RESEARCH PAPER

Implication of Thermodynamic Functions and Speciation Diagrams in the Analysis of Solvent Extraction Behavior of Samarium from Acidic Solutions

Hamed Tavakkoli[1], Mohammad Reza Aboutalebi[1,*], Seyed Hosein Seyedein[1], Seyed Nezameddin Ashrafizadeh[2]

* *mrezab@iust.ac.ir*
[1] School of Metallurgy and Materials Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran.
[2] Professor, School of Chemical Engineering, Iran University of Science and Technology (IUST), Narmak, Tehran, Iran.

Received: January 2021 Revised: April 2021 Accepted: May 2021
DOI: 10.22068/ijmse.2105

Abstract: *Solvent extraction of samarium from aqueous solutions by two different types of extractants, namely D2EHPA and PC88A, in kerosene was investigated. Through identification of speciation diagrams, the chemically stable complex of samarium in different acidic solutions (H_2SO_4, HCl and HNO_3) were studied. Regarding the various types of samarium species in sulfate medium in comparison with other acidic environments, H_2SO_4 and HNO_3 media were chosen to examine the extraction behavior of samarium complexes. Thermodynamic parameters of samarium extraction reactions by D2EHPA and PC88A from aqueous solutions of HNO_3 and H_2SO_4 were calculated as $\Delta G°$D2EHPA-HNO_3 , $\Delta G°$D2EHPA-H_2SO_4 , $\Delta G°$PC88A-HNO_3 , $\Delta G°$PC88A-H_2SO_4 equal to -5.58, 3.40, 6.70 and 14.26, and the corresponding $\Delta H°$ values were equal to -9.38, -2.75, 4.01 and 16.95 kJ/mol, respectively. According to the results, D2EHPA seemed to be a more efficient extractant than PC88A and nitric aqueous solution was a better media than the sulfuric type. The synergistic effect of binary extractants revealed that synergistic factors were 2.94 and 5.74 in sulfuric and nitric solutions, respectively, for a D2EHPA:PC88A ratio of 2:3. The compositions of extracted complexes by D2EHPA and PC88A in sulfuric and nitric solutions were SmH_3A_6 and SmH_3B_6, respectively. Thermodynamic parameters of extraction reactions were calculated as: K_e equal to 9.513, 0.254, 0.067, 0.003 and $\Delta S°$D2EHPA-HNO_3 , $\Delta S°$D2EHPA-H_2SO_4 , $\Delta S°$PC88A-HNO_3 , $\Delta S°$PC88A-H_2SO_4 values were equal to -12.75, -20.64, -9.03, and 9.03 ($J\ mol^{-1}$) respectively.*

Keywords: *Samarium; Speciation diagram; Solvent Extraction; D2EHPA; PC88A.*

1. INTRODUCTION

Rare earth elements (REEs) have been widely used in batteries, chemicals, metallurgical processes, and production of advanced materials. Among the rare earth elements, samarium (III), as one of the most abundant and important REEs, has extensive applications in many fields including the production of permanent magnets, heat insulating ceramics, and catalysts [1, 2]. Recently lanthanide elements have attracted increasing attention and a considerable number of explorations have been performed on extraction and application of these materials [3]. Among various applications of the natural (non-radioactive) elements, samarium is one of the best absorbers of thermal neutrons by the capture process [4].

The purification and separation of rare earth elements (REEs) by liquid-liquid extraction process have attracted attentions worldwide due to the vast application of these elements in advanced technological areas [5–9]. The most common organic materials used for extraction are: di-(2-ethylhexyl) phosphoric acid (D2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (HEH/EHP), tributyl phosphate (TBP), 2-octylaminopyridine (2-OAP), Cyanex 272 and Cyanex 923.

Lenz et al. [10] studied solvent extraction behavior of samarium by D2EHPA diluted in Amsco from different acidic solutions. It was found that Sm was extracted from chloride media by the conventional ion-exchange reaction at low, moderate and high concentrations. Equilibrium data for the perchlorate and nitrate systems differed considerably from those of the chloride system due to the appearance of a second extraction reaction. El-hefny et al. used Cyanex 272 to extract Sm from chloride solutions. They found that the extracted ion was Sm $(OH)A_2$ 2HA and the chloride ions of the solution had a negligible effect on samarium extraction [11]. El-Nadi et al. conducted a research on recovery of La

(III) and Sm (III) from nitrate containing solutions by the use of Cyanex grade extractants (Cyanex 921, Cyanex 923, and Cyanex 925). They studied the effect of different parameters on the extraction of these ions. They sorted these extractants regarding to their efficiency as: Cyanex 921> Cyanex 923≥ Cyanex 925 [12]. Different grades of phosphorous based acids have been successfully used in the industry for the extraction of rare earth metals [11] where high selectivity and efficiency were achieved by using a combination of these extractants [13–20]. Torkaman et al. [5] investigated the solvent extraction of Sm (III) from aqueous nitrate solution using Cyanex301 alone and in combination with D2EHPA. The synergistic effect showed that addition of D2EHPA to Cyanex301 extraction system led to an increase in the extraction efficiency of Cyanex301 in low concentration range (0.01–0.05 M). Furthermore, mixtures of the extractants provided a better stripping performance at low acid concentration in comparison with D2EHPA system.

