetone (TTA) chelating agent

The extraction of Ba(II), Sr(II) and Se(IV)from aqueous solution was investigated by using two different solvent systems: thenoyltrifluoroacetone (TTA) and tri-butyl phosphate (TBP).The optimization of the solvent extraction process involves achieving the best extraction conditions in which the uptake of metal ion occurs to the largest extent. To accomplish this goal, this study considered the extraction behavior of the Ba(II), Sr(II) and Se(IV) with the (TTA) and (TBP). The effect of the variables that mostly affect the metal extraction process, namely extractant concentration, pH, shaking time and temperature were studied. As extraction measurement parameter, the metal extraction percentage (E%) and the metal distribution coefficient (D) were used.

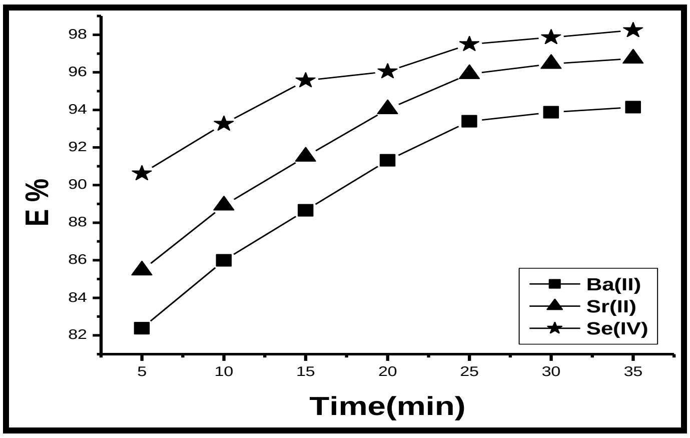


Figure 1: Effect of shaking time on extraction of Ba(II), Sr(II) and Se(IV) and extraction percentage using extractant (TBP)

The results indicate that the extraction capability of the three selected metal ions follows a general order of Se(IV) > Sr(II) > Ba(II) under given conditions. As well it is seen that, as expected, the extraction percentage increases at higher concentrations of the extractant. In liquid-liquid extraction (TTA) has been better extractant than (TBP). The TTA enolate ion forms highly extractable metal chelates of the form where z is the charge on the uncomplexed metal ion.

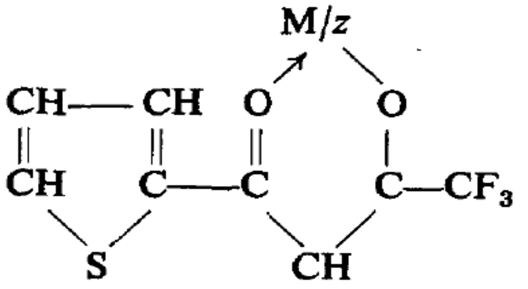


Table 2: The effect of extractant (TBP) concentration on extraction E% of Ba(II), Sr(II) and Se(IV)

Conc.TBP	Ba(II)	Sr(II)	Se(IV)
	E%	E%	E%
0.010	63.24	74.01	82.29
0.030	68.17	77.70	91.41
0.050	74.41	80.40	92.27
0.075	76.87	81.26	92.87
0.100	78.84	82.37	93.29
0.125	79.52	83.12	93.71
0.150	80.18	83.39	93.83

Effect of pH

The effect of initial acidity of aqueous phase on the degree of extraction of metal ions was studied.

The effect of pH on the extraction of Ba(II), Sr(II) and Se(IV) with (TTA) and (TBP) was investigated at a phase ratio of 1:1. In general, as shown in Fig. (3) the extraction percentage of each metal ions increase when the initial pH of the aqueous feed solution increases.

