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鹽酸溶液에서 單獨 및 混合抽出劑에 의한 네오디뮴의 溶媒抽出†

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Solvent Extraction of Nd from Chloride Solution with Individual and Mixed Extractants†

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요 약

PC88A, D2EHPA, Cyanex272, Versatic acid10, D2EHPA+Alamine-304-1, D2EHPA+Alamine-308, D2EHPA+TBP, D2EHPA+TOPO, PC88A+Alamine-336, PC88A+TBP와 같은 단독 및 혼합추출제를 사용하여 Nd의 용매추출실험을 수행했다. 수용액의 평형 pH와 추출제의 농도가 증가함에 따라 Nd의 추출율은 증가하였다. 그러나 D2EHPA와 TBP 혼합추출제로 추출시에는 추출제의 농도증가에 따라 Nd의 추출율이 감소하였다. PC88A에 TBP를 첨가하는 것은 Nd의 추출에 거의 영향을 미치지 않았으나, Alamine336을 첨가하면 동일한 조건에서 추출율이 증가하였다. 실험결과로부터 단독 및 혼합추출제에 의한 Nd의 추출에 대해 고찰하였다.

주제어 : 네오디뮴, D2EHPA, TBP, 용매추출

Abstract

An extraction study of neodymium (Nd) was investigated with different individual and mixer of extractants such as PC88A, D2EHPA, Cyanex 272, Versatic acid 10 and D2EHPA+Alamine-304-1, D2EHPA+Alamine-308, D2EHPA+TBP, D2EHPA+TOPO, PC88A+Alamine-336 and PC88A+TBP respectively. In all cases, it was observed that the extraction percentage of Nd increased with increasing equilibrium pH and extractant concentration but rather opposite observation was found that the extraction percentage of Nd decreased with increasing TBP concentration along with D2EHPA. Adding TBP to PC88A had no favorable effect on the extraction of Nd, whereas use of a mixture of PC88A with Alamine336, increased the extraction percentage of Nd under the same condition. Based on our experimental studies, this paper reports the results on the basic approach and extraction of neodymium.

Key words: neodymium, D2EHPA, TBP, solvent extraction,

1. Introduction

Neodymium (Nd) is one of the most abundant elements in the rare earths but never found in nature as the free element. Nd occurs in ores such as monazite, bastnasite and xenotime[1,2] that contain small amounts of all the rare earth metals. Neodymium is not rare at all. Its abundance in the earth crust is about 38 mg/kg, which is the second highest among rare-earth elements, after cerium. The neodymium has been used as a

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component in the alloys used to make high-strength neodymium magnets. These magnets are widely used in such products as microphones, professional loudspeakers, in ear headphones, and computer hard disks. Due to growing demand of high purity neodymium and continuous diminution of high grade ores, selective recovery of metal values from various raw material resources becomes an important issue. Based on the above importance, several methods have been used for separation of Nd from different sources (ores/or scrap/ or spent catalysts, etc.) but solvent extraction method is one of the great interest due to its high selectivity, significant importance and cost saving.

The literature survey suggested that the organo phosphorous reagents are suitable for extraction of Nd from acidic aqueous media[3-6] and the survey also indicating that less number of studies have been done on the extraction of neodymium. H. C. Kao et al studied the extraction equilibria and kinetics of single and binary La (III) and Nd (III) from nitrate medium using PC 88A in kerosene and reported that PC88A is better than D2EHPA in separation performance.[7] Similar studies have been investigated by K. Kondo et al. on the extraction equilibria and kinetics of neodymium with diisodecylphosphoric (DIDPA) in different diluents and temperatures[8] at chloride medium and described that Nd extractability with DIDPA is much greater than that of D2EHPA and PC88A. N. V. Thakur et al. developed a process and mathematical model for the production of magnet grade Nd_2O_3 with the purity of 97% by using saponified PC 88A as an extractant in kerosene.[9]

The present work discusses on the extraction behavior of Nd with different individual and mixed extractants in escaid diluent from chloride solutions. Various studies have been carried out by us on the extraction of Nd with different extractant systems.