In some studies, the effect of acidic solution on the extractive behavior of rare earth elements due to differences in their stable ionic complexes has been investigated. The extraction of some lanthanides with D2EHPA from hydrochloric acid and sulfuric acid solutions has been declared to be similar, while the extraction is lower than that from of nitric acid solution [2, 21]. Agarwal [22] studied yttrium extraction from different acidic media by PC88A. In this research, it was found that the extractability of Y (III) with PC88A in different acidic media follows the order of HCl ≥ HNO3 >H2SO4. Also, Agarwal et al. [23] studied the solvent extraction of cerium (III) and samarium (III) from mixed solutions of all rare earth elements (REEs) using PC88A. The results revealed that HNO_3 and HCl were found adequate media for the solvent extraction of both Sm (III) and Ce (III). The results also showed that H_2SO_4 at pH=2 provided the best separation between Sm(III) and Ce(III).

Given these findings, a limited number of studies have been published in terms of the solvent extraction of samarium by various types of extractants and different acid solutions. As such, in this research solvent extraction of samarium from sulfate and nitrate solutions using the acidic extractants of D2EHPA and PC88A were thoroughly investigated. In this regard, the interaction of the type of extractant and the acidic solution was studied. Furthermore, the effect of aqueous media on the synergistic parameter was considered. Therefore, the speciation diagrams of samarium species in various acidic media were first identified through simulation using Medusa/Hydra software. The effects of operating parameters including the initial pH of the aqueous solution, extractant concentration, temperature, and synergistic effect of both extractants on the extraction behavior of samarium were investigated and the stoichiometric coefficients of the extraction were obtained. Due to the lack of a thorough investigation devoted to the speciation diagram of samarium species as well as their extraction using D2EHPA and PC88A reagents in sulfate and nitrate media, the present paper aims to report such experimental data on the mentioned subjects.

2. EXPERIMENTAL

2.1. Reagents and analysis

Samarium oxide and samarium nitrate (99.9% purity) were obtained from Middle East Ferro Alloy Company (Iran). The extractants, D2EHPA and PC88A were obtained from Merck (Germany) and from Daihachi Chemical Industry Co. Ltd (Japan), respectively. Both extractants were used as-received without any further purification. D2EHPA (H_2A_2) and PC88A (H_2B_2) are acidic organophosphorus extractants and have P=O and P-O-H groups, as shown in Fig. 1 [14].

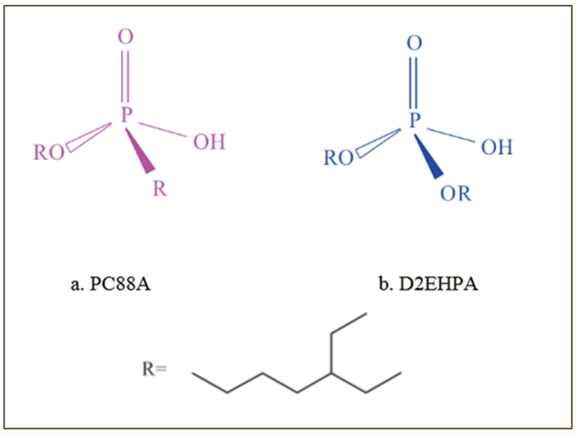

Fig. 1. Structural formulas of PC88A and D2EHPA [14].

Kerosene, which was used as organic diluent, was obtained from Alfa Aesar, (USA). Ammonium hydroxide, and nitric and sulfuric acid solutions were obtained from Chem-Lab (Belgium).

[DOI: 10.22068/ijmse.2105]

2.2. Identification of samarium speciation diagrams

The stability of samarium diverse complexes in either of aqueous sulfuric, nitric and hydrochloric solutions was identified through simulation by Medusa/Hydra software (version 15) [24]. This software calculates the equilibrium conditions based on the input information (Hydra) and then plots the results (Medusa). The concentrations used to plot these diagrams were

400 mg/L (ppm) of dissolved samarium and 0.1 M of either of nitrate, sulfate and chloride ions.

2.3. Batch experiments

Liquid-liquid extraction experiments were conducted in beakers while stirring was provided by means of magnetic stirrers. The aqueous phases used for batch experiments contained 2.66 mM (400 ppm) samarium in nitrate or sulfate solutions because the concentration of samarium in our real industrial solutions was about 400 ppm. Nitrate solutions were prepared by dissolving Samarium (III) nitrate hexahydrate salt in distilled water and further dilution. Sulfate solutions were prepared by dissolving appropriate amounts of samarium oxide in concentrated sulfuric acid (60% v/v) at the temperature of 80 °C and subsequent dilution by distilled water. The pH of the aqueous solution was adjusted to the desired value through addition of either dilute ammonium hydroxide, or sulfuric or nitric acid solutions.

For each experiment, 20 mL of the aqueous solution with known pH was mixed with 20 mL of the organic phase at room temperature and the mixture was agitated at 350 rpm for 30 minutes by a magnetic stirrer. After attaining equilibrium, the mixture was transferred into a separation funnel where the phases were allowed to separate. The equilibrium pH was measured by a digital pH meter (Mettler Toledo- Seven Compact S220) after complete phase separation. The pH meter was calibrated with specified buffer solutions (pH=1.68, 4.01, 7.01 and 10.01) according to the manufacturer's instructions on a daily basis. The equilibrium pH values at specific ionic strength of each solution are the measured proton activities. The concentration of samarium ions in the aqueous solutions before and after the extraction was determined using an AGILENT 735 inductively coupled plasma optical emission spectrometry (ICP-OES). The calibration of the device was performed in two steps: first at the beginning of the analyzing the samples and second at the end of analyzing the samples. In both steps, we used 1, 5, 10 and 20 ppm standard solutions to calibrate the device, each for 5 times. We found that the precision of the device to be constant and about 1 ppm.

