

Solvent extraction equilibrium of dysprosium(III) from nitric acid solutions with 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester

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Abstract: In view of the importance of solvent extraction of rare earth metals with the acidic organophosphorous reagent, the development of a chemically based model applicable to high concentration is desired. In the present study, the equilibrium distribution of dysprosium(III) between an aqueous nitric acid solution and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) was measured in the range of an initial aqueous dysprosium(III) concentration from 1.0×10^{-3} to 1.0×10^{-1} kmol/m³ and PC88A concentration from 0.16 to 0.65 kmol/m³ in Shellsol D70 as the diluent. The obtained data were analyzed using the chemically based model in order to correlate the equilibrium distribution ratios. In this model, dysprosium(III) was assumed to be extracted with the PC88A dimer as a 1:3 complex, the activities were considered for the aqueous species, and the effective concentration of the PC88A dimer was calculated using Alstad's empirical equation. As a result, the apparent extraction equilibrium constant was determined to be $253 (\text{kmol} \cdot \text{m}^{-3})^{-2}$ with an excellent correlation between the experiment and calculation results in the wide range of the logarithm of the distribution ratio from -2 to 3.5 . In conclusion, the methodology in this model would be effective for quantitative description of solvent extraction behavior of general rare earth elements as well as dysprosium.

Key words: solvent extraction; dysprosium; 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A); nitric acid; equilibrium

1 Introduction

Solvent extraction using acidic organophosphorus extractants has shown its effectiveness to separate and recover rare earth (RE) metals because of the high extraction and separation efficiencies[1–6]. In order to make the process more efficient, a chemically-based mathematical model for the numerical simulation applicable in the range from low ($\sim 10^{-5}$ kmol/m³ RE) to high ($> 10^{-2}$ kmol/m³ RE) metal concentrations should be developed. As the initial step, it is desired to establish an extraction equilibrium model for RE. Up to now, the fundamental extraction equilibrium studies of RE using acidic organophosphorus extractants were carried out mainly under the ideal conditions: low metal concentration with a constant ionic strength and activity coefficients of chemical species[2, 7–12]. There are only few studies[13–16] on the extraction equilibrium of RE at high concentrations.

In this work, by considering the recent increasing importance of dysprosium due to the use as the dopant to the neodymium magnet and the limited reserve in nature, the distribution of dysprosium(III) between aqueous nitric acid solution and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC88A) is measured in the range of an initial aqueous dysprosium(III) concentration from 1.0×10^{-3} to 1.0×10^{-1} kmol/m³ and PC88A concentration from 0.16 to 0.65 kmol/m³ in Shellsol D70 as the diluent. The data obtained are analyzed in order to develop a chemically based extraction equilibrium model employing the activities for the aqueous species and the effective concentration of the extractant in the organic phase.

2 Experimental

The aqueous working solutions were prepared by diluting dysprosium(III) nitrate hexahydrate ($\text{Dy}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Wako, 99.5% purity) with nitric acid at different

concentrations. The original concentrations of $\text{Dy}(\text{NO}_3)_3$ and HNO_3 in the aqueous phase solutions were from 0.001 to 0.1 kmol/m^3 and 0 to 0.8 kmol/m^3 , respectively. The organic phase contained PC88A (Daihachi) and Shellsol D70 (C11-C14 paraffins and naphthenes, Shell Chemicals), which were used as extractant and diluent, respectively. The concentration of PC88A in the organic phase was varied from 0.16 to 0.65 kmol/m^3 as monomer. The concentration of the extractant was determined by the nonaqueous neutralization titration.

Equal volume (20 cm^3) of the aqueous and organic working solutions was continuously shaken for 4 h in a water bath kept at (298 ± 0.1) K to attain equilibrium. Then the two phases were separated centrifugally for 5 min. The pH values of the aqueous phases were measured using an HM-60G pH meter (TOA-DKK). The concentrations of Dy in the aqueous phases were determined by EDTA titration and by ICP-AES (ULTIMA 2, Horiba) when they were relatively high and low, respectively. The concentrations of Dy in the organic phases were measured by the same method after completely stripping Dy from the organic phases into 2 kmol/m^3 HNO_3 . The distribution ratio, D , was calculated as the ratio of the total Dy molar concentration in the organic phase to that in aqueous phase, i.e.,

$$D = \frac{c(\overline{\text{Dy}})_T}{c(\text{Dy})_T} \quad (1)$$

where c , the subscript T, and over bar denote the molar concentration, the total concentration, and the organic phase, respectively.

