Extraction Kinetics of Ytterbium with Salicylaldehyde *n*-Octanohydrazone into 1,2-Dichloroethane in the Presence of Both Tributyl Phosphate and Perchlorate

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The kinetics of the solvent extraction of ytterbium(III) from aqueous media with a 1,2-dichloroethane solution of salicylaldehyde *n*-octanohydrazone (SOH or H_2L) in the presence of both tributyl phosphate (TBP) and perchlorate have been studied at 25±0.1°C and an ionic strength of 0.2 M (1 M=1 mol dm^{-3}). The rate of extraction was first-order with respect to the concentrations of ytterbium(III) in the aqueous phase and SOH in the organic phase, inversely first-order with respect to the hydrogen-ion concentration and zero- and first-order with respect to the TBP concentration in the organic phase. Two mechanisms operate for this extraction, depending on the TBP concentration in the organic phase. One is a mechanism in which the formation of the first complex, $[Yb(HL)]^{2+}$, between Yb^{3+} and HL^- in the region of $\log [TBP]_{org} < -0.95$ becomes the rate-determining step, and the other is that in which the formation of the first complex, $[Yb(HL)(TBP)]^{2+}$, between $[Yb(TBP)]^{3+}$ and HL^- in the region of $\log [TBP]_{org} > -0.85$ is the rate-determining step. The rate constant and activation parameters for the former reaction were calculated, but those for the latter one could not be determined.

In a previous work[1)] the extraction equilibria of praseodymium, europium, and ytterbium ions with salicylaldehyde *n*-alkanohydrazones (SAAH or H_2L) from aqueous solutions containing both tributyl phosphate (TBP) and perchlorate into 1,2-dichloroethane were investigated. As the result, it was found that these lanthanoid ions (Ln^{3+}) were extracted in the form of $(Ln^{3+})(HL^-)_2(TBP)_3(ClO_4^-)$ and SAAH having a long alkyl chain in its molecule such as salicylaldehyde *n*-octanohydrazone (SOH or H_2L) is a very useful extractant for the lanthanoid ions because the distribution of the SAAH and its lanthanoid complexes into 1,2-dichloroethane is very large. In order to more fully understand the extraction behavior and clarify the extraction mechanism, the extraction of the above three lanthanoid ions with SOH into 1,2-dichloroethane in the presence of both TBP and perchlorate has kinetically been investigated in this work. Unfortunately, no reliable results were obtained for the extraction kinetics of praseodymium(III) and europium(III) because their extraction rates were too fast to measure, so the results on the extraction kinetics of ytterbium(III) are described here.

Experimental

Reagents and Apparatus. Standard Ytterbium(III) Solution. Prepared by dissolving ytterbium oxide of 99.999% grade in dilute nitric acid.

SOH Solution. Prepared by dissolving SOH synthesized in the previous work[1)] in 1,2-dichloroethane.

Buffer Solutions. Solutions of 0.2 M (M=mol dm^{-3}) 2-morpholinoethanesulfonic acid (MES)-0.2 M sodium hydroxide system were used.

Other reagents and apparatus were the same as those used in the previous work.[1)]

Procedure. The kinetic runs were carried out under pseudo-first-order excess of SOH in the organic phase over ytterbium(III) in the aqueous phase.

A 10-cm^3 portion of an aqueous solution containing 42.6 μg of ytterbium(III), 2 cm^3 of 0.2 M MES buffer solution and a sufficient amount of 1 M sodium perchlorate solution to keep the ionic strength at 0.2 M was placed in a 100-cm^3 separating funnel. After thermal equilibration (ca. 30 min), an equal volume of 1,2-dichloroethane containing SOH and TBP was added carefully. The reaction was begun by shaking. The experiments were carried out in the "plateau" region where a further increase in shaking speed had no effect on the rate of extraction. After shaking for a predetermined time (from 5 to 30 min), the funnel was allowed to stand for 10 min to ensure complete phase separation. The ytterbium concentration in the organic phase was determined by measuring the absorbance of the extract at 371 nm against a reagent blank prepared under identical conditions. The concentration of ytterbium in the aqueous phase was calculated by subtracting the concentration in the organic phase from the initial concentration.