The distribution coefficient (D) and extraction efficiency (E) are defined as follows:

$$D = \frac{[M]_o}{[M]_a} \quad (1)$$

$$\%E = \frac{D\times 100}{\left[D+\left(\frac{V_a}{V_o}\right)\right]} \quad (2)$$

Where $[M]_o$ and $[M]_a$ express the concentrations of samarium ions in the organic and aqueous phase, and V_a and Vo are the volumes of the aqueous and organic phases, respectively.

To determine the optimum operating conditions, pH isotherm tests were carried out at different extractant concentrations from 0.01 to 0.4 M. At the optimum concentrations of extractants, isotherm experiments were then carried out at different pH values from 0.2 to 2.5. Another set of extraction experiments was also carried out at different temperatures of 298, 308, 318 and 328 K to study the effect of temperature on the extraction of samarium complexes.

3. RESULTS AND DISCUSSION

3.1. Speciation diagrams of samarium

Speciation diagrams are useful in characterizing the distribution of species in a range of pH values. A speciation diagram can prepare a visual and quantitative exhibition of species availability. Speciation diagrams can be constructed as a function of a variety of parameters such as pH and metal ion concentration [24].

The stability of samarium diverse complexes in aqueous sulfuric, nitric and hydrochloric solutions was simulated by Medusa/Hydra software (version 15) [25]. The results show that the behavior of complexes is almost the same at chloride and nitrate solutions, as shown in Figure 2 (b-c). It is obvious that up to pH=2 the Sm^{3+} complex is the most abundant specie in chloride and nitrate solutions while in sulfate solution the $(Sm(SO4))^{+}$ complex is the most abundant (Figure 2 (a)).

[DOI: 10.22068/ijmse.2105]

[DOI: 10.22068/ijmse.2105]

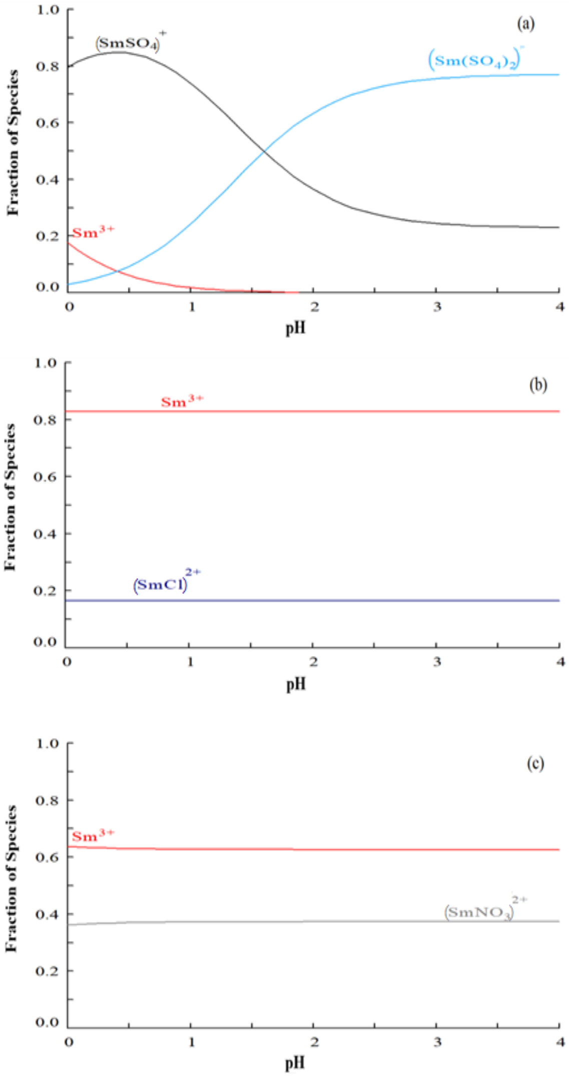

Fig. 2. Speciation diagrams constructed by Medusa software for (a) Sm-sulfate, (b) Sm-chloride and (c) Sm-nitrate (concentration of samarium species = 400 ppm, concentration of nitrate, sulfate and chloride ions = 0.1M).

It seems that in each acidic medium the main existing complex differs and would determine the extractive behavior of this element. For example, in the aqueous sulfate system, it would be appropriate to know the available sulfate ions concentrations as a function of pH. At low pH values, a major part of the sulfate is complexed with hydrogen, the complexed sulfates are not available for reaction as sulfate. On the other hand, at high pH values, nearly all sulfates are dissociated from hydrogen ions. Dissociated sulfates are readily available to react with other species.

3.2. Samarium extraction reactions

Both extractants of D2EHPA and PC88A exist as dimer species in kerosene [5, 6, 26] and the extraction reaction of samarium by these extractants can thus be written as Eq. (3):

$$Sm^{n+}_{aq} + m(HL)_{2,org} \overset{K_{eq}}{\Leftrightarrow} [(SmL)_n(HL)_{2m-n}]_{org} + nH^+_{aq} \quad (3)$$

Figures 3 and 4 show the logarithm of distribution coefficient (D) versus equilibrium pH; the slope of the distribution curve is about 3 for both extractants and both acidic media. It is thus confirmed that three moles of hydrogen ion are released when one mole of samarium is extracted into the organic phase.

