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Solvent Extraction of Lanthanoids(III) and Yttrium(III) with *N*-(2,2-Dimethylvaleryl)-*N*-phenylhydroxylamine

Tohru SAITOH,* Manabu OKUYAMA, Tamio KAMIDATE, Hiroto WATANABE, and Kensaku HARAGUCHI†
Faculty of Engineering, Hokkaido University, Kita-ku, Sapporo, Hokkaido 060
†Hokkaido National Industrial Research Institute, Toyohira-ku, Sapporo, Hokkaido 062

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Lanthanoids(III) and yttrium(III) were extracted with *N*-(2,2-dimethylvaleryl)-*N*-phenylhydroxylamine (DV-PHA) having a tertiary alkyl group attached to the carbonyl group. The distribution ratio of a lanthanoid(III) ion between the carbon tetrachloride and the aqueous phases was measured as functions of the pH and DV-PHA concentration at 298 K and an ionic strength of 0.1 ($NaNO_3$). The aqueous phase involved sodium tartrate (1.0×10^{-2} mol dm^{-3}). Lanthanoids(III) were extracted as a self-adducted chelate, $ML_3(HL)_3$, with DV-PHA (HL). The separation factors for pairs of Yb/Eu and Yb/Y were considerably greater than those of bis-(2-ethylhexyl)hydrogenphosphate. The excellent selectivity of DV-PHA was attributable to a greater inductive effect of the tertiary alkyl group than those of the primary and secondary alkyl groups.

In hydrometallurgical separations, chelating extractants with long-chain alkyl substituents have received a great deal of attention.[1] This is not only due to the formation of a stable chelate with a variety of metal ions at an appropriate pH, but also due to the easy back extraction of the chelate by a slight modification of the pH. However, limited studies have been made on the effect of alkyl substituents on the selectivity of the chelating extractants.[2,3]

Previously, we had tested a series of *N*-alkylcarbonyl substituted *N*-phenylhydroxylamines (R-PHAs) having primary and secondary alkyl groups for the extraction of lanthanoids(III).[4] Of the R-PHAs tested, *N*-(2-hexyldecanoyl)-*N*-phenylhydroxylamine (HD-PHA) with a secondary alkyl substituent was superior to R-PHAs, such as *N*-octanoyl-*N*-phenylhydroxylamine (C8-PHA), having a primary alkyl substituent for intragroup separations of heavy lanthanoids (III). The branching of alkyl substituents seems to enhance the selectivity of R-PHAs. Hence, in the present study we were concerned with an evaluation of the selectivity of *N*-(2,2-dimethylvaleryl)-*N*-phenylhydroxylamine (DV-PHA) having a tertiary alkyl substituent in the extraction of lanthanoids(III).

Experimental

Reagents. DV-PHA was synthesized by the addition of 2,2-dimethylvarelyl chloride (14.1 g, 0.95 mol) into an ether solution (300 cm^3) containing phenylhydroxylamine (10.9 g, 0.10 mol) and sodium hydrogencarbonate (12.6 g, 0.15 mol) at 0 °C. A white crystalline product was obtained by the recrystallization in a 1 : 1 ether/petroleum ether solution. The conformation was made by an elemental analysis and measuremts of the H-NMR, IR, and mass spectra. Other R-PHAs used were synthesized and purified in a similar manner and had already been prepared in our previous studies.[4,5] They were *N*-butyryl-*N*-phenylhydroxylamine (C4-PHA), *N*-(2-propylvaleryl)-*N*-phenylhydroxylamine (PV-PHA), and *N*-(2,2-dimethylpropionyl)-*N*-phenylhydroxylamine (*t*C5-PHA). Stock solutions of metal ions(III) (1.0×10^{-2} mol dm^{-3}) were prepared by dissolving their nitrate hexahydrates (99.99%, Raremetalic Inc.) in 0.01 mol dm^{-3} nitric acid. They were standardized by EDTA titration. All of the other reagents used were of analytical grade.

Apparatus. DV-PHA extracted into the organic phase was determined using a Hitachi 320 double-beam spectrophotometer equipped with 1-cm quartz cells. The concentration of lanthaniods(III) in the aqueous phase was measured with a Shimadzu GVM-1000P inductively plasma atomic emission spectrometer. A Toa HM-15A pH meter was employed for measuring the pH in the aqueous phase. A Yamato SA-31 shaker was used for mixing the two phases. A Kokusan H-200 centrifuge was also used for a rapid and complete separation of the two phases.