Results and Discussion

In general, since the rate of complexation in the extraction depends on the concentrations of metal ion, ligand, hydrogen ion and adductant, the rate of formation of the ytterbium complex can be assumed as

$$-\frac{d[Yb^{3+}]}{dt} = k'[Yb^{3+}]^a[H_2L]^b_{org}[H^+]^c[TBP]^d_{org}, \quad (1)$$

where t is the reaction time, k' is the rate constant, a, b, c, and d are the reaction orders with respect to the concentrations of ytterbium ion, SOH, hydrogen ion, and TBP, respectively, and the subscript org denotes the concentration in the organic phase.

Reaction Order with Respect to Yttebium-Ion Concentration. Under a pseudo-first-order excess of SOH and at a constant pH and constant concentrations

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of SOH, TBP, and perchlorate, the rate of extraction of ytterbium(III) into 1,2-dichloroethane is expressed as

$$-\frac{d[Yb^{3+}]}{dt} = k_{obsd}[Yb^{3+}]^{a}, \tag{2}$$

where k_{obsd} is the observed pseudo-first-order rate constant. If a=1, we can integrate Eq. 2 and derive Eq. 3:

$$\ln\frac{[Yb^{3+}]_{t=0}}{[Yb^{3+}]_{t=t}} = k_{obsd}t, \tag{3}$$

where $[Yb^{3+}]_{t=0}$ and $[Yb^{3+}]_{t=t}$ are the concentrations of ytterbium ion in the aqueous phase at t=0 and t=t, respectively. The plots of $\ln([Yb^{3+}]_{t=0}/[Yb^{3+}]_{t=t})$ versus t when ytterbium(III) was extracted with changing the pH and keeping the other variables constant are shown in (A) in Fig. 1, and those when ytterbium(III) was likewise extracted with changing the SOH concentration in (B) in Fig. 1. The plots in both cases are linear through the origin, which indicates that the complexation reaction of ytterbium(III) with SOH in this extraction system is first-order with respect to the ytterbium(III) concentration, i.e., a=1.

Reaction Order with Respect to Hydrogen-Ion Concentration. Taking the above results into considerations, Eq. 4 is finally obtained from Eqs. 1 and 2:

$$\log k_{obsd} = \log k' + b\log[H_2L]_{org} - c\,pH + d\log[TBP]_{org}. \tag{4}$$

The plot of $\log k_{obsd}$ versus pH when $[SOH]_{org}$, $[TBP]_{org}$, and $[ClO_4^-]$ are kept constant gave a straight line with a slope of unity as shown in (A) in Fig. 2, which indicates that the reaction order with respect to the hydrogen-ion concentration is inversely first-order, i.e., $c=-1$.

Reaction Order with Respect to Extractant Concentration. The plot of $\log k_{obsd}$ versus $\log [H_2L]_{org}$ with keeping the other valiables constant was linear with a slope of unity as shown in (B) in Fig. 2, indicating that the reaction order with respect to the extractant concentration is first-order, i.e., b=1.

Reaction Order with Respect to TBP Concentration. The plot of $\log k_{obsd}$ versus $\log [TBP]_{org}$ was independent of the TBP concentration for $\log [TBP]_{org} < -0.95$ but its slope increased with an increase in the value of $\log [TBP]_{org}$ until the slope approaches unity as shown in (C) in Fig. 2. This indicates that the reaction order with respect to the TBP concentration depends on the TBP concentration and in particular is zero-order, i.e., d=0 in the lower concentration region of TBP, but first-order, i.e., d=1 in the higher concentration region of TBP.

Reaction Mechanisms. Since the major species of ytterbium(III), the extractant and the adductant in the aqueous phase under the conditions studied are considered to be Yb^{3+}, HL^-, and TBP, Eqs. 5, 6, 7, 8, 9, and 10 are involved in the equilibria and reactions in this extraction system:

$$H_2L_{org} \rightleftharpoons H_2L \quad K_{D,L} = [H_2L]_{org}/[H_2L] \tag{5}$$

$$H_2L \rightleftharpoons H^+ + HL^- \quad K_a = [H^+][HL^-]/[H_2L] \tag{6}$$

$$TBP_{org} \rightleftharpoons TBP \quad K_{D,TBP} = [TBP]_{org}/[TBP] \tag{7}$$

$$Yb^{3+} + TBP \rightleftharpoons [Yb(TBP)]^{3+}$$
$$\beta = [[Yb(TBP)]^{3+}]/[Yb^{3+}][TBP] \tag{8}$$