Duplicated experiment under 18 different conditions indicated that the $\lg D$ was reproduced with the standard deviation of 0.040.

3 Results and discussion

The dependencies of $\lg D$ on the measured pH value, pH_a , at different initial concentrations of PC88A and $\text{Dy}(\text{NO}_3)_3$ (i.e. $c(\overline{\text{HR}})_{\text{in}}$ and $c(\text{Dy}^{3+})_{\text{in}}$) are shown in Figs.1 and 2, respectively. In Fig.1, the distribution ratios increase with increasing pH and $c(\overline{\text{HR}})_{\text{in}}$. When $c(\overline{\text{HR}})_{\text{in}}$ is constant and $c(\text{Dy}^{3+})_{\text{in}} \leq 0.01$ kmol/m^3 , $\lg D$ changes little with increasing $c(\text{Dy}^{3+})_{\text{in}}$ and increases linearly with increasing pH_a as shown in Fig.2. When $c(\text{Dy}^{3+})_{\text{in}} = 0.1$ kmol/m^3 , however, $\lg D$ approaches the constant value with increasing pH_a . This is because the initial Dy concentration exceeds the extraction capacity of the extractant.

It is accepted that Dy^{3+} is extracted by PC88A through the following cation exchange reaction at the low acid concentration [7, 14, 17], where $(\text{HR})_2$ is a dimer of PC88A:

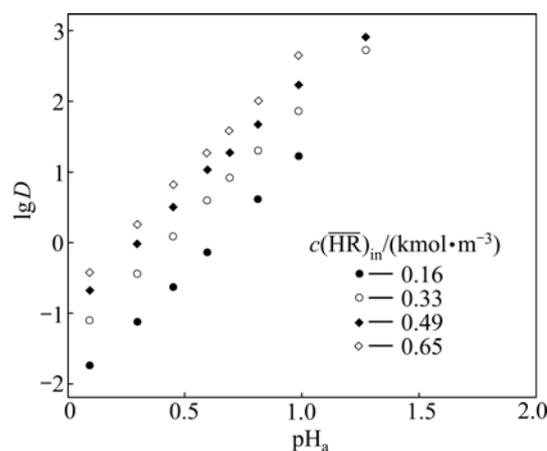


Fig.1 $\lg D$ vs pH_a for extraction of Dy with PC88A ($c(\text{Dy}^{3+})_{\text{in}} = 0.001$ kmol/m^3)

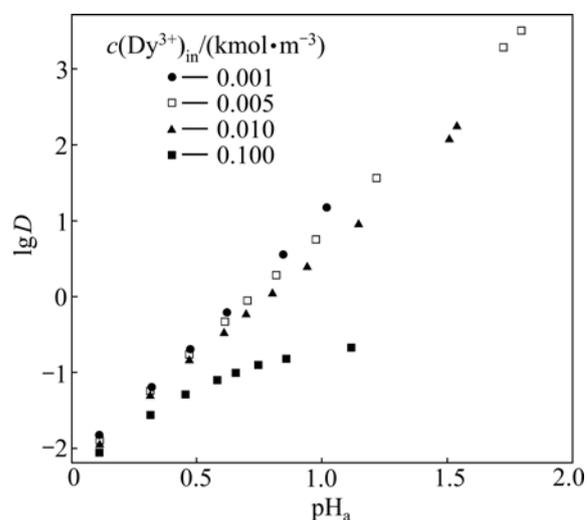


Fig.2 $\lg D$ vs pH_a for extraction of Dy with PC88A ($c(\overline{\text{HR}})_{\text{in}} = 0.16$ kmol/m^3)

The apparent extraction equilibrium constant, K_{ex} , is defined as

$$K_{\text{ex}} = \frac{c[\overline{\text{DyR}_3 \cdot (\text{HR})_3}] [a(\text{H}^+)]^3}{\{c[(\overline{\text{HR}})_2]\}^3 a(\text{Dy}^{3+})} \quad (3)$$

Here a is the activity related to c by

$$a = \gamma c \quad (4)$$

where γ is the activity coefficient. When $\overline{\text{DyR}_3 \cdot (\text{HR})_3}$ is the only extracted species in the organic phase, Eqs.(3) and (4) lead to

$$\lg D = \lg K_{\text{ex}} + 3\text{pH} + 3\lg c[(\overline{\text{HR}})_2] + \log \gamma(\text{Dy}^{3+})_T \quad (5)$$

where $\text{pH} = -\lg a(\text{H}^+)$.