Procedure for Extracting DV-PHA. A 50.0-cm^3 portion of an aqueous solution and a 5.00-cm^3 portion of carbon tetrachloride containing 1.00×10^{-4} mol dm^{-3} of DV-PHA were shaken in a 60-cm^3 glass vial for 1 h, which was sufficient for equilibration, at 298±1 K. The pH of the aqueous solution was controlled by the addition of a phosphate buffer (0.01 mol dm^{-3}) in conjunction with sodium hydroxyde. The ionic strength was kept at 0.1 with sodium nitrate. The DV-PHA concentration in the organic phase was determined by measuring the absorbance at 260 nm. The concentration in the aqueous phase was calculated on the basis of the material balance of DV-PHA.

Procedure for the Extraction of Lanthanoids(III). A 30.0-cm^3 aliquot of an aqueous solution containing a specified metal ion (5.00×10^{-5} mol dm^{-3}), sodium nitrate (0.1mol dm^{-3}), sodium tartrate (1.0×10^{-2} mol dm^{-3}), and an appropriate buffer component (1×10^{-3} mol dm^{-3}) was shaken, with a 5.00-cm^3 aliquot of carbon tetrachloride in which the DV-PHA concentration was in the range from 1.58×10^{-3} to 1.58×10^{-2} mol dm^{-3} for 1 h equilibration at 298±1 K. The buffer components used were 2-(*N*-morphorino)ethanesulfonic acid, tris(hydroxymethyl)-aminomethane, and 3-cyclohexylaminopropanesulfonic acid. The ionic strength was kept at 0.1 with sodium nitrate. Sodium tartrate was employed in order to prevent the hydrolysis of the lanthanoids(III). After centrifuging for 10 min at 1500 rpm, the aqueous phase was submitted to a determination of the pH as well as the metal-ion concentrations.

The metal concentration in the organic phase was calculated by using a material-balance technique.

Synthesis of Ytterbium(III) Chelates and Their IR Spectra. The ytterbium(III) chelate with PV-PHA precipitated from dilute solutions of the components in near-stoichiometric compositions at pH 8 and 60 °C. Here, PV-PHA was dissolved in aqueous ethanol. The chelate was dried in vacuo at 45 °C. Other chelates with C4-PHA and *t*C5-PHA were prepared by the same method as mentioned above. The IR spectra of these chelates were taken in potassium bromide pellets with an FT-IR instrument (Perkin–Elmer 1600).

Results and Discussion

Distribution Equilibrium of DV-PHA. The distribution ratio (D_L) of DV-PHA (HL) between the two phases can be expressed as a function of hydrogen-ion concentration ($[H^+]$),

$$\log D_L = \log K_d - \log(1 + K_a[H^+]^{-1}), \quad (1)$$

where K_a is the acid dissociation constant and K_d is the distribution constant of DV-PHA. A plot of log D_L against the pH in the aqueous phase is given in Fig. 1. A curve-fitting method[6] was applied to determine a set of $K_a$and K_d values for DV-PHA. The thus-obtained pK_a and log K_d values are 10.05 and 1.96, respectively.

Distribution Equilibria of Lanthanoids(III). Since the tartrate ion is present in the aqueous phase, the distribution ratio (D_M) of a metal ion (M^{n+}) between the two phases can generally be expressed by

$$D_M = [ML_n(HL)_m]_o/[M^{n+}]\alpha_M, \quad (2)$$

where one subscript (o) denotes the organic phase and α_M is the side-reaction coefficient of a metal ion for complexation with tartrate, tart^{2-}. The side reaction coefficient is defined by

