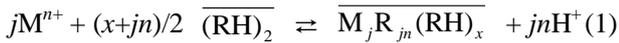


Liquid-Liquid Equilibrium of Sodium with Organophosphorus Acid as Extracting Agent

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1. Introduction

Solvent extraction is one of the important methods to separate metals, such as rare earth metals [1], where the metals are distributed between aqueous phase and organic phase containing extracting agent. Organophosphorus acid, e.g., 2-ethylhexyl-2-ethylhexylphosphonate (PC-88A) for rare earth metal extraction, is widely used as an extracting agent. In the extraction, the metal is exchanged with hydrogen in the extracting agent as,



where M^{n+} is metal ion in aqueous phase and $\overline{(RH)}_2$ is the extracting agent dimer in organic phase. This transfer of hydrogen into aqueous phase reduces the metal extraction degree. In order to avoid this unfavorable hydrogen transfer, the extracting agent is saponified with any appropriate metal, such as, sodium, in the practical extraction process[2,3,4]. In this thesis, liquid-liquid equilibrium of sodium with organophosphorus extracting agent was studied for rare earth metal extraction.

2. Experimental

Neodymium was selected as a rare earth metal. Sodium chloride or neodymium chloride hexahydrate was the source of the metals. The pH of the aqueous phase was adjusted with hydrochloric acid or sodium hydroxide at initial. The organic solvent phase was kerosene solution of 2-ethylhexyl-2-ethylhexylphosphonate (PC-88A). All materials were used without further purification. **Tables 1** and **2** show the experimental conditions. The specified amounts of aqueous and organic phases were brought into contact in a conical flask. These phases in the flask were shaken in the constant temperature bath to be equilibrated. After equilibration, settling, and phase separation, both liquid phases were analyzed using ICP-AES (SPS7800, Hitachi High-Tech Science Corporation) and pH meter (F-52, Horiba).

3. Results and Discussion

The material balance of the metal is written as,

$$V_{aq} C_{M, aq, 0} + V_{org} C_{M, org, 0} = V_{aq} C_{M, aq, eq} + V_{org} C_{M, aq, eq} \quad (2)$$

The concentration of metals in organic phase was calculated using this equation with that in aqueous phase. The extraction yield, E_M , and distribution ratio, D_M , of the metal were defined as,

$$E_M = C_{M, org, eq} V_{org} / (C_{M, aq, 0} V_{aq}) \quad (3)$$

$$D_M = C_{M, org, eq} / C_{M, aq, eq} \quad (4)$$

Table 1 Experimental conditions in solvent extraction of sodium

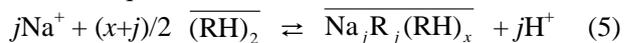
Feed	aqueous solution of sodium, Na (NaCl)
Volume, V_{aq} [m^3]	2.0×10^{-5}
Concentration of Na^+ , $C_{Na, aq, 0}$ [$kmol m^{-3}$]	0.25 ~ 1
pH, pH_0	0 ~ 14 (adjusted by HCl, NaOH)
Solvent	kerosene solution of PC-88A
Volume, V_{org} [m^3]	2.0×10^{-5}
Concentration of PC-88A, $C_{RH2, org, 0}$ [$kmol m^{-3}$]	0.25
Temperature [K]	298
Time [h]	12

Table 2 Experimental conditions in solvent extraction of neodymium

Feed	aqueous solution of neodymium, Nd ($NdCl_3 \cdot 6H_2O$)
Volume, V_{aq} [m^3]	2.0×10^{-5}
Concentration of Nd^{3+} , $C_{Nd, aq, 0}$ [$kmol m^{-3}$]	0.005
pH, pH_0	0 ~ 2.0 (adjusted by HCl)
Solvent	kerosene solution of PC-88A w/ or w/o saponification
Volume, V_{org} [m^3]	2.0×10^{-5}
Concentration of PC-88A, $C_{RH2, org, 0}$ [$kmol m^{-3}$]	0.25
Temperature [K]	298
Time [h]	12