The variations of logarithm of distribution coefficient versus equilibrium concentration of D2EHPA [H2A2] and PC88A [H2B2] in organic phases in both acidic media are given in

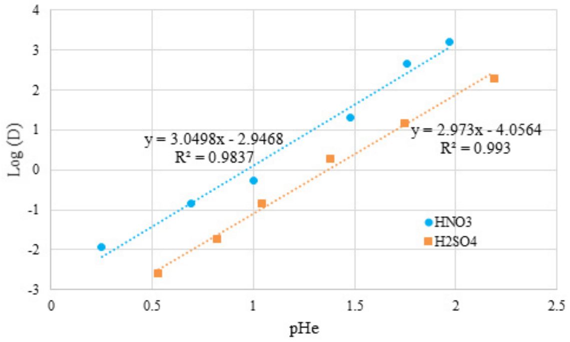

Fig. 3. Distribution coefficient (D) versus equilibrium pH in both solutions by D2EHPA ([D2EHPA] = 0.05 M, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm, T = 298 K).

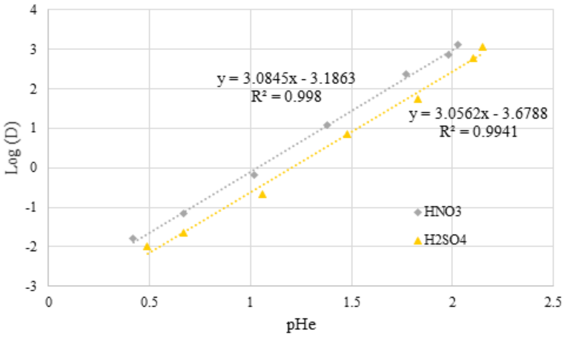

Fig. 4. Distribution coefficient (D) versus equilibrium pH in both solutions by PC88A ([PC88A] =0.4 M, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm, T = 298 K).

Figures 5 and 6. To calculate the equilibrium concentration of extractants, the following relationship is used:

$$[D2EHPA\ or\ PC88A]_{eq} = [D2EHPA\ or\ PC88A]_{initial} - [M^{n+}]_{initial} \times p \times \frac{D}{1+D} \quad (4)$$

Where $[M^{n+}]_{initial}$ indicates the initial concentration of samarium ions in the aqueous solution and p is the slope of the curved line of distribution coefficient variations based on the equilibrium concentration of the extractants.

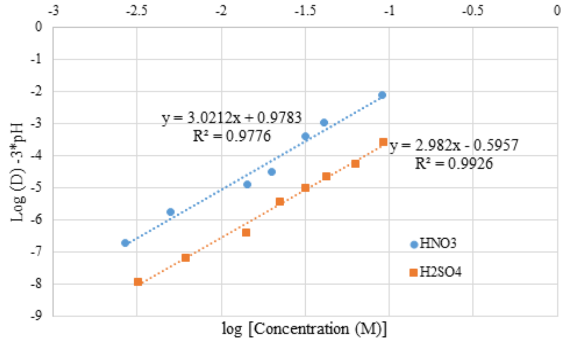

Fig. 5. Distribution coefficient (D) versus concentration of D2EHPA in nitric and sulfuric acid solutions (initial aqueous pH = 2.5, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm, T=298 K).

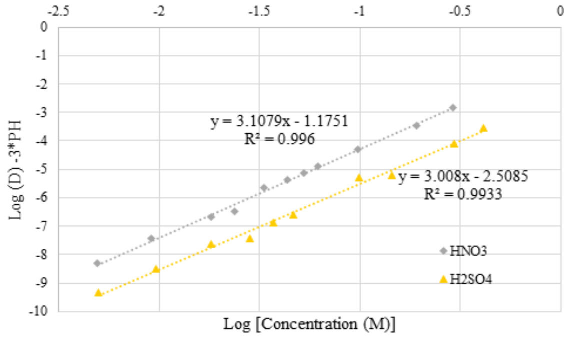

Fig. 6. Distribution coefficient (D) versus concentration of PC88A in nitric and sulfuric acid solutions (initial aqueous pH = 2.5, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm, T=298 K).

The slope of log–log linear relationships among the equilibrium extractant concentrations and the relative distribution ratios are determined to be around 3 in all systems. This shows that three moles of D2EHPA and/or PC88A participate in the extraction of each samarium ion.

From these results, the reactions could be deduced as Eqs. (5) and (6):

$$Sm^{3+} + 3H_2A_2 \overset{K_{eq}}{\Leftrightarrow} SmH_3A_{6(O)} + 3H^+ \quad \text{(nitric and sulfuric acid solutions)} \quad (5)$$

$$Sm^{3+} + 3H_2B_2 \overset{K_{eq}}{\Leftrightarrow} SmH_3B_{6(O)} + 3H^+ \quad \text{(nitric and sulfuric acid solutions)} \quad (6)$$

From the distribution coefficient curves plotted in Figures 5 and 6, the equilibrium constant of the reactions can be measured, the values of which are given in Table 1.

Table 1. The values of intercepts and equilibrium constants for all systems.

System	intercept	K_e
$Sm(HNO_3)$/D2EHPA	0.9783	9.513
$Sm(H_2SO_4)$/D2EHPA	-0.5957	0.254
Sm (HNO_3)/PC88A	-1.1751	0.067
Sm (H_2SO_4)/PC88A	-2.5085	0.003

Regarding the results shown in Figs. 5 and 6, the intercepts of plots provide $\log K_{eq}$. The equilibrium constant and standard free energy for extraction reaction of samarium from aqueous HNO_3 solutions by D2EHPA, which exhibits the maximum extraction, are calculated as:

$\log K_{eq} = 0.9783$

$\Delta G^0 = -5.58\ kJmol^{-1}$

Also, the equilibrium constant and free energy for the extraction reaction of samarium from aqueous H_2SO_4 solutions by D2EHPA are obtained as:

$\log K_{eq} = -0.5957$

$\Delta G^0 = 3.40\ kJmol^{-1}$

It is clear that the system of D2EHPA/HNO_3 has a much bigger equilibrium constant than the other systems.

