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Equilibrium distributions of trivalent actinides and lanthanides in the liquid–liquid extraction system of TBP and molten $Ca(NO_3)_2 \cdot 4H_2O$

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Abstract

The extraction distributions of Am, Cm and lanthanides between tri-butyl phosphate solution and molten calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$) were studied radiochemically. The apparent equilibrium constants of the extraction reaction were determined and their systematics along the series was studied. By comparing the observed systematics with those obtained for other similar extraction systems it was found that there is a large difference in hydration effect between the lighter and heavier f-series in water-deficient hydrate melt systems. © 1998 Elsevier Science S.A.

Keywords: Actinide; Hydrate melt; Hydration; Lanthanide; Solvent extraction; TBP

1. Introduction

The extraction distribution of trivalent actinides and lanthanides between tri-butyl phosphate (TBP) and nitric acid solutions has been studied extensively by Best et al. [1] and Hesford et al. [2] and their extraction behavior has been systematically elucidated. The extraction of some trivalent f-elements between TBP and fused hydrated salts (generally called hydrate melt) has been studied by Akatsu [3], Aratono [4] and Mitsugashira [5], and a difference from the aqueous systems has been demonstrated. We also find scientific interest in TBP extraction using hydrate melts because of the water-deficiency by which we can expect magnified appearance of ligand solvation and hydration. Therefore, we systematically studied the distribution of trivalent actinides and lanthanides in the $Ca(NO_3)_2 \cdot 4H_2O$/TBP–dodecane system, and attempted to elucidate the characteristic behavior of this system.

2. Experimental details

The distribution ratios were determined radiochemically throughout the experiment. ^{241}Am and ^{242}Cm for trivalent actinides, and ^{140}La, ^{141}Ce, ^{142}Pr, ^{147}Nd, ^{153}Sm, ^{152m}Eu, ^{160}Tb, ^{166}Ho, ^{171}Er, ^{170}Tm, ^{169}Yb and ^{177}Lu for trivalent lanthanides were used as tracers. Radioactive tracers were dissolved in nitric acid and the solution was evaporated to dryness to obtain the nitrates. The final residue was dissolved in molten $Ca(NO_3)_2 \cdot 4H_2O$ by warming, and this was used as the source inorganic solution. All the organic solutions of varying TBP concentration prepared from 99.9% pure TBP and dodecane were pre-equilibrated with fresh molten $Ca(NO_3)_2 \cdot 4H_2O$ at 50°C. A few grams of both phases were stirred vigorously in a glass vial for over 1 h in a waterbath thermostated at 53°C. The vials were quickly centrifuged for perfect phase separation after mixing. Weighed small portions of both phases were taken for γ-spectrometric analysis to determine the distribution ratios of ^{241}Am and lanthanides. The self-absorption of low energy γ-rays in the salt samples were corrected as needed. The distribution ratio of ^{242}Cm was computed from the ratio of ^{242}Cm and ^{241}Am in the organic phase which was determined by α-spectrometry performed after quantitative backextraction into water.

All quantifications of samples and reagents were performed gravimetrically to avoid the large error associated with volumetric treatment. For the analysis of equilibrium constants, the concentrations of the species and radioactivity were all converted to volumetric concentrations using the density of the solutions. The chemical reagents used were all of analytical grade. Supplementary experiments were performed to study the distribution of lanthanides between an anhydrous molten eutectic mixture of $LiNO_3$ and KNO_3 and various TBP solutions. They were per-

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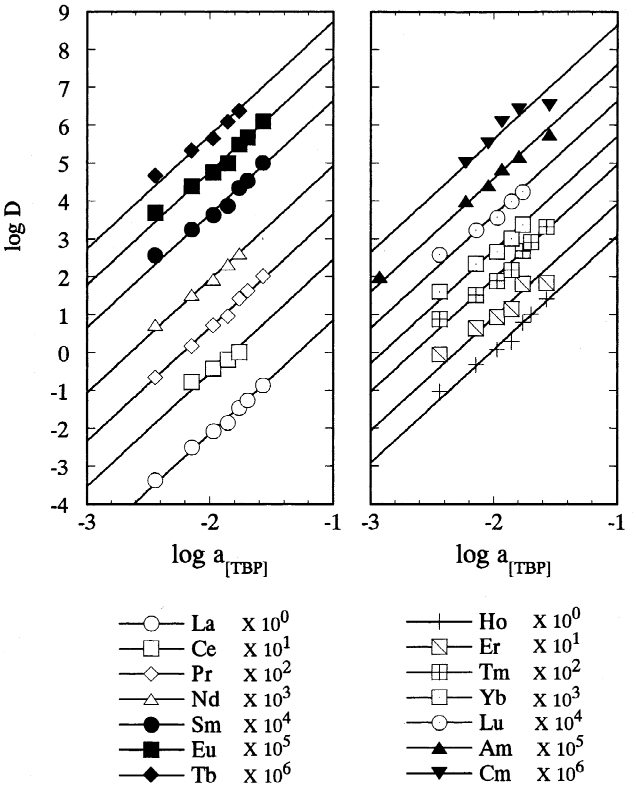
formed in almost the same manner as the experiment for $Ca(NO_3)_2 \cdot 4H_2O$ except that the extraction was performed in an oil bath thermostated at 150°C.