At pH_{eq} higher than 5, white turbidity in the aqueous phase was observed and the turbidity was kept even after the settling at $pH_{eq}=5$. This might result from the surface active effect by the extracting agent saponified with sodium [6]. In the range of high sodium concentration, heterogeneous three phases were formed at equilibrium. The results of sodium extraction are shown in **Figure 1**. Figure 1(a) shows the comparison between the initial and equilibrium pHs, pH_0 , pH_{eq} . While, in the range of $pH_0 < 3$, pH_{eq} was almost the same as pH_0 , pH_{eq} decreased after equilibration, where $6 < pH_0$.

The Eq.(1) is rewritten for Na^+ as,



The equilibrium constant of Na^+ , K_{Na} , is, thus, represented with D_{Na} as,

$$K_{Na} = D_{Na} C_{H, aq, eq}^j / (C_{Na, aq, eq}^{j-1} C_{RH2, org, eq}^{(x+j)/2}) \quad (6)$$

Based on this equation, $\log[D_{Na} / (C_{Na, aq, eq}^{j-1} C_{RH2, org, eq}^{(x+j)/2})]$ was plotted over $\log(1/C_{H, aq, eq}) = pH_{eq}$ in Figure 1(d), which is so-called slope analysis.

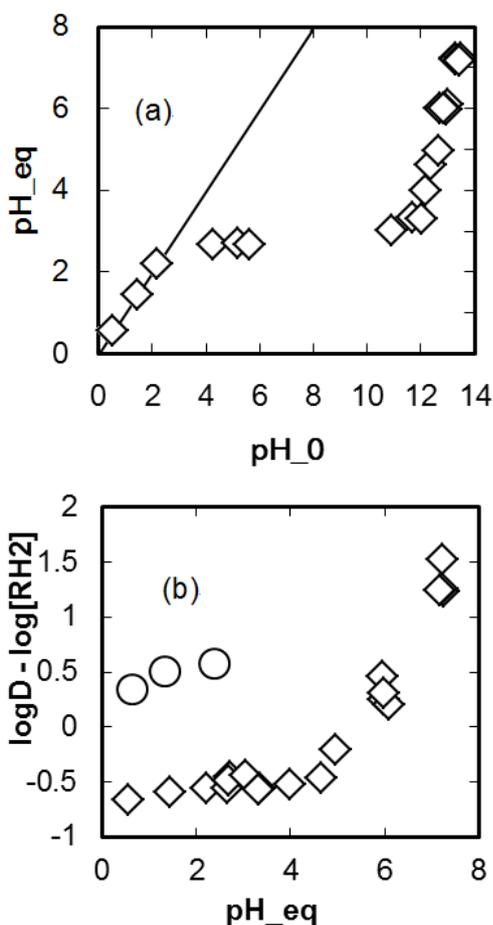
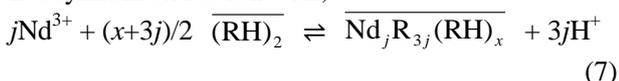


Fig. 1 Results of sodium, Na, extraction (\diamond -without saponification, \circ -with saponification): (a) pH change; (b) slope analysis under $C_{Na,aq,0}=2.5 \times 10^{-1} \text{ kmol/m}^3$

In the range of $5 < \text{pH}_{eq}$, these plots gave straight line with $j=1$, $x=1$, and $K_{Na}=3.12 \times 10^{-6}$. Shono *et al.* reported $j=2$ and $x=2$ for sodium extraction with bis (2-ethylhexyl) hydrogen phosphate (D2EHPA), when pH_{eq} was higher than 4.0[5]. Where pH_{eq} was lower than 5, $\log[D_{Na}/(C_{Na,aq,eq}^{j-1} C_{RH2,org,eq}^{(x+j)/2})]$ was higher and almost constant over pH_{eq} . Although this was qualitatively attributed to the effect of chloride ion and it was reported that the chloride ion might enhance the extraction of metal by forming complex with metal [7, 8], further study is required.