$$Yb^{3+} + HL^- \xrightarrow{k_1} [Yb(HL)]^{2+} \tag{9}$$

$$[Yb(TBP)]^{3+} + HL^- \xrightarrow{k_2} [Yb(HL)(TBP)]^{2+} \tag{10}$$

where $K_{D,L}$ and $K_{D,TBP}$ are the partition coefficients of SOH and TBP, respectively, between 1,2-dichloroethane and water, K_a is the acid dissociation constant of SOH, β is the formation constant of the $[Yb(TBP)]^{3+}$ complex and k_1 and k_2 represent the rate constants of the two reaction paths expressed by Eqs. 9 and 10, respectively. If it is assumed that the rate-determining steps of this extraction system are formation of the $[Yb(HL)]^{2+}$ complex in the aqueous phase (expressed by Eq. 9) for extraction in the lower TBP concentration region and that of the $[Yb(HL)(TBP)]^{2+}$ complex in the aqueous phase (expressed by Eq. 10) for extraction in the higher TBP concentration region, the following equations can be derived as the rate equations:

(i) for $\log [TBP]_{org} < -0.95$

$$-\frac{d[Yb^{3+}]}{dt} = k_1[Yb^{3+}][HL^-] = k_1[Yb^{3+}]\frac{K_a[H_2L]_{org}}{K_{D,L}[H^+]} \tag{11}$$

(ii) for $\log [TBP]_{org} > -0.85$

$$-\frac{d[Yb^{3+}]}{dt} = k_2[Yb\cdot TBP^{3+}][HL^-] = k_2\beta[Yb^{3+}]\frac{K_a[H_2L]_{org}[TBP]_{org}}{K_{D,L}K_{D,TBP}[H^+]} \tag{12}$$

Equations 11 and 12 are consistent with the kinetic experimental results described above that the rate of the extraction is always first-order with respect to the concentrations of ytterbium(III) and SOH, inversely first-order with respect to the hydrogen-ion concentration and zero- and first-order with respect to the TBP concentration.

Therefore it can be concluded that there are two mechanisms for the extraction of ytterbium(III) with SOH in the presence of both TBP and perchlorate: One is a reaction occurred in the region of $\log [TBP]_{org} < -0.95$, where the formation of $[Yb(HL)]^{2+}$ is the rate-determining step, and the other is one occurred in the region of $\log [TBP]_{org} > -0.85$, where the complexation of $[Yb(TBP)]^{3+}$ with HL^- is the rate-determining step. The first mechanism is independent of the TBP concentration, first-order dependent on the concentrations of ytterbium(III) and SOH and inversely first-order dependent on the hydrogen-ion concentration, the second