The experimental values of $\lg D - 3\lg c[(\overline{\text{HR}})_2] - \log \gamma(\text{Dy}^{3+})_T$ with different extraction conditions are plotted versus pH according to Eq.(5) in Fig.3, where the

straight line with the slope of 3 is fitted by the least squares method. The K_{ex} value of $117 \text{ (kmol}\cdot\text{m}^{-3})^{-2}$ has been obtained as the antilogarithm of the intercept of the solid line. In Eq.(5), y values are calculated using an OLI Analyzer 2.0, a comprehensive analysis tool for complex aqueous and multisolvent electrolyte solution chemistry [18]. Here, the material balance of the extractant and the charge balance, respectively, shown as Eqs.(6) and (7) were considered. However, the linearity of the analysis results of the experimental data is not good as shown in Fig.3.

$$c(\overline{\text{HR}})_{in} = 2c[(\overline{\text{HR}})_2] + 6c[\overline{\text{DyR}}_3 \cdot (\overline{\text{HR}})_3] \quad (6)$$

$$c(\text{HNO}_3)_{in} = c(\text{H}^+) - 3c[\overline{\text{DyR}}_3 \cdot (\overline{\text{HR}})_3] \quad (7)$$

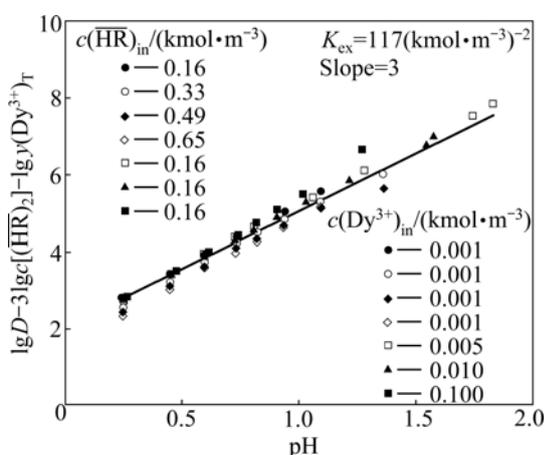


Fig.3 Analysis of extraction equilibrium data of Dy with PC88A based on Eq.(5)

The experimental values of $\lg D - 3\text{pH} - \lg y(\text{Dy}^{3+})_T$ with different initial HNO_3 concentrations (i.e., $c(\text{H}^+)$) when $c(\text{Dy}^{3+})_{in}$ is 0.001 kmol/m^3 are plotted versus $\lg c[(\overline{\text{HR}})_2]$ in Fig.4. The slope value of the fitted straight line is 2.3 that is less than the theoretical value of 3 shown in Eq.(5). Due to this fact together with the

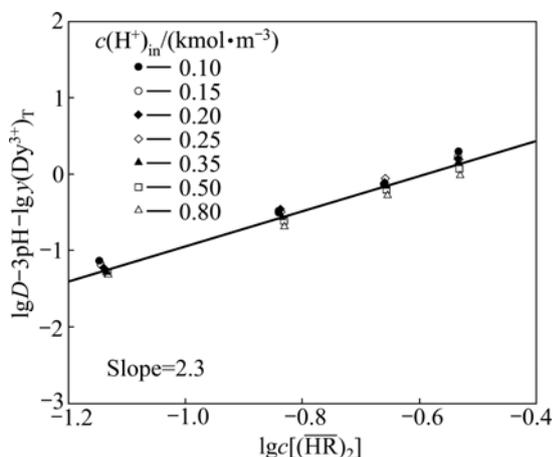


Fig.4 Analysis of extraction equilibrium data of Dy with PC88A at $c(\text{Dy}^{3+})_{in}$ of 0.001 kmol/m^3 based on Eq.(5)

unsatisfied linearity of the experimental data in Fig.3, it is concluded that the model based on Eq.(5) cannot describe the extraction equilibria successfully.