The results indicate that the optimum pH for extraction of metal ions were at pH = 6.0 which is giving higher percentage of extraction (E). Metal ions extraction at low pH seems to be caused by the occurrence of strong intermolecular hydrogen bonding and protonation of most hydroxyl groups in the extractant molecule [6]**.** When there is sufficient excess of H^+ ions in the strongly acidic solution in comparison to metal ion, most of oxygen pair electrons coordinate rather with H^+ than with metal cations. In the case of the high pH of aqueous solution, where limited amount of H^+ ions is present, the interaction between oxygen lone pair electrons of extractant and vacant orbital of metal ions is possible [7]. Similar profile of percent Pb(II) loading to the organic phase versus pH of aqueous phase was found for dimetoxycalixarene di(carboxylic acid) with cone conformation [8]**.**

The extraction Sr(II) was achieved between 67.64% and 91.22% whereas between 68.43% and 88.17 % for (TTA) and (TBP) respectively. There is no significant difference in E% for Se (IV) with two extraxtant. The extraction of metal ions in the higher pH may not be precise because of the metal ions hydrolysis and the hydroxide precipitation that can interfere with the metal-ligand complex formation and cause decline of process efficiency.

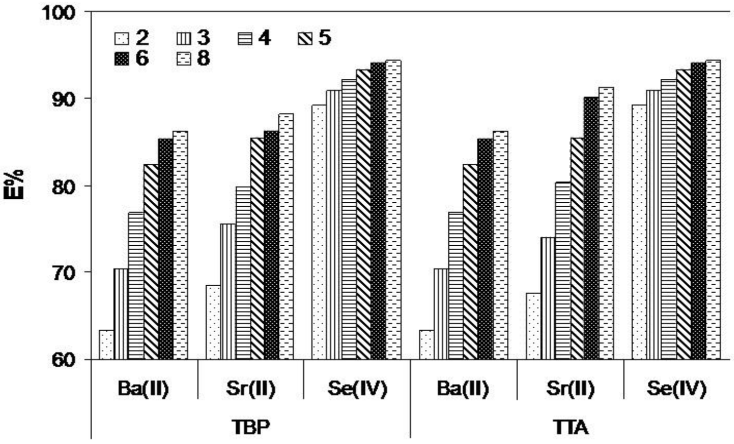


Figure 3: The effect of pH on extraction E% of Ba(II), Sr(II) and Se(IV) using extractant (TBP)and TTA

Equilibrium constants of the extraction reaction

The distribution ratio of each metal ion in the liquid–liquid distribution was representing the total analytical concentration of the metal ion in the organic phase (extract) with respect to its analytical concentration in the aqueous phase (raffinate). The values of D for Ba(II), Sr(II) and Se(IV) increases with increasing the extractant concentration due to their solvating character .Equilibrium constants and the proposed stoichiometry of the extraction reaction can also be confirmed.

The equation for the extraction of a metal ion with charge z+, M^{z+}, can be simply written as

$$M^{Z+}_{aq} + zHT_{org} = [MT_z]_{org} + zH^+_{aq} \ldots\ldots\ldots\ldots \quad (3)$$

The equilibrium constant *K* can be given as: Equation (4) can be rewritten as

$$K = \frac{[MT_z]_{org}\ [H^+_{aq}]^z}{[M^{Z+}_{aq}]\ [HT_{org}]^z} \ldots\ldots\ldots\ldots \quad (4)$$

$$\text{Log } D = \log K + z\log HT_{org} + z\,pH \ldots\ldots\ldots \quad (5)$$

To get the information about the equilibrium constants and the proposed stoichiometry of the extraction reaction it is necessary to arrange the experimental information and plot it as log D vs. log [HT] at constant pH or plot it as log D vs. log pH at constant concentration, as shown in equation (5). Using the slope method, if the stoichiometries of the extraction reaction follow that proposed as most probable in equation (5), straight lines should be obtained. The slopes of the straight lines would verify the proposed stoichiometry, and from the intercepts of the plots the corresponding apparent equilibrium constants can be obtained.

The obtained plots of the logarithmic relation of the metal ions distribution ratio *vs*. extractant concentration are straight lines whose slopes are < 1.5 close to 2, which might be attributed to the extraction of a species of 2:1 (extractant /metal) stoichiometry.