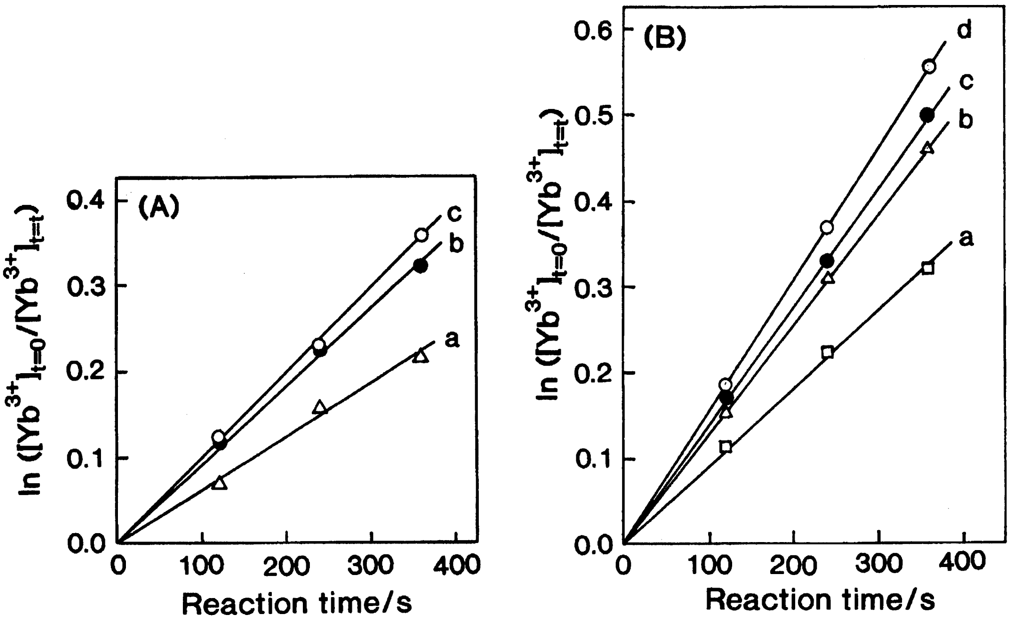

Fig. 1. Plots of log $\{[Yb^{3+}]_{t=0}/[Yb^{3+}]_{t=t}\}$ vs. t for the ytterbium(III)–SOH system when(A) pH was varied and (B) SOH concentration was varied. Yb(III), 2.46×10^{-5} M; pH–a, 5.45; b, 5.37; c, 5.20 in (A); 5.38 in (B); SOH–5.64×10^{-4} M in (A); a, 4.23×10^{-4}M; b, 5.64×10^{-4}M; c, 6.24×10^{-4}M; d, 7.05×10^{-4} M in (B); TBP, 12% (v/v); ionic strength, 0.2 M(NaClO$_4$); temperature, 25±0.1°C;$v_{aq}=v_{org}=10$ ml.

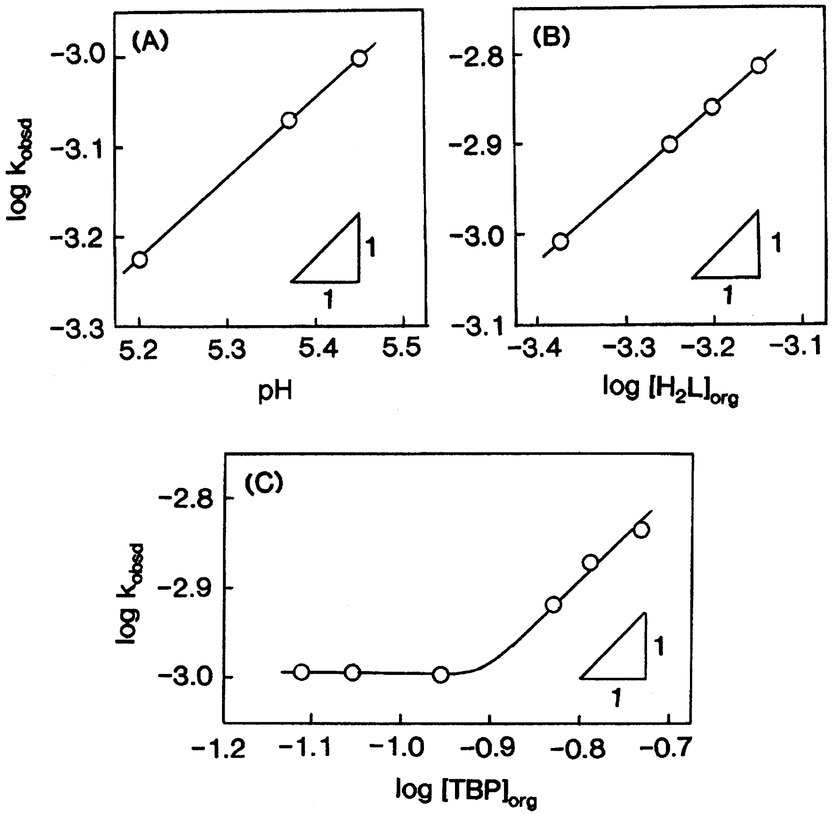

Fig. 2. Plots of (A) log k_{obsd} vs. pH, (B)log k_{obsd}vs. log $[H_2L]_{org}$ and (C)log k_{obsd} vs. log $[TBP]_{org}$ for the ytterbium(III)-SOH system. Yb(III), 2.46×10^{-5}M; SOH, 5.64×10^{-4} M in (A) and (C); pH, 5.38 in (B) and 5.56 in (C); TBP, 12% (v/v) in (A) and (B); ionic strength,0.2 M (NaClO$_4$); temperature, 25±0.1°C;$v_{aq}=v_{org}=10$ ml.

one being first-order dependent on the concentrations of ytterbium(III), TBP and SOH and inversely first-order dependent on the hydrogen-ion concentration.

Rate Constants and Activation Parameters.