Several researchers pointed out for the acidic organophosphorous extractants that when aliphatic solvents were used as diluents, the slope values of the $\lg D$ vs logarithm of extractant dimer concentration plot were close to 2.5 in the extractant concentration range of $10^{-2} - 1 \text{ kmol/m}^3$ [19–22]. The negative deviation from the third-order dependence can be attributed to the nonideality of $(\overline{\text{HR}})_2$ caused by weak solute-solute interactions [22], where the interacting solute species is the PC88A dimer. This nonideality can be corrected by the effective concentration of the PC88A dimer, $c^*[(\overline{\text{HR}})_2]$, which is defined as

$$c^*[(\overline{\text{HR}})_2] = y^*[(\overline{\text{HR}})_2]c[(\overline{\text{HR}})_2] \quad (8)$$

where $y^*[(\overline{\text{HR}})_2]$ is the coefficient for the effective concentration of the extractant. The value of $y^*[(\overline{\text{HR}})_2]$ is assumed to vary with $c[(\overline{\text{HR}})_2]$ on the basis of the empirical equation by ALSTAD et al [23] as

$$\lg y^*[(\overline{\text{HR}})_2] = -A \cdot \{c[(\overline{\text{HR}})_2]\}^{0.5} \quad (9)$$

where A is a constant. Thus, K_{ex} is redefined as

$$K_{ex} = \frac{c[\overline{\text{DyR}}_3 \cdot (\overline{\text{HR}})_3][a(\text{H}^+)]^3}{c^*[(\overline{\text{HR}})_2]^3 a(\text{Dy}^{3+})} \quad (10)$$

Eq.(5) is rewritten as

$$\lg D = \lg K_{ex} + 3\text{pH} + 3\lg c[(\overline{\text{HR}})_2] - 3A \cdot c\{[(\overline{\text{HR}})_2]\}^{0.5} + \lg y(\text{Dy}^{3+})_T \quad (11)$$

When the K_{ex} and A values are given, the value of the right hand side of Eq.(11) can be obtained from the experimental data. Therefore, the least squares method minimizing the difference between both sides of Eq.(11) was applied in order to determine K_{ex} and A . As a result, the values of $K_{ex} = 253 \text{ (kmol}\cdot\text{m}^{-3})^{-2}$ and $A = 0.473 \text{ (kmol}\cdot\text{m}^{-3})^{-0.5}$ were obtained, where the standard deviation in terms of $\lg D$ of Eq.(11) was 0.021.

Figs.5 and 6 show the analysis results using Eq.(11) in which the nonideality of the extractant was considered. It is observed that the linearity of Fig.5 becomes better as compared with Fig.3 and the slope of the fitting line in Fig.6 is increased to 3.0 which is 2.3 in Fig.4.

Fig.7 is the graphical expression for the result of the least squares analysis of Eq.(11) showing that the data points lie on the straight line of the unit slope with the y-intercept of $\lg K_{ex}$ in which the coefficient of determination, R^2 , is close to 1.

The value of A in this research is in the same order as that reported by ALSTAD et al [23] for the extraction

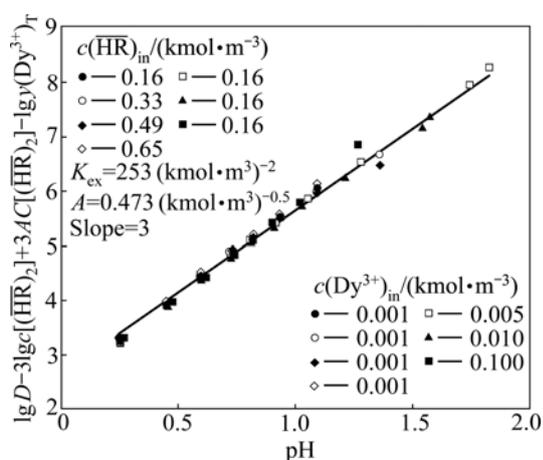


Fig.5 Analysis of extraction equilibrium data of Dy with PC88A based on Eq.(11)