A plot of log *D* vs. pH at constant concentration in all cases straight lines was obtained, confirming that the proposed equations would effectively represent the chemical reactions of the extraction process. Summarizes the results of the apparent equilibrium constant stable, K_{eq} (intercepts) for Ba(II), Sr(II) and Se(IV) with (TTA) and (TBP) and slopes (m) for all the extraction experiments performed at constant pH are presented in Table (3) and at constant concentration are presented in Table (4).

It can be deduced that the stoichiometric coefficient would generally equal to the charge of the metal ion extracted. An average of ≈ 2 for the slope has been observed by researchers using non-polar solvents. According to [9], the metals ions were solvated by two simple molecules of extractant, a supposition that stem from the slope obtained using the equilibrium slope method. In conclusion, the number of molecules of the extractant determined by all researchers was unanimously 2, even when using different extractant and diluent combinations. Even though the oxidation number of Se (IV) is more than 2, it was found that the slope of the log *D* versus pH plot is 1.607. This is due to Se(IV) forming a complex with O_2 that results in the formation of SeO_2^{2+}, thus the equilibrium slope of 2.

Table 3: the equilibrium constants, K and the proposed stoichiometry of the extraction reaction at constant pH

Metal ions	TTA			TBP		
	Slope	Intercept	R^2	Slope	Intercept	R^2
Ba(II)	1.81	0.86	0.980	1.95	0.717	0.91
Sr(II)	1.91	0.80	0.901	2.15	0.883	0.99
Se(IV)	1.81	1.33	0.980	1.90	1.33	0.98

Table 4: The equilibrium constants and the proposed stoichiometry of the extraction reaction at constant concentration

Metal ions	TTA			TBP		
	Slope	Intercept	R^2	Slope	Intercept	R^2
Ba(II)	1.93	0.211	0.64	2.02	0.168	0.882
Sr(II)	2.20	0.334	0.81	2.00	0.352	0.969
Se(IV)	1.61	0.841	0.91	1.61	0.841	0.914

Thermodynamic studies

The critical role of temperature is because of the temperature effect on solubility and equilibrium constant of the reaction. The introduction of a neutral complex into a solution phase involves a number of processes that can be associated with large changes in enthalpy (solvation processes) and in entropy (solvent orientation and restructuring), leading to considerable temperature effects [10]**.**

For demonstrate the effect of temperature on the extraction of Ba(II), Sr(II) and Se(IV) from aqueous phase by use (TTA) and (TBP). Experiments were carried out by varying temperatures in the range of 295 to 323 K. The results reveal that the elevation of the temperature positively influences the extraction of each metal ion with (TTA) and (TBP) extractant.

The free energy change Δ*G* was calculated from the relationships.
$\log K_{ex} = \log D_M - 2pH - 2\log[HA]$

$\Delta G = -2.303RT \log K_{ex}$ ………………… …………(6)

Thermodynamic functions, namely the changes of enthalpy (ΔH),and entropy (ΔS) can be calculated from the well known Van't Hoff relation. Applying this relation to the equilibrium of extraction of metal ions gives:

$\log K_{ex} = -\Delta H_{ex}/2.303RT + \Delta S_{ex}/2.303R$ ………………(7)

where R is the gas constant equal to 8.314 J $mol^{-1}K^{-1}$.A graphical illustration of the Van't Hoff relation (log K_{ex} vs. 1/T) should be a straight line with the slope B = $\Delta H_{ex}/2.303R$ and intercept A = $\Delta S_{ex}/2.303R$. Its general expression is as follows:

$\log K_{ex} = B/T + A$……………………………………………(8)

The experimental values of the extraction constant (K_{ex}) of Ba(II), Sr(II) and Se(IV)determined for each (TTA) and (TBP) extractant at constant composition of the aqueous and organic phases Fig(4) were correlated with the reciprocal of the absolute temperature (T) ranging from 295 to 323 K . Coefficients A, and B in the equation (8) are determined by the multiple regression analysis separately for each extractant. Thermodynamic functions, namely the changes of enthalpy (ΔH), free energy change Δ*G* and entropy (ΔS) can be calculated and illustrated in Table (5 and 6). The negative values of the enthalpy change indicate the exothermic character of the extraction of metal ions.

