Solid-Liquid Extraction of Some Lanthanide Complexes with 1-Nitroso -2- Naphthol

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Abstract: The extraction behavior of Sm(III), Eu(III) ,Er(III) and Yb(III) with 1- nitroso -2-naphthol (HA) in paraffin has been studied. The composition of extracted complexes has been determined to be LnA_3 by slope analysis method. The effect of temperature on extraction system is also investigated and thermodynamic parameters are obtained.

Keywords: Solid-liquid, lanthanide, 1-nitroso-2-naphthol.

1-Nitroso-2-naphthol (HA) is a highly selective reagent for the spectrophotometric determination of Co (III)[1]. Rao *et al*. have studied the equilibrium extraction behavior of mixed ligand complexes of trivalent Sm, Eu and Dy ions with 1-nitroso-2-naphthol and trioctylphosphine oxide[2], Dyrssen *et al*. have examined the complex formation of Th (IV) with 1-nitroso-2-naphthol and 2-nitroso-1-naphthol[3], however, there is no report for the extraction mechanism of lanthanides being attempted with this reagent. In recent years, our lab has done some work on the solid - liquid extraction of rare earth ions[4]. This paper investigates the extraction behavior of trivalent Sm, Eu, Er and Yb with HA at 70℃ using paraffin wax as a diluent. The extraction equilibrium constants and the thermodynamic data have been obtained. The results show that extraction reaction is endothermic and raising temperature is favourable to extraction of lanthanides with HA.

At constant pH, the percentage extraction was observed by varying the concentration of HA in paraffin wax. At fixed concentration of HA, the plot of logD *vs*. pH yields straight lines with slopes close to 3. Therefore, in the system of Ln(III) - HA - PC, the extraction reaction can be described as follows:

$$Ln^{3+} + 3\,HA_{(o)} === (LnA_3)_{(o)} + 3H^+ \qquad (1)$$

At constant Ln^{3+} and HA concentration, varying temperature of the extraction reaction, the distribution ratios of the lanthanides and the pH value of the aqueous phase are determined. The relationship between logK and $1/T\mathrm{x}10^3$ is plotted in **Figure 1**. Supposing in the experiment temperature range, the value of the enthalpy change (ΔH) is constant, then eq. (2) is obtained as follows:

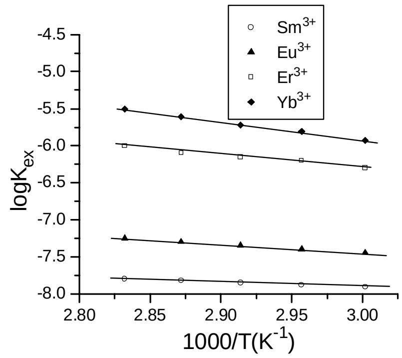
$$\log K = -\frac{\Delta H}{2.303\,R\,T} + C \qquad (2)$$

Based on eq. (2) , the value of the enthalpy change (ΔH_{ex}) can be calculated from the slope. The value of the entropy change (ΔS_{ex}) and the value of the Gibbs free energy (ΔG_{ex}) are obtained from the following expressions.

$$\Delta S = \frac{\Delta H - \Delta G}{T} \qquad (3)$$

$$\Delta G = -RT2.303\log K_{ex} \qquad (4)$$

Figure 1 Plot of $\log K_{ex}$ *vs*. $1/T \times 1000$ for the extraction with HA



$Ln^{3+} = 2 \times 10^{-5}$ mol/L. $[HA]_o = 0.024$ mol/L. Sm, pH = 6.56; Eu, pH = 6.42; Er, pH = 6.24; Yb, pH = 6.15.

The above results are listed in **Table 1.** According to **Table 1,** ΔH_{ex} value is positive and increases gradually from Sm^{3+} to Yb^{3+}. This indicates that the reaction is endothermic and higher temperature is helpful to the extraction of the lanthanide ions. For the Gibbs free energy, the value is positive and reduces gradually with increasing atomic number. The values of the entropy change increase gradually from negative to positive. On the basis of these results, we think that a higher temperature is favourable to the extraction. Moreover, for the heavy rare earth elements , extraction efficiency is relatively better.

Table 1. Thermodynamic parameters at 70℃ for system Ln^{3+} (2.0×10^{-5} mol/L) /$NaClO_4$ - $HClO_4$ (μ =0.10) /HA-PC

Ion	ΔH_{ex} (KJ)	ΔG_{ex} (KJ)	ΔS_{ex} ($J \cdot K^{-1}$)
Sm	15.96	51.58	- 103.79
Eu	25.53	48.10	- 65.76
Er	30.64	40.08	- 27.51
Yb	43.76	37.46	18.36

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