2. Experimental

2.1. Apparatus and reagents

Spectro arcos model atomic emission spectrophotometer (ICP-OES) and Fisher Scientific accumet (XL 15 model) pH meter were used for the determination of metal concentrations in the aqueous phase and for measuring the pH values, respectively. D2EHPA (di 2-ethyl hexyl phosphoric acid), PC 88A (2-ethyl hexyl phosphonic acid mono 2-ethylhexyl ester) Cyanex 272 (2, 4, 4 tri methyl pentyl phosphinic acid), Versatic acid 10 (a highly branched-C10 tertiary carbaxlic acid) were purchased. Alamine 304-1 (Tridodecyl Amine), Alamine 308 (tri iso-octyl amine) and Alamine 336 (tri C8-10 alkyl amines), Aliquat 336 (Tricaprylmethylammonium chloride) were purchased from Cognis and used without any purification. TBP (tri butyl phosphate, Yakuri pure chemicals co. Ltd.) and TOPO (tri octyl phosphine oxide, Sigma-Aldrich) were used. Escaid was used as diluent and all the other chemicals used were of analytical grade.

2.2. Solvent extraction procedure

The stock solution of Nd (III) was prepared by digesting the corresponding rare earth oxide in minimum concentrated hydrochloric acid and evaporated to near dryness and then made up to the mark with double distilled water. The desired initial pH values of the Nd (III) solution was adjusted with NaOH. Equal volume (20 ml) of aqueous and organic solution were taken in a 100 mL screwed cap bottle for shaking up to 30 minutes (initial experiments showed that equilibrium was attained within 5 minutes). The aqueous and organic phases were allowed to separate clearly after shaking experiments and the metal concentration in the aqueous phase was determined with ICP-OES after suitable dilutions and the concentration of metal in the organic phase was calculated from the mass balance. The distribution ratio (D) was calculated as the ratio of the concentration of metal present in the organic phase to that part in the aqueous phase at equilibrium and all the experiments were conducted at ambient temperature.

3. Results and discussion

3.1. Effect of equilibrium pH on extraction of Nd with different extractants

The extraction of Nd was carried out over the equilibrium pH range of 1 to 3 using different extractants such as PC88A, Cyanex 272, D2EHPA and versatic acid-10 in escaid diluent at unit phase ratio. The distribution coefficient of Nd increased with increasing of equilibrium pH in aqueous solution. The plot of log

D vs eq. pH (Fig. 1) is a linear line with the slope of 3.5, 2.2, 2.8, 0.08, showing that the extractants such as PC88A, Cyanex 272, D2EHPA, and versatic acid -10 release the protons 3.5, 2.2, 2.8 and nil, respectively. Among the above studied extractants, D2EHPA is showing well extraction efficiency than other extractants. Solvent extraction of Nd with the above extractants can be represented as follows:

$$Nd^{3+}{}_{aq}+3HA_{org}=NdA_{3,org}+3H^{+}{}_{aq} \quad (1)$$

$$Nd^{3+}{}_{aq}+3H_2A_{2org}=[Nd(HA_2)_3]_{,org}+3H^{+}{}_{aq} \quad (2)$$

where HA and H_2A_2 represent the monomer of the extractant (D2EHPA, Cyanex 272, Versatic acid 10) and dimer form of the PC 88A in escaid and aq and org denote aqueous and organic phases, respectively.