$$\alpha_M = 1 + \Sigma\beta_i[\text{tart}^{2-}]^i. \quad (3)$$

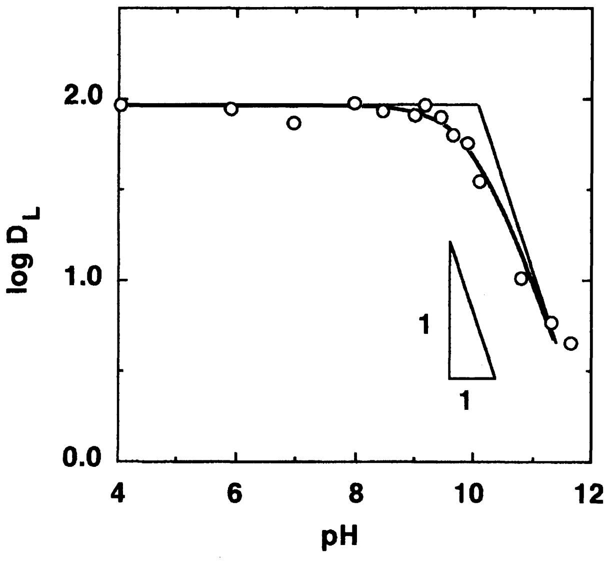

Fig. 1. Log D_L as a function of the pH.

Here, β_i is the stability constant for a tartrate complex and the numerical index (i) on the stability constant gives the number of tartrate ions in the complex, M-$(\text{tart})_i^{(3-2i)}$. Thus, Eq. 2 is reduced to

$$D_M = K_{ex}\alpha_M[HL]_o^{(n+m)}/[H^+]^n, \quad (4)$$

where K_{ex} is the extraction constant defined by

$$K_{ex} = [ML_n(HL)_m]_o[H^+]^n/[M^{n+}][HL]_o^{(n+m)}. \quad (5)$$

The second acid dissociation constant of tartaric acid (H_2tart) is $10^{-3.94}$[7] and, thus, the dianion, tart^{2-}, should be present exclusively under the present conditions where the pH range is above 3.94. Accordingly, the α_M term can be regarded as being a constant. We can therefore define the conditional extraction constant (K'_{ex}) in combination of α_M with K_{ex}. Therefore, Eq. 4 is reduced to

$$\log D_M = \log K'_{ex} + n\text{pH} + (n+m)\log[HL]_o, \quad (6)$$

where $K'_{ex} = K_{ex}\alpha_M$.

Based on Eq. 6, we can elucidate the extracted species by a slope analysis of the equilibrium data. A plot of log D_M against the pH at the constant concentration of DV-PHA in Fig. 2 gave a slope of 3 for lanthanoids(III) and yttrium(III). In addition, a plot of (log D_M − 3pH) against log $[HL]_o$ exhibited a slope of 6 (Fig. 3). It is thus concluded that all of the metal ions were extracted to be a type of $ML_3(HL)_3$ chelate. This is different from extraction with other R-PHAs having primary and secondary alkyl substituents,[4] where a $ML_3(HL)_2$ type chelate was extracted. The logarithms of the thus-obtained conditional extraction constants (log K'_{ex}) are

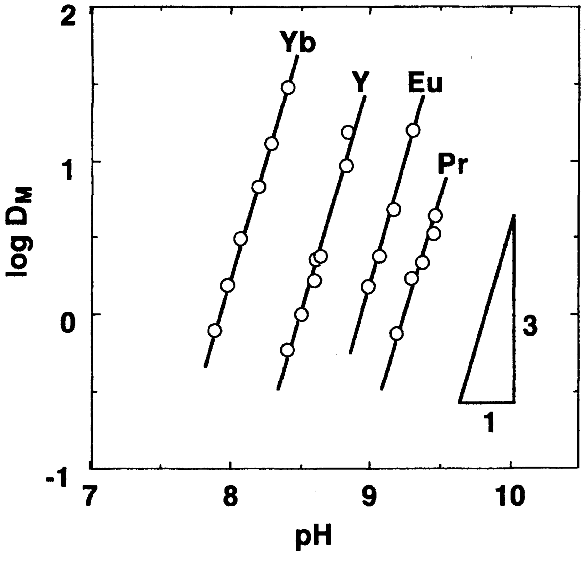

Fig. 2. Log D_M as a function of pH. The aqueous phase contains 5.00×10^{-5} mol dm^{-3} metal ion, 1.00×10^{-2} mol dm^{-3} tartrate and 0.1 mol dm^{-3} sodium nitrate. The carbon tetrachloride phase involves 1.00×10^{-2} mol dm^{-3} DV-PHA.