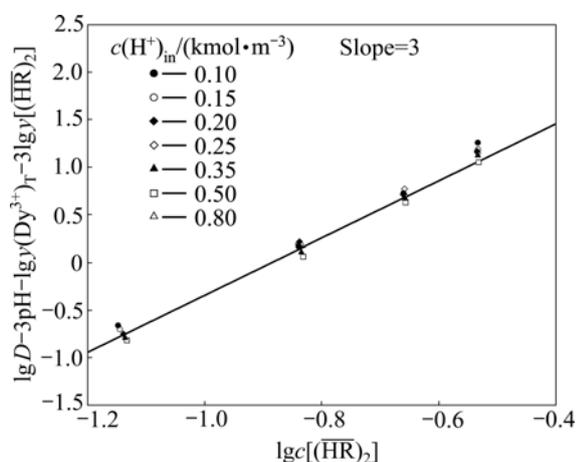


Fig.6 Analysis of extraction equilibrium data of Dy with PC88A at $c(\text{Dy})_{\text{in}}$ of 0.001 kmol/m^3 based on Eq.(11)

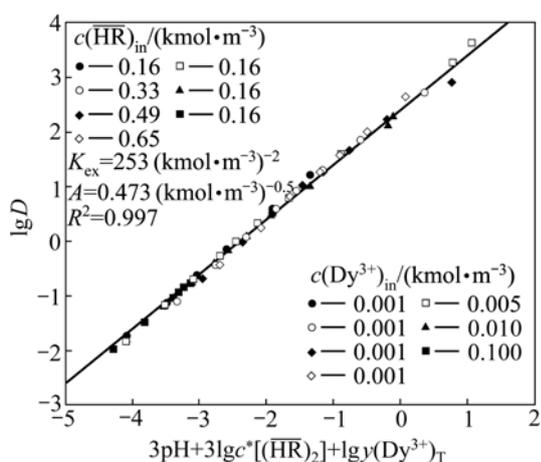


Fig.7 Relationship between experimental data of $\lg D$ and $3\text{pH} + 3\lg c^*[(\text{HR})_2] + \lg y(\text{Dy}^{3+})_{\text{T}}$

of rare earth metals by di(2-ethylhexyl)phosphoric acid diluted in Shellsol T ($0.83 \text{ (kmol}\cdot\text{m}^{-3})^{-0.5}$).

From the good analysis results shown in Figs.5–7, it is concluded that Eq.(11) is successful to describe the extraction equilibrium of Dy with PC88A. Because of

the similarity of the extraction behavior, the methodology in this model would be effective also for the quantitative description of the extraction equilibria of other rare earth metals with PC88A.

4 Conclusions

The equilibrium distribution of Dy(III) between the aqueous nitric acid solution and the organic phase containing PC88A as the extractant and Shellsol D70 as the diluent was measured over wide concentration ranges of dysprosium, hydrogen ion and PC88A. A chemical equilibrium model considering the activities of the aqueous species and the effective concentration of the extractant was developed by analyzing the distribution data. The Alstad's empirical equation was found to be applicable for calculating the effective concentration of the PC88A dimer. As a result, excellent correlation between the model and the experiment was obtained in the wide $\log D$ range from -2 to 3.5 with the apparent extraction equilibrium constant of $253 \text{ (kmol}\cdot\text{m}^{-3})^{-2}$. Consequently, the methodology in this model would be effective for quantitative description of solvent extraction behavior of general RE elements as well as dysprosium.

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Appendices

- a* Activity
- A* Constant in the Alstad's empirical equation $((\text{kmol}\cdot\text{m}^{-3})^{-0.5})$
- c* Concentration ($\text{kmol}\cdot\text{m}^{-3}$)
- c** Effective concentration of the extractant ($\text{kmol}\cdot\text{m}^{-3}$)
- D* Distribution ratio
- HR Extractant monomer
- K_{ex} Apparent extraction equilibrium constant $((\text{kmol}\cdot\text{m}^{-3})^{-2})$
- R^2 Coefficient of determination
- y* Activity coefficient
- y** Coefficient for the effective concentration of the extractant
- Superscript (—) Organic phase
- Subscript T Total

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