3.3. The effect of operating variables on the extraction of samarium

3.3.1. Effect of pH

Extraction of samarium by either of 0.05 molar D2EHPA and PC88A extractants in kerosene from two aqueous acidic solutions was investigated. The results which are presented in Figures 7 and 8 show that the maximum extraction of samarium was obtained at a pH value of about 2 in nitric solution when using D2EHPA and at a pH value approximately of 2.8 when using PC88A. Meanwhile, the slope of extraction for HNO_3 solution is much higher than that of H_2SO_4 solution for both D2EHPA and PC88A extractants. It is also clear that the ability of D2EHPA in the extraction of samarium is higher than that of PC88A in both solutions. The maximum samarium extraction by PC88A is

[DOI: 10.22068/ijmse.2105]

about 90% (at initial pH>2.5), while the extraction by D2EHPA reaches 100%.In sulfuric medium, the maximum extraction of samarium was obtained at pH values of about 2.2 and 2.7 for D2EHPA and PC88A, respectively. Also, the maximum extraction of samarium was obtained at pH values more than 2.5 for D2EHPA and PC88A in both aqueous solutions.As such, this pH was chosen as the optimum pH for the extraction of samarium species. From the extractant point of view, comparison between the performances of PC88A in both solutions reveals that PC88A has a better performance in HNO_3 solution.

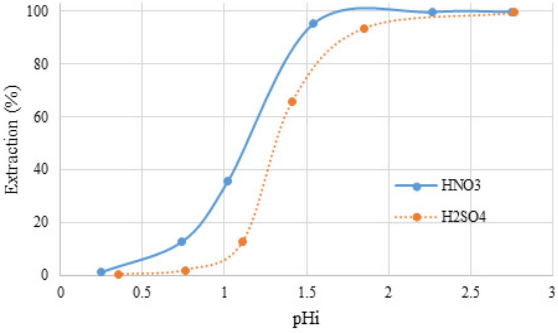

Fig. 7. The extraction of samarium versus initial pH by D2EHPA ([D2EHPA] = 0.05 M, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm, T=298 K).

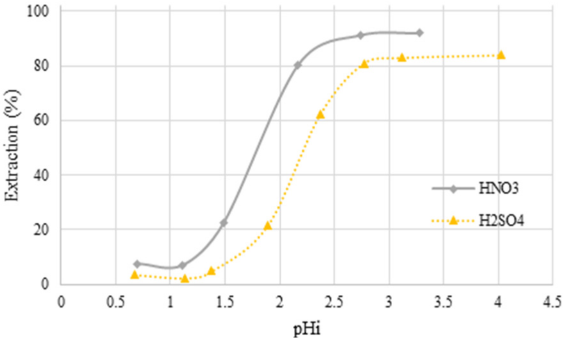

Fig. 8. The extraction of samarium versus initial pH by PC88A ([PC88A] = 0.05 M, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm, T=298 K).

Therefore, the samarium extraction would occur in the following order:

D2EHPA-HNO_3 > D2EHPA-H_2SO_4 > PC88A-HNO_3 > PC88A-H_2SO_4 at similar conditions. In all experiments equilibrium pH was either equal or lower than the initial pH of acidic solutions due to the release of H^+ ions from acidic extractants with progress of the solvent extraction reaction.

3.3.2. *Effect of extractant concentration*

One of the important factors in the solvent extraction of metal species is the concentration of used extractants. As mentioned before, in this research two different types of organophosphorus extractants, D2EHPA and PC88A, were used. The results of extraction versus extractant concentration in the organic phase for both extractants are shown in Figure 9.

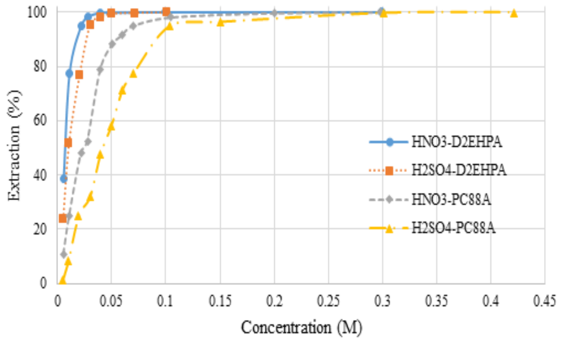

Fig. 9. The extraction of samarium versus extractant concentration in two different aqueous acidic solutions (Initial aqueous pH= 2.5, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm, T=298 K).

As it is shown, the slope of the extraction curve is remarkably higher for D2EHPA in both acidic media. It is also apparent that the maximum extraction is obtained at 0.04 M concentration for D2EHPA from both acidic solutions while for PC88A the maximum extraction is achieved at 0.2 and 0.3 M extractant from nitric and sulfuric media, respectively. Obviously, increasing the extractant concentration from the mentioned values did not result in any further extraction.

It was thus concluded that D2EHPA has a better performance than PC88A in extracting samarium species at similar pH and aqueous media. Meanwhile, the concentrations of 0.05 M for D2EHPA and 0.4 M of PC88A were chosen as the optimum extractant concentrations.

The abovementioned observation can be interpreted by hard and soft acid-base principle (HSAB) [27], where anions of PC88A have a soft factor and anions of D2EHPA have a hard one. According to the mentioned theory, lanthanides are more willing to react with the hard anions. As such, lower amounts of D2EHPA can extract higher amounts of samarium in comparison with PC88A at similar conditions. Also, solvent

[DOI: 10.22068/ijmse.2105]

extraction of samarium using PC88A was more affected by acidic solution media than that of D2EHPA.