Figure 2 presents the results of neodymium extraction with and without sodium. Figure 2(a) shows the pH change by neodymium extraction. The pH_{eq} was the same as or lower than pH_0 without sodium. The addition of sodium could prevent the pH reduction as mentioned above. Figure 2(b) shows the extraction yield of neodymium. Neodymium was extracted into solvent phase. The yield increased with pH_0 and exceeded 0.9 at higher pH_0 . The yield could be improved by the addition of sodium as predicted. Figure 2(c) shows the slope analysis for neodymium extraction with,



The experimental results could be well fitted by this

reaction formula with $j=1$, $x=3$, and $K_{Nd}=0.0136$, which was much higher than that of sodium, 3.12×10^{-6} . The saponification of extracting agent with sodium did not affect the neodymium equilibrium, whereas neodymium enhanced the sodium extraction as shown in Figure 1(b).

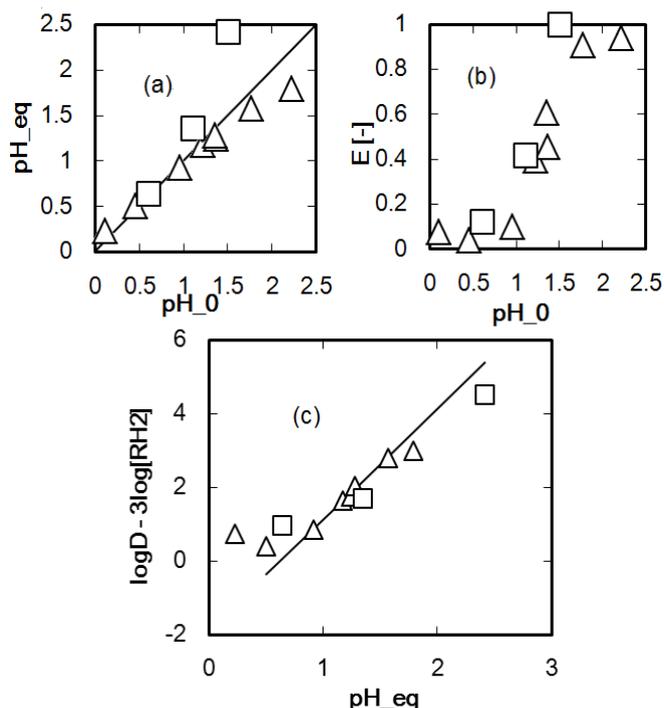


Fig. 2 Results of neodymium, Nd, extraction (\triangle -without saponification, \square -with saponification): (a) pH change; (b) extraction yield; (c) slope analysis

4. Conclusions

The liquid-liquid equilibrium of sodium with the extracting agent of PC-88A was clarified. It was confirmed that the extraction of neodymium was improved by the saponification of extracting agent with sodium.

References

- [1] 塩川二郎, 足立吟也, 希土類元素の化学, 49, (1981)
- [2] Man-Seung Lee et al. Separation Purification Technology 46 (2005) 72-78
- [3] I.Kojima et al. Journal of Inorganic and Nuclear Chemistry 31 (1969) 1815-1820
- [4] Isao Komasaawa et al. Journal of Chemical Engineering of Japan 16 (1983) 210-217
- [5] 庄野厚ほか 化学工学論文集 24 (1998) 609-614
- [6] Hailong Hou et al. Chinese Journal of Chemical Engineering 24 (2016) 79-85
- [7] F.J.Alguacil et al. Revista de Metalurgia Madrid 35 (1999) 255-260
- [8] Thomas Charles Owens Retrospective Theses and Dissertations Iowa State University (1967)