The values of enthalpy of extraction demonstrate the degree of electrostatic association between cation and extractant as well as shows the degree of approach one another, where the more approach one another giving more stable complex extracted, also the large radius of ions as well as the probable to giving stable species in aqueous phase effect to decrease the approach between ions and extractant with temperature increase, and this results emphasize the participation of organic solvent in ion pair complex extracted as solvent separated complex loose ion pair[7]. The positive value of ΔS reveals the increased randomness at the solid- solution interface during the fixation of the metal ion on the active site of the adsorbent. Since the adsorption process is endothermic, it follows that under these conditions the process becomes spontaneous because of the positive entropy change.

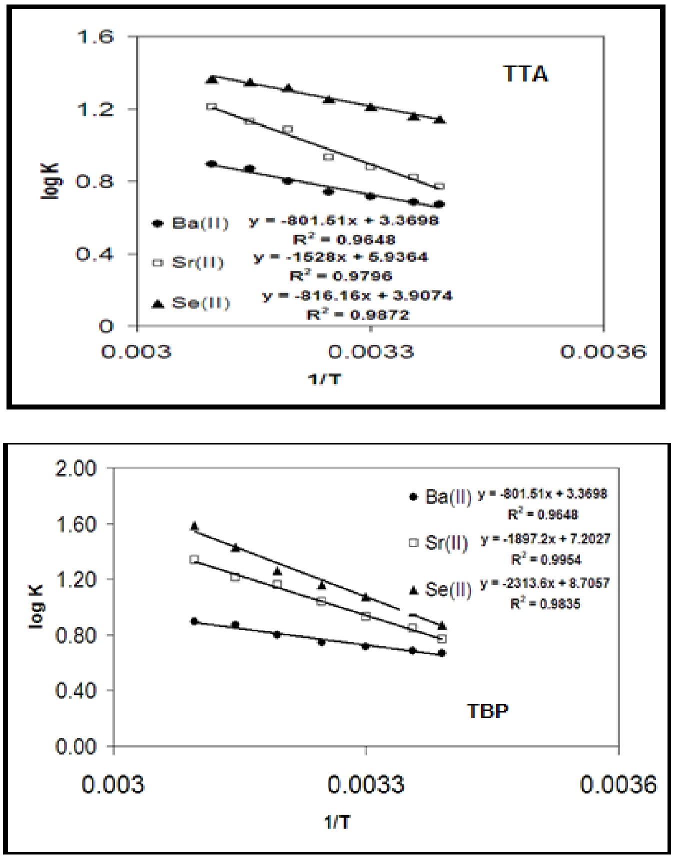


Figure 4: The effect of the reciprocal of the absolute temperature on the extraction constant (K_{ex}) of Ba(II), Sr(II) and Se(IV)

Table 7: Separation factor of Se(IV),Sr(II) and ,Ba(II) at different pH , using extractant (TTA) and (TBP)

pH	Extractant (TTA)			Extractant (TBP)		
	D_{Se}/ D_{Ba}	D_{Se}/ D_{Sr}	D_{Sr}/ D_{Ba}	D_{Se}/ D_{Ba}	D_{Se}/ D_{Sr}	D_{Sr}/ D_{Ba}
2.00	4.77	3.94	1.21	4.77	3.79	1.26
3.00	4.15	3.49	1.19	4.15	3.20	1.30
4.00	3.52	2.88	1.22	4.02	2.96	1.36
5.00	2.97	2.36	1.26	3.77	2.36	1.60
6.00	2.74	1.75	1.56	3.93	2.54	1.54
8.00	2.67	1.29	2.06	3.80	2.24	1.69

Separation factor at different extractant concentration
A series of experiments in order to measure separation factor of Ba(II), Sr(II) and Se(IV) using (TTA) and (TBP) as extractant were made. The experiments were performed using varying extractant concentration in the range of 0.01to 0.15M.