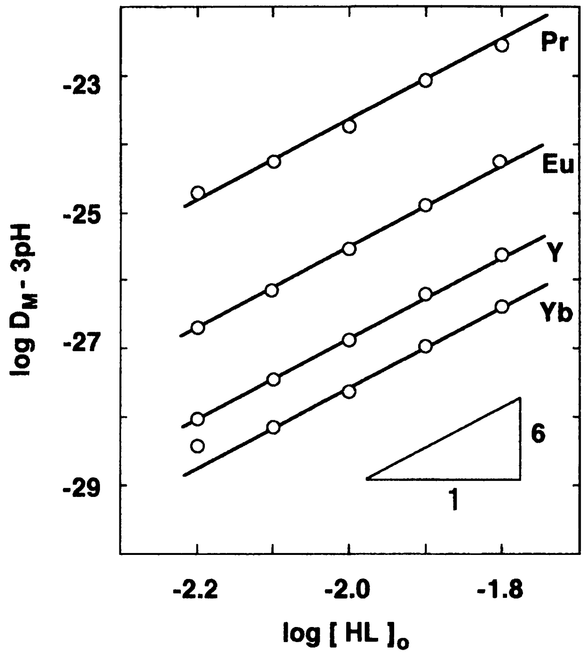

Fig. 3. Log $D_{\rm M}$−3pH as a function of log $[{\rm HL}]_{\rm o}$. The conditions of the aqueous phase are the same as described in Fig. 2.

presented in Table 1.

Separation Factor of Lanthanoids(III). The log $K'_{\rm ex}$ values of DV-PHA given in Table 1 can not simply be compared with those obtained previously for other R-PHAs. This is because the stoichiometric composition of the chelates with DV-PHA is different from that with other R-PHAs. Hence, we compared the selectivity of R-PHAs on the basis of a separation factor (SF) for a pair of metal ions. Three pairs (Eu/Pr, Yb/Eu, and Yb/Y) were chosen. The former two pairs were chosen as representatives for intragroup separations of lighter and heavier members of lanthanoids(III), and the latter to describe the separation of heavier members of lanthanoids(III) from yttrium(III). The separation factor is defined as the ratio of the $K'_{\rm ex}$ values for a pair of metal ions,

$$({\rm SF}) = K'_{\rm ex}({\rm I})/K'_{\rm ex}({\rm II}), \tag{7}$$

where subscripts (I) and (II) refer to two different metal ions.

As is evident from Table 2, the log (SF) values of DV-PHA for pairs of Yb/Eu and of Yb/Y are much greater than those of other R-PHAs[4] with primary and secondary alkyl groups and of bis(2-ethylhexyl)hydrogenphosphate (DEHPA)[8] currently used for intragroup separaitons of lanthanoids(III). The separation factor increased in the order: primary < secondary < tertiary. In this respect, DV-PHA should be most promising for mutual separations of heavy members of lanthanoids(III) as well as yttrium(III).

Table 1. Equilibrium Data on the Extraction with DV-PHA

	log $K'_{\rm ex}$		log $K'_{\rm ex}$
Pr	−15.68	Ho	−12.89
Nd	−15.80	Er	−12.26
Eu	−14.78	Tm	−11.96
Gd	−14.39	Yb	−11.69
Tb	−13.76	Lu	−11.45
Dy	−13.07	Y	−13.52

Table 2. Separation Factors of DV-PHA and Other Extractants

Extractant	log (SF)		
	Eu/Pr	Yb/Eu	Yb/Y
DV-PHA	0.90	3.09	1.83
C8-PHA[a)]	1.23	1.71	0.51
HD-PHA[a)]	1.02	2.64	1.32
PV-PHA[a)]	1.14	2.10	1.50
DEHPA[b)]	1.26	2.70	1.02

a) Obtained in our previous study (Ref. 5). b) Taken from Ref. 8. C8-PHA: *N*-octanoyl-*N*-phenylhydroxylamine, HD-PHA: *N*-hexyldecanoyl-*N*-phenylhydroxylamine.