3. Results

In Fig. 1, the distribution ratios of actinides and lanthanides observed in the $Ca(NO_3)_2 \cdot 4H_2O$ system are plotted logarithmically versus the activity of TBP in the organic phase ($a_{[TBP]}$). The activity of TBP was computed by multiplying activity coefficients [4] by the initial mole concentration of the TBP solutions. Because it was revealed that a large amount of TBP is consumed by the extraction of calcium nitrate at TBP concentrations higher than $a_{[TBP]}=0.05$, the analysis was performed only on the data at TBP concentrations lower than $a_{[TBP]}=0.05$. All actinides and lanthanides showed a quite satisfactory third-power law, which can be seen by the best fit third-power lines in the figure. This demonstrates that, in this low TBP concentration region, there is a negligible interfering effect of Ca extraction and that the solvation number of TBP to trivalent cation is three. It was also found that there is no singularity of Am and Cm to lanthanides and that there is little difference between the distributions of Am and Cm.



Observed distribution ratios are shown with adequate multiplication by10^n for avoiding visual confusion.

Fig. 1. Distribution ratios of lanthanides, Am, and Cm in the $Ca(NO_3)_2 \cdot 4H_2O$/TBP–dodecane system (53°C).

4. Discussion

4.1. Systematics of the extraction equilibrium over the series

Based on the above observations in the low TBP concentration region, the entire extraction mechanism of trivalent f-elements is considered to comprise the following equilibria

$$M(H_2O)_m^{3+} + 3NO_3^- + 3TBP_{inorg} \overset{K_1}{\leftrightarrow} M(NO_3)_3(TBP)_{3\ inorg} + mH_2O \qquad (1)$$

$$TBP_{inorg} \overset{K_2}{\leftrightarrow} TBP_{org} \qquad (2)$$

$$M(NO_3)_3(TBP)_{3\ inorg} \overset{K_3}{\leftrightarrow} M(NO_3)_3(TBP)_{3\ org} \qquad (3)$$

The suffixes "org" and "inorg" indicate species in the organic and inorganic phase, respectively. Because the observed distribution ratio D is defined by Eq. (4), it is expressed by Eq. (5) as a function of the equilibrium constants of reactions (1) to (3)

$$D = \frac{[M(NO_3)_3(TBP)_{3\ org}]}{[M(NO_3)_3(TBP)_{3\ inorg}] + [M(H_2O)_m^{3+}]} \qquad (4)$$

$$D = K_3\left(1 + \frac{K_2^3}{K_1} a_{[H_2O]}^{m} a_{[NO_3^-]}^{-3} a_{[TBP]_{org}}^{-3}\right)^{-1} \qquad (5)$$

When $a_{[TBP]}$ is relatively small, the first term of Eq. (5) can be neglected, and the logarithm of D is given by Eq. (6). The first term of Eq. (6) represents the extractability of the element in the system, and it can be obtained as the intercept of the third-power relation of $\log D$ on $a_{[TBP]}$. In this paper, this term is denoted $\log K'$ which is defined by Eq. (7). $\log K'$ can be seen as the apparent equilibrium constant of the overall extraction reaction under a specific experimental condition

$$\log D = \log K_3 \frac{K_1}{K_2^3} a_{[H_2O]}^{-m} a_{[NO_3^-]}^{3} + 3 \log a_{[TBP]_{org}} \qquad (6)$$

$$\log K' = \log K_3 \frac{K_1}{K_2^3} a_{[H_2O]}^{-m} a_{[NO_3^-]}^{3} \qquad (7)$$

The intercepts of the third-power lines for all trivalent elements were then determined by adapting the least squares fitting method to the observed data points. The $\log K'$ are plotted in Fig. 2 as functions of the inverse of their ionic radii ($1/R$). The ionic radii of trivalent lanthanides quoted are those of coordination number 8 given by Shannon [6], and those of trivalent actinides are those recommended by David [7]. It is noted that $\log K'$ increases linearly with increasing $1/R$ for the lighter lanthanides, attains a maximum for the mid-lanthanides, and then decreases slightly for the heavier lanthanides. Am