3.2. Effect of equilibrium pH on extraction of Nd with different mixer of extractants

Fig. 2 shows the effect of different extractants mixed with organophosphorous reagent (D2EHPA) for the extraction of Nd over the equilibrium pH ranges from 1-2.5 at equal phase ratio. The results indicate that the distribution coefficient of Nd increases with the rise in the equilibrium pH of the aqueous solution and the slopes were found to be 2.7, 2.6, 4.0 and 3.8 with 1M D2EHPA + 0.5M Alamine 304-1, 1M D2EHPA + 0.5M Alamine 308, 1M D2EHPA+0.5M TBP and 1M D2EHPA+0.5M TOPO, respectively. In the extraction with D2EHPA, it is found from the above results that the number of protons released during the extraction is the same in the extraction with D2EHPA mixed with amines but different in the extraction mixed with TBP and TOPO. The slight increase in Nd slope value with D2EHPA+TBP and D2EHPA+TOPO may be due to polymerization reaction of the extracted species in the organic phase. Employing D2EHPA+Alamine 336 and D2EHPA + Aliquat 336 in the extraction of Nd showed that aqueous phases were not clear even after long period, which means longer separation time is needed.

Fig. 3 shows the effect of varying TBP concentration from 0.5-2M mixed with D2EHPA for extraction of Nd at equilibrium pH range from 0.9-2. The distribution coefficient of Nd increases with increasing of equilibrium pH and decreases with increasing of TBP concentration. The plot of log D vs eq. pH having linear lines with the slope of 4.0, 4.1 and 3.7, shows that there was no marginal effect of TBP concentration on the extracted species of Nd with D2EHPA and it releases maximum 4 protons irrespective of the TBP concentration. The decreasing of distribution coefficient of Nd with increasing TBP concentration might be ascribed to the interaction between D2EHPA

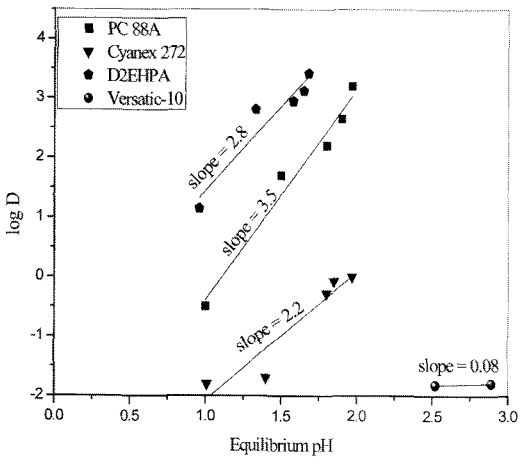

Fig. 1. Plot of log D vs Equilibrium pH for Nd extraction. Experimental conditions: PC 88A, Cyanex 272, D2EHPA, Versatic-10 acid = 1M; Nd = 0.01M.

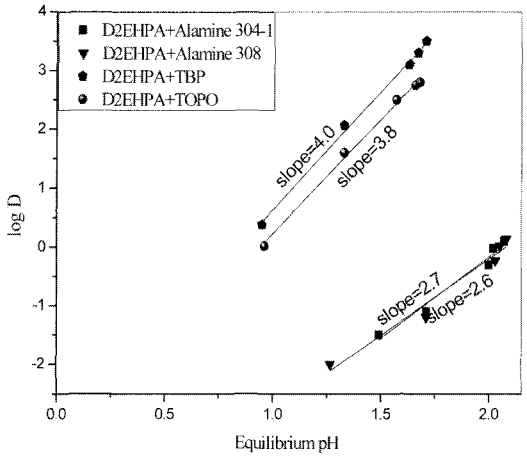

Fig. 2. Plot of log D vs Equilibrium pH for Nd extraction. Experimental conditions: D2EHPA = 1M; Alamine 304, Alamine 308, TBP and TOPO = 0.5M; Nd = 0.01M.

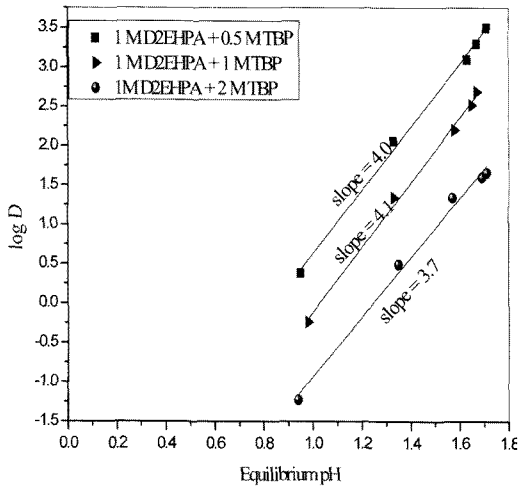

Fig. 3. Plot of log D vs Equilibrium pH for Nd extraction. Experimental conditions: D2EHPA = 1M; TBP = 0.5-2 M; Nd = 0.01M.