3.3.3. *Effect of temperature*

The effect of temperature on the solvent extraction of samarium at fixed initial concentrations of 30 mM of D2EHPA, 70 mM of PC88A in the organic phase, and 2.67 mM of Sm(III) in the aqueous phase was investigated. The initial pH was 2.5 and the temperature was changed from 298 K to 328 K in increments of 10 K. The volume ratio of organic to aqueous phases (O/A) was fixed at 1:1 and the extraction time was 10 min. In all experiments (especially at temperatures above ambient temperature) the final volume of the aqueous solution was carefully measured and was taken into account in the calculations.

As it can be seen from Figure 10(a), the temperature rise is reversely relative to the extraction efficiency of samarium from both acid solutions when D2EHPA was used as extractant. Therefore, it can be concluded that the extraction reaction by D2EHPA is exothermic, resulting in stronger bonds in the extraction reaction product. However, in the case of using PC88A, the samarium extraction was increased by increasing temperature (Figure 10(b)). So, the extraction reaction with PC88A is exothermic. As a general conclusion, it can be said that the type of aqueous solution has much less effect than the type of extractant in the exothermic or exothermic

The results shown in Figure 10(a) exhibit that the extraction reaction of samarium from nitric solutions via D2EHPA was the best in comparison with other conditions. The logarithmic variations of the distribution coefficient versus temperature for PC88A extractant is shown in Fig 10(b). As it can be observed, by increasing the temperature, the extraction from both aqueous acidic solutions decreased where using D2EHPA. It is obvious that Sm/(HNO_3)/D2EHPA presented the maximum extraction.

In order to calculate the thermodynamic parameters of samarium extraction reaction, one should plot the logarithm scale of distribution curve versus temperature. Using such a procedure, the enthalpy and entropy of reactions were calculated from equations (7) to (9) and the results are presented in Table 2.

$$\log D = \log K_{eq} + m\log[(HL)_{2,org}] + npH \qquad (7)$$

$$[\frac{\partial \log D}{(\partial)\frac{1}{T}}]_{[(HL)_{2,org}],pH} = [\frac{\partial \log K_{eq}}{(\partial)\frac{1}{T}}]_{[(HL)_{2,org}],pH} \qquad (8)$$

$$[\frac{\partial \log D}{(\partial)\frac{1}{T}}]_{[(HL)_{2,org}],pH} = -\frac{\Delta H^{\circ}}{2.303R} \qquad (9)$$

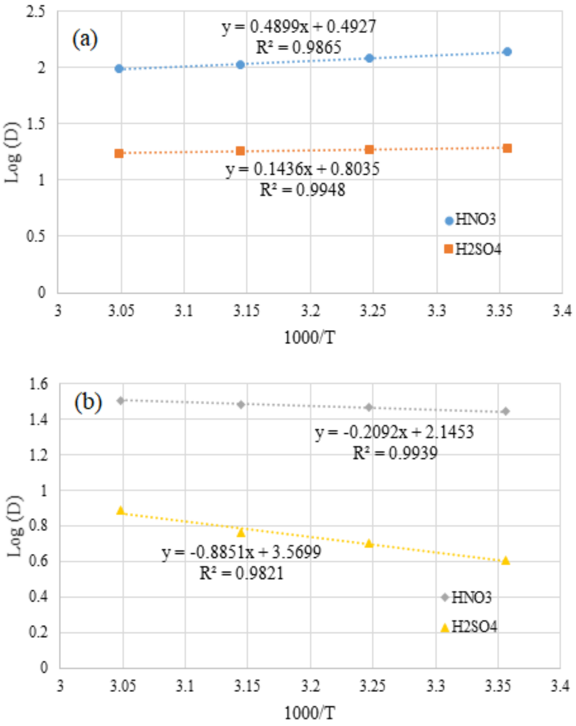

Fig. 10. Distribution of samarium versus temperature for a) D2EHPA, b) PC88A (initial aqueous pH= 2.5, [D2EHPA] = 0.03 M, [PC88A] = 0.07 M, aqueous/organic phase volume ratio = 1, stirrer speed= 350 rpm).

3.4. Synergic effect of extractants

To examine the possible synergic effect of using both extractants, instead of single ones, experiments were conducted by incorporating a mixture of both extractants in the organic phase. The synergistic factor (R) could be obtained according to the synergistic extraction theory [5].

$$R = \frac{D_{mix}}{D_A + D_B} \qquad (10)$$

Where D_{mix}, D_A, and D_B represent the distribution ratios when samarium is extracted with D2EHPA + PC88A, D2EHPA and PC88A, respectively. Meanwhile, synergistic and antagonistic effects on the extractions are exhibited by R >1 and R <1, respectively. For investigating the synergic effect of extractants, the extraction experiments were carried out with binary mixtures in a diverse ratio, as indicated in Table 3.

[DOI: 10.22068/ijmse.2105]

Table 2. Calculated thermodynamic parameters for various extraction systems under investigation.

System	**ΔG°(KJ mol^{-1})**	**ΔH°(KJ mol^{-1})**	**ΔS°(J mol^{-1})**
$Sm(HNO_3)$/D2EHPA	-5.58	-9.38	-12.75
$Sm(H_2SO_4)$/D2EHPA	3.40	-2.75	-20.64
Sm (HNO_3)/PC88A	6.70	4.01	-9.03
Sm (H_2SO_4)/PC88A	14.26	16.95	9.03

Table 3. The synergic factor for binary extractant systems.