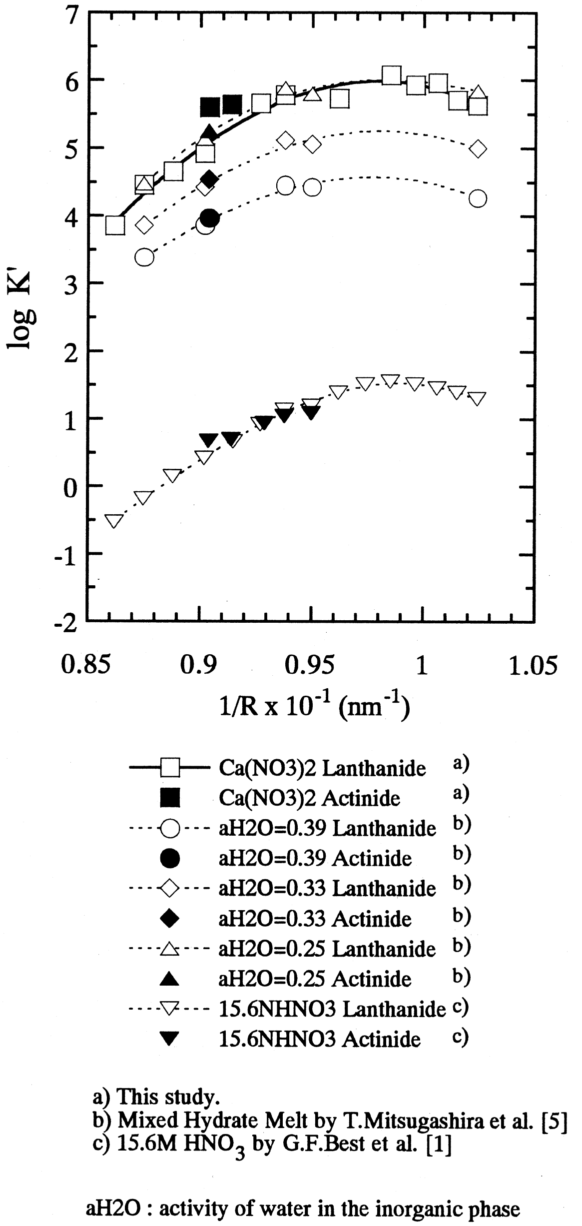


Fig. 2. Dependence of the equilibrium constant on the inverse of the ionic radius for various hydrate melt systems.

and Cm showed a slight difference from the lanthanides, but are considered to be in agreement considering the relatively larger error of the α-activity analysis. The proportionality in the lighter series for $1/R$ suggests that the extraction reaction is controlled by electrostatic interaction. On the contrary, the depression from linearity for the heavier series suggests the presence of a strong competing interaction which specifically occurs on the smaller elements.

The observed systematics of this study can be compared with those of similar water-deficient extraction systems. In Fig. 2, the systematics reported for a mixed hydrate melt of calcium and magnesium nitrate [5] and a 15.6 M HNO_3 aqueous system [1] are shown together. Although there are some differences in the water content ($a_{[H2O]}$) of the systems, as listed in Table 1, they show a quite similar tendency along the series.

4.2. Analysis on the hydration effect

The solvation reaction (1) of the aquo-ion in hydrate melt systems can be divided hypothetically into two fundamental reactions defined by Eqs. (8) and (9). The equilibrium constant K_1 is expressed by Eq. (10)

$$M^{3+} + mH_2O \overset{K_{\mathrm{hyd}\ M^{3+}}}{\leftrightarrow} M(H_2O)_m^{3+} \tag{8}$$

$$M^{3+} + 3NO_3^- + 3TBP_{\mathrm{inorg}} \overset{K_{\mathrm{solv}\ M^{3+}}}{\leftrightarrow} M(NO_3)_3(TBP)_{3\ \mathrm{inorg}} \tag{9}$$

$$K_1 = \frac{K_{\mathrm{solv}\ M^{3+}}}{K_{\mathrm{hyd}\ M^{3+}}} \tag{10}$$

The suffixes M^{3+} and HM specify that the constants are those of the hydrate melt system and bare tripositive cations. Because K_2^3 and $a_{[H_2O]}^{-m} a_{[NO_3^-]}^3$ in Eq. (7) are fixed by the composition of the inorganic system, Eq. (7) for hydrate melt systems is then rewritten as Eq. (11)