In Eq. 7 the separation factor is defined as being the ratio of two conditional extraction constants including the term $\alpha_{\rm M}$. Lanthanoid(III) ions are accepted to be present largely in the form of a ditartrate complex in the presence of tartrate.[9] Hence, Eq. 3 is reduced to

$$\alpha_{\rm M} = \beta_2[{\rm tart}^{2-}]^2. \tag{8}$$

Then, the intrinsic separation factor, i.e., the ratio of the two extraction constants, can be written in a logarithmic form as

$$\log\,(K_{\rm ex}({\rm I})/K_{\rm ex}({\rm II})) = \log\,[({\rm SF})(\beta_2({\rm I})/\beta_2({\rm II}))]. \tag{9}$$

The logarithms of β_2 for Pr(III), Eu(III), Yb(III), and Y(III) are reported to be 6.9, 7.4, 7.3, and 6.9, respectively.[7,10] Thus, the logarithms of the intrinsic separation factor of DV-PHA were calculated to be 1.4 for Eu/Pr, 3.0 for Yb/Eu, and 2.2 for Yb/Y, respectively. These values are only slightly smaller than those of the separation factors given in Table 2. From these results, we can conclude that DV-PHA is excellent for hydrometallurgical separations of heavy lanthanoids(III). Tertiary branching at the α position of the carbonyl group will be a good means for enhancing the selectivity of R-PHAs in the extraction of heavy lanthanoids(III) and ytterium(III).

Separation Factor and Taft σ^* Polar Substituent Constant. We previously reported on the correlation of the separation factor of R-PHAs for a pair of Ni(II)/Co(II) with a steric parameter, STERIMOL B_1, of an alkyl substituent.[11] The parameter represents the steric effect of the alkyl substituent located at the neighbor of the carbonyl group.[12] The separation factor decreased in the order: primary > secondary > tertiary.

Provided that the steric requirements of branched chains are of great importance in enhancing the selectivity of R-PHAs for heavy lanthanoids(II), the separation factor should decrease in the same order as mentioned above. Although we have attempted to test the correlation between log (SF) and STERIMOL B_1, no distinct correlation was found. In addition DV-PHA forms an adduct chelate of the type $ML_3(HL)_3$, while the other R-PHAs, having a primary or a secondary alkyl substituent, form an adduct of the type $ML_3(HL)_2$. DV-PHA favors formation of highly adducted chelates with lanthanoids (III), irrespective of having a bulky tertiary alkyl group. These results indicate that the steric explanation is improbable in the present study.

We then tested the correlation between the separation factor and Taft polar substituent constant (Taft σ^*). The latter represents the inductive effect of a substituent.[13] The numerical values of Taft σ^* for the alkyl groups in question in the present study are not available in the literature. Their values were thus assumed to be approximately equal to those for appropriate substituents having structures similar to the alkyl groups in question. Table 3 lists the values of Taft σ^* employed as well as alternates of the alkyl groups.

As is shown in Fig. 4 (A and B), a fairly good inverse correlation has been obtained between log (SF) and the Taft σ^* values. This provides good evidence indicating the inductive effect of alkyl substituents in the extraction of heavy lanthanoids(III) with R-PHAs. The inductive effect may also have a significant effect on the acid dissociation of a hydroxyl group binding to the nitrogen atom of R-PHAs. Indeed, the pK_a value (10.05) for DV-PHA is larger than that of R-PHAs having a secondary alkyl substituent (9.74 for HD-PHA, 9.26 for PV-PHA).[5] However, the increase in log (SF) can not be explained by the increase in the pK_a value of the hydroxyl group. Generally, there is a free-energy relationship between the stability constants for pairs of metal chelates of a series of chelating reagents having different acidity.[14] Hence, the ratio of the stability constants for a pair of metal chelates, i.e. the separation factor, should be independent of the acidity of the chelating reagent. Accordingly, it seems certain that the inductive effect of the alkyl substituents enhances the binding strength between the carbonyl oxygen and the lanthanoids(III). This was further confirmed by measuring the wavenumber of the C=O stretching band on ytterbium(III) chelates having different alkyl substituents.

Table 3. Alternate Alkyl Groups for R-PHAs and Their Taft σ^* Polar Parameter

Extractant	Alternate of alkyl group	Taft σ^*
C8-PHA	$CH_3(CH_2)_6-$	−0.130
*t*C9-PHA	$(CH_3)_3CCH_2-$	−0.165
PV-PHA	$(C_2H_5)_2CH-$	−0.210
HD-PHA	$(C_2H_5)_2CH-$	−0.210
DV-PHA	$(CH_3)_3C-$	−0.300

*t*C9-PHA : *N*-(2,4,4-trimethylhexanoyl)-*N*-phenylhydroxylamine.