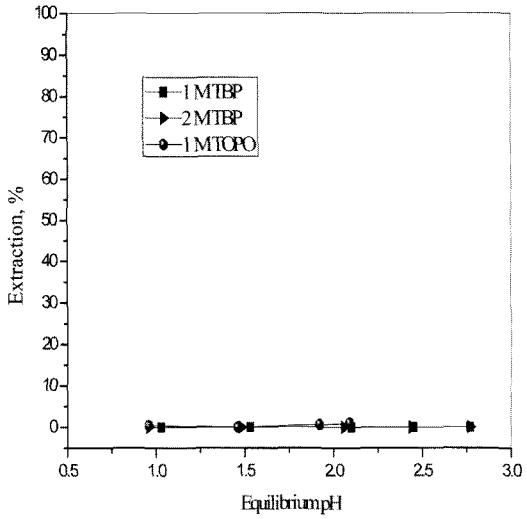

Fig. 4. Effect of equilibrium pH on extraction of Nd with TBP and TOPO. Experimental conditions: TOPO = 1M; TBP = 1.0-2M; Nd = 0.01M.

and TBP and similar studies have been reported earlier unambiguously with mixer of D2EHPA and TOPO system.[10]

3.3. Effect of equilibrium pH on extraction of Nd with solvating extractants

Extraction experiments of Nd were carried out as a function of equilibrium pH range from 1.0-2.8 using TBP and TOPO extractants in escaid diluent at unit phase ratio. The experimental results (Fig. 4) show that the extraction percentage of Nd was nil in all equilibrium pH of the aqueous solution and the results suggest that the solvating extractant alone is not suitable for the extraction of Nd in our pH range.

3.4 Effect of equilibrium pH and PC 88A concentration on extraction of Nd

The extraction of Nd was carried out at unit phase ratio in the equilibrium pH range from 0.7-1.0 using PC88A concentrations from 1 to 3M. The plot log D vs eq. pH (Fig. 5) shows that the distribution coefficient of Nd increases with increasing PC88A concentration and equilibrium pH of the solution. Comparing Fig. 1 and Fig. 5 indicates that the distribution coefficient of Nd decreases with increasing metal concentration in aqueous chloride solutions and the reaction between Nd and PC88A can be written as:

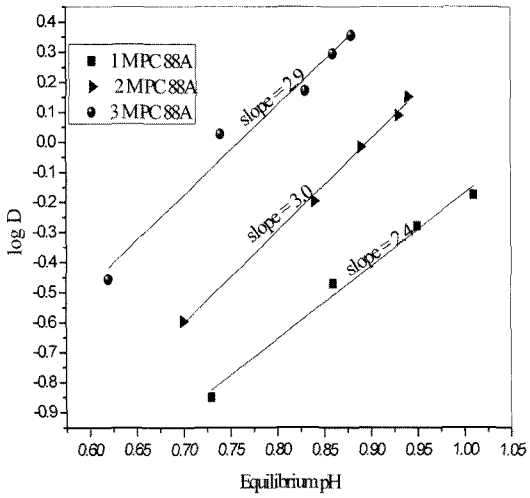

Fig. 5. Effect of equilibrium pH on extraction of Nd at different PC 88A concentrations; $[NdCl_3]$ = 0.1M.

$$Nd^{3+}{}_{aq} + 3H_2A_{2org} = [Nd(HA_2)_3]_{,org} + 3H^+{}_{aq} \quad (3)$$

where H_2A_2, aq and org represents the dimer form of PC 88A and aqueous and organic phases with respectively.