Nitric Solutions	**Distribution coefficient (D)**			**R Value**
	D2EHPA	**PC88A**	**Binary Extractants**	
$Sm(HNO_3)$/ D2EHPA(0.05M)	1054	0	1054	1
$Sm(HNO_3)$/D2EHPA(0.04M)+PC88A(0.01M)	499	0.33	702.33	1.41
$Sm(HNO_3)$/D2EHPA(0.03M)+PC88A(0.02M)	150.78	1.16	271.25	1.78
$Sm(HNO_3)$/D2EHPA(0.02M)+PC88A(0.03M)	17.88	2.46	116.12	5.71
$Sm(HNO_3)$/D2EHPA(0.01M)+PC88A(0.04M)	3.58	5.06	29.12	3.37
$Sm(HNO_3)$/PC88A(0.05M)	0	4.84	4.84	1
Sulfuric Solutions	D2EHPA	PC88A	Binary Extractants	R Value
$Sm(H_2SO_4)$/D2EHPA(0.05M)	160.02	0	160.02	1
$Sm(H_2SO_4)$/D2EHPA(0.04M)+PC88A(0.01M)	38.44	0.09	47.30	1.23
$Sm(H_2SO_4)$/D2EHPA(0.03M)+PC88A(0.02M)	27.56	0.42	51.60	1.84
$Sm(H_2SO_4)$/D2EHPA(0.02M)+PC88A(0.03M)	5.24	0.84	17.86	2.94
$Sm(H_2SO_4)$/D2EHPA(0.01M)+PC88A(0.04M)	0.92	1.49	5.30	2.20
$Sm(H_2SO_4)$/PC88A(0.05M)	0	1.83	1.83	1

In both acidic solutions, by increasing the ratio of PC88A/D2EHPA, the synergic effect increases and reaches its maximum value at a ratio of 3:2 for both acidic solutions; where the synergic factors of R=5.71 in nitric solution and R=2.94 in sulfuric solution were obtained. Afterwards, through further addition of PC88A to the binary mixture, the obtained synergic factor declined to 1.

4. CONCLUSIONS

Samarium speciation diagrams in sulfate, chlorate and nitrate aqueous media were identified through simulation with Medusa software. Solvent extraction of samarium by the abovementioned extractants from two different acidic solutions, i.e.

H_2SO_4 and HNO_3, was investigated. It was shown that almost all of samarium ions were extracted from all solutions at the initial pH value of 2.5, 30 mM D2EHPA and 300 mM PC88A from a solution containing 2.67 mM Sm(III) at room temperature and a phase ratio of 1. Also, the equilibrium constants were measured and it was verified that the efficiency of Sm(III) extraction follows this order:

HNO_3/D2EHPA>H_2SO_4/D2EHPA>HNO_3/PC88A >H_2SO_4/PC88A

Additionally, it was shown that the effect of the acidic solution on the solvent extraction of samarium by PC88A was greater than that of D2EHPA. The negative enthalpies of extraction reactions by D2EHPA show that the samarium chemical bonds in the organic phase are stronger than the same bonds in the aqueous solutions. It was also shown that the Sm extraction increases with increasing temperature when PC88A is used as extractant. The maximum extraction of samarium was obtained in HNO_3 aqueous solution with D2EHPA. In both sulfuric and nitric acidic solutions, D2EHPA was proved to be more effective than PC88A under similar conditions. The latter observation was attributed to the fact that lanthanides preferentially tend to react with hard anions like D2EHPA. The optimum ratio of the binary mixture of extractants was obtained at

[DOI: 10.22068/ijmse.2105]

PC88AA/D2EHPA 3:2, for both aqueous solutions, where the highest synergic factor was obtained as R=5.71 in nitric acid solution.

ACKNOWLEDGMENTS

This research was financially supported by Iranian Mines and Mining Industries Development and Renovation Organization (IMIDRO). The authors appreciate the support of research council at Iran University of Science and Technology (IUST). The first author would like to thank Dr. H. Aghajani (Associate Professor at Tabriz University) for many useful discussions, comments and suggestions that greatly improved the manuscript.

REFERENCES

[1] He,Y., Pei, J., Srinivasakannan,C., Li, S., Peng, J., Guo, S., Zhang, L., Yin, S.,"Extraction of samarium using a serpentine Y-junction microreactor with 2- ethylhexyl phosphonic acid mono-2-ethylhexyl." Hydrometallurgy, 2018, 179, 175–180.

[2] Xie, F., Zhang,T.A., Dreisinger, D., Doyle, F.,"A critical review on solvent extraction of rare earths from aqueous solutions." Miner. Eng., 2014, 56, 10–28.

[3] Luo,Q.Y., Luo, H., Kuang, H.M., Chen,W.T., Wen, Y.X., "A novel samarium material: Synthesis, structure, photophysical properties and photoluminescence energy transfer mechanism." J. Solid State Chem., 2019, 270, 200–204.

[4] Herrera, M.S., Hernández, M.F., Cipollone, M., Conconi, M.S., Rendtorff, N.M., "Thermal behavior of samarium oxide – Ball clay mixtures for high macroscopic neutron capture cross section ceramic materials." Appl. Clay Sci., 2019, 168, 125–135.

[5] Torkaman, R., Moosavian, M.A., Torab-Mostaedi, M., Safdari, J., "Solvent extraction of samarium from aqueous nitrate solution by Cyanex301 and D2EHPA." Hydrometallurgy, 2013, 137, 101–107.