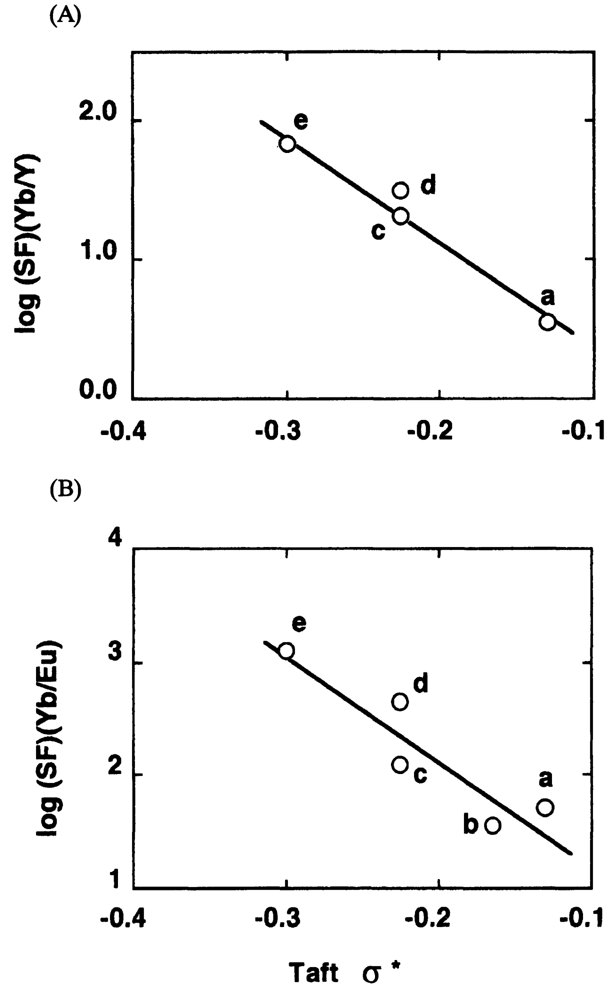

Fig. 4. Relationship between the logarithmic separation factor and Taft σ^* polar parameter. (A) log (SF)(Yb/Y) vs. Taft σ^*, (B) log (SF)(Yb/Eu) vs. Taft σ^*. Extractant: (a) C8-PHA, (b) *t*C9-PHA, (c) PV-PHA, (d) HD-PHA, (e) DV-PHA.

IR Spectra of Ytterbium(III) Chelates. The IR spectra of ytterbium(III) chelates with C4-PHA, PV-PHA, and DV-PHA were measured, respectively. Their wavenumber of the C=O stretching band was 1577 cm^{-1} for C4-PHA with a primary alkyl group, 1562 cm^{-1} for PV-PHA with a secondary group, and 1538 cm^{-1} for *t*C5-PHA with a tertiary alkyl group, respectively. The wavenumber of the C=O stretching band decreases in the following order: primary < secondary < tertiary. This is another way of stating the order of the binding strength between the carbonyl oxygen and ytterbium(III); that is, the tertiary alkyl group has the most significant effect on the binding strength.

In general, the smaller is the value of Taft σ^*, the greater is the electron donation.[13] Therefore, in combination with the data for the wavenumber and Taft σ^* value, it can be said that the log (SF) value tends to increase with an increase in the electron donation from the unshared electron pair of carbonyl oxygen to ytterbium(III). The tertiary alkyl group is the greatest substituent in regard to electron donation. This would be most favored in complexation with heavier members of lanthanoids(III), because of their smaller ionic radii than those of lighter members of the lanthanoids(III). Hence, the excellent selectivity of DV-PHA for heavy lanthanoids(III) is attributable to the inductive effect, which is most highly enhanced by the tertiary alkyl group.

Conclusion

DV-PHA having a tertiary alkyl substituent was promising for intragroup separations of heavy lanthanoids(III). The separation factors of DV-PHA for pairs of Yb/Eu and Y/Yb were considerably higher than those of DEPHA currently employed in hydrometallurgical separations of lanthanoids(III). The selectivity of R-PHAs for heavy lanthanoids(III) was best described in terms of Taft σ^* of alkyl groups. Taft σ^* schould be useful for the molecular design of chelating extractants with long-chain alkyl groups for the separation of heavy lanthanoids(III).

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