3.5. Effect of mixed extractants on extraction of Nd

Solvent extraction experiments were conducted in

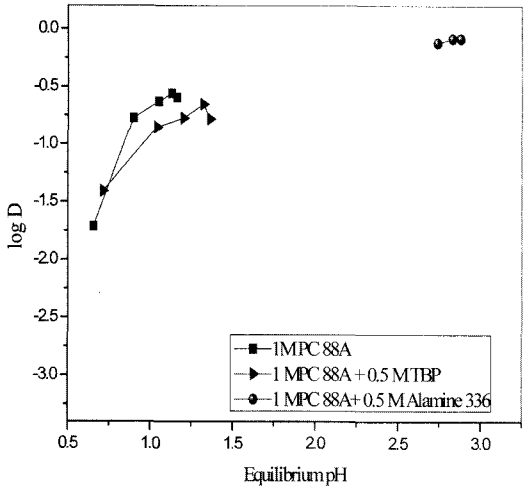

Fig. 6. Effect of equilibrium pH on extraction of Nd with mixer of extractants. TBP, Alamine 336 = 0.5 M; PC 88A = 1.0 M and [$NdCl_3$] = 0.1 M.

the equilibrium pH range from 0.7-3.0 using mixer of extractants such as 1M PC88A + 0.5 M Alamine 336 and 1M PC88A + 0.5M TBP in escaid diluent at unit phase ratio. The distribution coefficient of Nd increased with the increasing of equilibrium pH in all experimental systems shown in Fig. 6. Employing 1M PC88A + 0.5M TBP, it was observed that there is no marginal effect on the extraction of Nd in all equilibrium pH solutions. However, in the extraction of Nd by 1M PC 88A + 0.5M Alamine 336, the value of equilibrium pH was much higher than that by PC88A alone and 1M PC88A + 0.5M TBP. In the case of extraction with the mixture of PC88A and Alamine336, the equilibrium pH was around 3.3, while the equilibrium pH was from 0.7 to 1.5 in the extraction with PC88A alone and the mixture of PC88A and TBP.

The extraction behavior of Nd with the mixture of PC88A and Alamine336 can be explained by the following equations. In the extraction of Nd by 1M PC88A, some of the hydrogen ions are transferred into the aqueous phase and these hydrogen ions are again extracted into the organic phase by Alamine336 and the extraction reaction can be represented as:

$$Nd^{3+}{}_{aq} + 3Cl^{-}{}_{aq} + 3H_2A_{2org} + 3R_3N_{org} = [Nd(HA_2)_3]_{,org} + 3R_3NHCl_{org} \quad (4)$$

According to Eq. (4), no hydrogen ions are transferred to the aqueous phase during the extraction with mixture of PC88A and Alamine336 and the Fig. 6 clearly shows that the obtained equilibrium pH value of mixture of PC88A and Alamine336 is much higher than the PC88A/or the mixture of PC88A and TBP.

4. Conclusion

Solvent extraction studies have been carried out for extraction of neodymium using different individual and mixer of extractants such as PC88A, D2EHPA, Cyanex 272, Versatic acid 10 and D2EHPA + Alamine-304-1, D2EHPA + Alamine-308, D2EHPA + TBP, D2EHPA + TOPO, PC88A + Alamine-336 and PC88A + TBP. The parameters such as effect of equilibrium pH, metal concentration and mixer of extractants have been applied to the extraction of Nd. In all cases, the distribution coefficient of Nd increased with increasing equilibrium pH and extractant concentration. However, the distribution coefficient of Nd decreased with the increase of TBP concentration in the mixture with D2EHPA. Applying mixed extractant as PC88A + TBP to the extraction of Nd showed that no fringy effect but Alamine 336 gives an effective extraction with PC 88A. Various studies have been carried out on extraction process of Nd with different systems, which is indicating that basic approach and extraction possibilities of Nd.

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