[6] Lee, M.S., Lee, J.Y., Kim, J.S., Lee, G.S., "Solvent extraction ofneodymium ions from hydrochloric acid solution using PC88A and saponified PC88A." Sep. Purif. Technol., 2005, 46, 72–78.

[7] Atanassova, M., Dukov, I.L., "Solvent extraction and separation of lanthanoids with mixtures of chelating extractant and 1-(2-pyridylazo)-2-naphthol." Sep. Purif. Technol., 2006, 49, 101–105.

[8] Li, W., Wang, X., Zhang, H., Meng, S., Li, D., "Solvent extraction of lanthanides and yttrium from nitrate medium with CYANEX 925 in heptane." J. Chem. Technol. Biotechnol., 2007, 82, 376–381.

[9] Morais, C.A., Ciminelli, V.S.T., “Selection of solvent extraction reagent for the separation of europium (III) and gadolinium (III).” Miner. Eng., 2007, 20, 747–752.

[10] Lenz, T.G., Smutz, M., “The extraction of neodymium and samarium by di(2-ethylhexyl) phosphoric acid from aqueous chloride, perchlorate and nitrate systems.” J. Inorg. Nucl. Chem., 1968, 30, 621–637.

[11] El-Hefny, N.E., El-Nadi, Y.A., Daoud, J.A., El-Hefny, N.E., El-Nadi, Y.A., Daoud, J.A., “Equilibrium and mechanism of samarium extraction from chloride medium using sodium salt of CYANEX 272.” Sep. Purif. Technol., 2010, 75, 310–315.

[12] El-Nadi, Y.A., El-Hefny, N.E., Daoud, J.A., “Extraction of Lanthanum and samarium from nitrate medium by some commercial organophosphorus extractants.” Solvent Extr. Ion Exch., 2007, 25, 225–240.

[13] Wang, X., Li, W., Meng, S., Li, D., “The extraction of rare earths using mixtures of acidic phosphorus-based reagents or their thio-analogues.” J. Chem. Technol. Biotechnol., 2006, 81, 761–766.

[14] Zhang, C., Wang, L., Huang, X., Dong, J., Long, Z., Zhang, Y., “Yttrium extraction from chloride solution with a synergistic system of 2-ethylhexyl phosphonic acid mono-(2-ethylhexyl) ester and bis (2, 4, 4-trimethylpentyl) phosphinic acid.” Hydrometallurgy, 2014, 147, 7–12.

[15] Zhang, F., Wu, W., Bian, X., Zeng, W., “Synergistic extraction and separation of lanthanum (III) and cerium (III) using a mixture of 2-ethylhexylphosphonic mono-2-ethylhexyl ester and di-2-ethylhexyl phosphoric acid in the presence of two complexing agents containing lactic acid and citric acid.” Hydrometallurgy, 2014, 149, 238–243.

[16] Onoda, H., Kurioka, Y., “Selective removal and recovery of samarium from mixed transition metal solution using phosphoric acid.” J. Environ. Chem. Eng., 2016, 4, 4536–4539.

[17] Mohammadi, M., Forsberg, K., Kloo, L., Martinez De La Cruz, J., Rasmuson, Å., “Separation of ND(III), DY(III) and Y(III) by solvent extraction using D2EHPA and EHEHPA.” Hydrometallurgy, 2015, 156, 215–224.

[18] Zhang, Y., Li, J., Huang, X., Wang, C., Zhu, Z., Zhang, G., “Synergistic extraction of rare earths by mixture of HDEHP and HEH/EHP in sulfuric acid medium.” J. Rare Earths, 2008, 26, 688–692.

[19] Sinha, M.K., Pramanik, S., Kumari, A., Sahu, S.K., Prasad, L.B., Jha, M.K., Yoo, K., Pandey, B.D., “Recovery of value added products of Sm and Co from waste SmCo magnet by hydrometallurgical route.” Sep. Purif. Technol., 2017, 179, 1–12.

[20] Mishra, B.B., Devi, N., “Study on the Extraction and Separation of Samarium from Chloride Medium Using D2EHPA and [P 66614] [D2EHP] and Their Application to Monazite Ore.” Trans. Indian Inst. Met., 2020, 73, 2247–2257.

[21] Gupta, C.K., Krishnamurthy, N., “Extractive metallurgy of rare earths.” Int. Mater. Rev., 1992, 37, 197–248.

[22] Agarwal, V., Safarzadeh, M.S., Galvin, J., “Solvent extraction and separation of Y(III) from sulfate, nitrate and chloride solutions using PC88A diluted in kerosene.” Miner. Process. Extr. Metall. Rev., 2018, 39, 258–265.

[23] Agarwal, V., Safarzadeh, M.S., “Solvent extraction and separation of cerium (III) and samarium (III) from mixed rare earth solutions using PC88A.” Miner. Metall. Process., 2017, 34, 125–131.

[24] Free, M.L., Speciation and Phase Diagrams, John Wiley & Sons, Inc., Hoboken, The United State Of America, 2013.

[25] Puigdomenech, I., “Make Equilibrium Diagrams Using Sophisticated algorithms (MEDUSA).” Inorg. Chem., 2004.

[26] Zhang, F., Dai, J., Wang, A., Wu, W., “Investigation of the synergistic extraction behavior between cerium (III) and two acidic organophosphorus extractants using FT-IR, NMR and mass spectrometry.” Inorganica Chim. Acta, 2017, 466, 333–342.

[27] Pearson, R.G., “The HSAB Principle - mo