Table 1. Rate Constant and Activation Parameters at 25±0.1°C and an Ionic Strength of 0.2 M

Rate constant, k_1	1.28×10^8	$M^{-1}\ s^{-1}$
Activation energy, E_a	34.5	$kJ\ mol^{-1}$
Activation enthalpy, $\Delta H^\ddagger$	32.0	$kJ\ mol^{-1}$
Activation entropy, $\Delta S^\ddagger$	17.7	$J\ K^{-1}\ mol^{-1}$
Activation free energy, $\Delta G^\ddagger$	26.7	$kJ\ mol^{-1}$

From Eqs. 2, 11, and 12, Eqs. 13 and 14 are obtained:

$$\log k_{\mathrm{obsd}} = \log \frac{k_1 K_a}{K_{D,L}[H^+]} + \log [H_2L]_{\mathrm{org}} \qquad (13)$$

$$\log k_{\mathrm{obsd}} = \log \frac{k_2 \beta K_a [H_2L]_{\mathrm{org}}}{K_{D,L} K_{D,\mathrm{TBP}}[H^+]} + \log [\mathrm{TBP}]_{\mathrm{org}} \qquad (14)$$

Since the rate constant k_2 cannot be determined because the formation constant, β, of the $[\mathrm{Yb(TBP)}]^{3+}$ complex is unknown, only the rate constant k_1 was determined. As is obvious from Eq. 13, the value of k_1 can be calculated from the intercept of the plot of $\log k_{\mathrm{obsd}}$ versus $\log [H_2L]_{\mathrm{org}}$ shown in (B) in Fig. 2, the result being given in Table 1, where the following values were used: $\log K_a = 9.16$, $\log K_{D,L} = 4.43$,[1] and $\log [H^+] = -5.38$.

Figure 3 shows the temperature dependence of the rate constants k_1 and k_2 in the range 15—25°C. The graphs of $\log k_1$ versus $1/T$ and $\log (k_2\beta/K_{D,\mathrm{TBP}})$ versus $1/T$ (where T denotes absolute temperature) gave straight lines (Arrhenius plots). The activation energy, E_a, activation enthalpy, $\Delta H^\ddagger$, activation entropy, $\Delta S^\ddagger$, and activation free energy, $\Delta G^\ddagger$, at 25±0.1°C and an ionic strength of 0.2 M in the lower TBP concentration region were calculated, the results being also given in Table 1.

The k_1 value is large, but seems to be reasonable compared with rate constants for other complexation reactions of ytterbium(III), e.g., $1.3\times10^7\ M^{-1}\ s^{-1}$ for the complexation reaction with murexide at 12°C[2] and $6.3\times10^7\ M^{-1}\ s^{-1}$ for that with anthranilic acid at 12.5°C.[3] This indicates that it is not necessarily needful for this extraction system to take into consideration the interfacial reaction such as observed in the extraction of copper(II) and nickel(II) with 2′-hydroxy-5′-nonylbenzophenone oxime.[4] On the other hand, the values of E_a, $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta G^\ddagger$ are not so large. The data shown in Table 1 suggest that ytterbium(III) forms the complex with SOH very rapidly and easily and that the resultant complex has a rather soft, bulky structure.

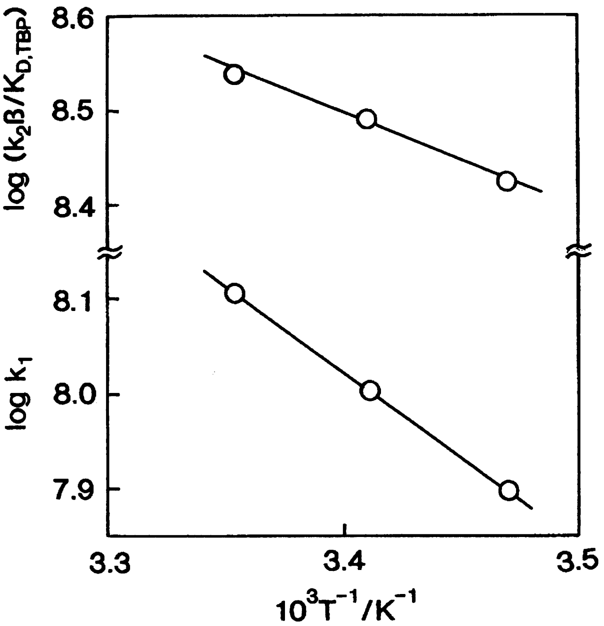

Fig. 3. Arrhenius plots. Yb(III), 2.46×10^{-5}M; SOH, 5.64×10^{-4}M; pH, 5.38; TBP, 12% (v/v); ionic strength, 0.2 M ($NaClO_4$); $V_{aq} = V_{org} = 10$ ml.

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