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,

\[ jM^{n+} + (x+j)n/2 \ \text{(RH)}_2 \rightleftharpoons M_j \text{R}_j \text{(RH)}_x + jnH^+ \] (1)

where \( M^{n+} \) is metal ion in aqueous phase and \( \text{(RH)}_2 \) 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 material, 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,

\[ V_{aq} C_{M,aq,0} + V_{org} C_{M,org,0} = V_{aq} C_{M,aq,eq} + V_{org} C_{M,org,eq} \] (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,

\[ E_M = C_{M,org,eq} V_{org}/C_{M,aq,0} V_{aq} \] (3)
\[ D_M = C_{M,org,eq}/C_{M,aq,eq} \] (4)

\[ jNa^+ + (x+j)n/2 \ \text{(RH)}_2 \rightleftharpoons Na_j \text{R}_j \text{(RH)}_x + jnH^+ \] (5)

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

\[ K_{Na^+} = D_{Na} C_{Na,org,eq}/(C_{Na,org,eq} + j^n C_{R_j,org,eq}) \] (6)

Based on this equation, \( \log(D_{Na}/C_{Na,org,eq}) \) was plotted over \( \log(C_{Na,org,eq}/C_{Na,org,eq}) \) in Figure 1(d), which is so-called slope analysis.
In the range of 5 < pH$_{eq}$, these plots gave straight line with $j$=1, $x$=1, and $K_{Na}$ = 3.12×10$^{-6}$. 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$_{Na,aq,eq}$] 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

\[ jNd^{3+} + (x+3j)/2 \text{ (RH)}_2 \rightarrow Nd_jR_{3j}^{'} \text{(RH)}_x^{'} + 3jH^+ \] (7)

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).

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

[8] Thomas Charles Owens Retrospective Theses and Dissertations Iowa State University (1967)