The separation factors *β* for both extractants were calculated and are plotted against extractant concentrations Table (8). These separation factors allow make it another one. It is clear that the separation of two or more metal ions will be more feasible as the separation factor β reaches values greater than 1.0. From Table (7) it was shown that the both extractant had relatively good separation factor and the capacity of these extractants to separate Se(IV)from Ba(II) and Sr(II) was apparent. Separation factor for each (TTA) and (TBP) were dependent on pH. Separation Se(IV)from Ba(II) by using (TBP)better than (TTA) **.** At initial pH 2 separation of Se(IV)from Ba(II) and Sr(II) were achieved, and it is not possible to separate Ba(II) from Sr(II) under these conditions. The separation factor of Se(IV) reached its maximum at pH range from of 2 to 3 for each extractant (TTA)and (TBP). While, Sr(II) and Ba(II) are difficult to separate because their separation factors *β* are all around 1.0.

Separation factor at different extractant concentration
A series of experiments in order to measure separation factor of Ba(II), Sr(II) and Se(IV) using (TTA) and (TBP) as extractant were made. The experiments were performed using varying extractant concentration in the range of 0.01to 0.15M.

The separation factors *β* for both extractants were calculated and are plotted against extractant concentrations Table (8). These separation factors allow make it possible to quantify how much of a metal ion is extracted with respect to another one. Although separation factors increased with increasing extractant concentrations, it is interesting that some degree of separation of the different metal ions was achieved. It is clear that the separation of two or more metal ions will be more feasible as the separation factor β reaches values greater than 1.0. - based on these separation factors, Table(8)shows that Se(IV) is the easiest to separate from the other ions. It is seen that the separation of Se (IV) from Ba(II) and Sr(II) and separation Sr(II)) from Ba(II) increase to a maximum around a (TTA) and (TBP) extractant concentration of 0.01M. Higher concentration of extractant was used affecting and diminishing the separation factors *β.*

Table 8: Effect of separation factor of Se(IV), Sr(II) and Ba(II) on different concentrations, using using extractant (TTA) and (TBP)

Conc. M	Extractant (TTA)			Extractant (TBP)		
	D_{Se}/ D_{Ba}	D_{Se}/ D_{Sr}	D_{Sr}/ D_{Ba}	D_{Se}/ D_{Ba}	D_{Se}/ D_{Sr}	D_{Sr}/ D_{Ba}
0.010	5.40	3.26	1.65	3.016	4.60	3.02
0.030	4.97	3.04	1.63	3.038	3.84	3.04
0.050	4.10	2.91	1.41	2.908	3.12	2.91
0.075	3.92	3.00	1.30	3.005	2.74	3.00
0.100	3.73	2.97	1.25	2.974	2.36	2.97
0.125	3.83	3.02	1.27	3.023	1.63	3.02
0.150	3.76	3.03	1.24	3.030	1.52	3.03

Conclusion

Liquid extraction of heavy metals is widely applied in many fields ranging from the environmental to the biomedical discipline. In the environmental field, some of the more prominent applications include: removal and recovery of metal ions and dyes from wastewater.

The equilibrium slope method and its utility in estimating the stoichiometry of the resulting organic complexes has been reviewed for multiple metal ions. The number of protons involved generally dictates the slope of the log D versus pH plot. A slope of 2 is common for each metal under study, thus attributing that the general organic complexes obtained from these extraction processes are in the form of dimers. The negative values of the enthalpy change indicate the exothermic character of the extraction of metal ions. The positive value of ΔS reveals the increased randomness at the solid-solution interface during the fixation of the metal ion on the active site of the adsorbent. Since the extraction process is endothermic, it follows that under these conditions the process becomes spontaneous because of the positive entropy change. The selectivity of extractant for desired metal separation can be quantified using separation factor. The highest value of the separation factor corresponds to the highest selectivity in metals separation.

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