Table 1
Experimental conditions of the various systems

Inorganic phase	Temperature (K)	$X(H_2O)$	$a(H_2O)$[a]
$Ca(NO_3)_2 \cdot 4H_2O$[b]	326	0.8	0.27
$(Ca+Mn)(NO_3)_2 \cdot xH_2O$[c]	333	0.8–0.875	0.27, 0.33, 0.39
15.6 M HNO_3[d]	298	0.6	0.23
$LiNO_3 + KNO_3$[b]	423	0	0

[a] Activity of H_2O in the inorganic phase was determined by the equilibrium vapor pressure of water.
[b] This study.
[c] Ref. [5].
[d] Ref. [1].

$$\log K'_{\mathrm{HM}} = \log K_{3\ \mathrm{HM}} + \log K_{\mathrm{solv\ M^{3+}}} - \log K_{\mathrm{hyd\ M^{3+}}} + \mathrm{const.} \qquad (11)$$

The relative gradation of the observed $\log K'_{\mathrm{HM}}$ on $1/R$ thus appears as the sum of the dependence of the first three terms on the right-side of Eq. (11).

In order to compare the results for the hydrate melt system with those for a system having no influence of water, an extraction with TBP using an anhydrous molten eutectic mixture of $LiNO_3$ and KNO_3 was performed in a separate experiment [8]. In this system, because there is no competing extraction of bulk salt even at high TBP concentrations, a wide range of TBP concentration was analyzed. The observed distribution ratios were fitted to Eq. (5) with $a_{[\mathrm{H2O}]}$ excluded, and $\log K_3$ and $\log K_{\mathrm{solv}}$ were determined. They are denoted as $\log K_{3\ \mathrm{Anhyd}}$ and $\log K_{\mathrm{solv\ Anhyd}}$ for lanthanides, and are shown versus $1/R$ in Fig. 3. Quite linear relations were obtained both for $\log K_{3\ \mathrm{Anhyd}}$ and $\log K_{\mathrm{solv\ Anhyd}}$ and even for $\log K_{3\ \mathrm{Anhyd}} + \log K_{\mathrm{sol}\upsilon\ \mathrm{Anhyd}}$. Their linearity for anhydrous systems implies that the free energy change of solvation is proportional to $1/R$, hence it is of electrostatic interaction throughout the series. The linearity of $\log K_{3\ \mathrm{Anhyd}}$ also suggests that the free energy change of the transfer of the extracted complex between two phases is also electrostatically controlled.

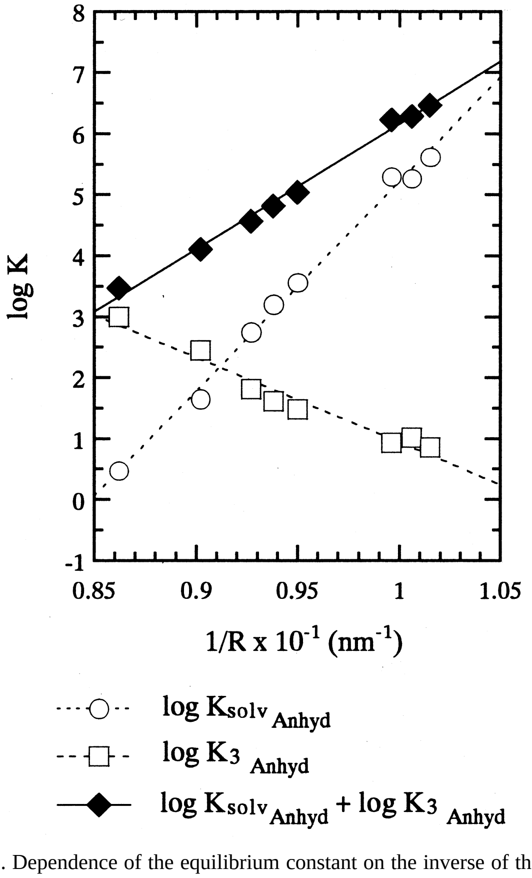


Fig. 3. Dependence of the equilibrium constant on the inverse of the ionic radius for the anhydrous $LiNO_3+KNO_3$/TBP–dodecane system (150°C).

Comparison of the absolute values of $\log K'$ between different systems is difficult because of differences in the solution conditions. However, the dependence of $\log K'$ on atomic number (or $1/R$), i.e. relative differences in $\log K'$ between the elements, can be compared among the different systems. The difference in the temperature of the system may change the absolute value of $\log K'$, but it does not produce a remarkable change in the dependence on atomic number [5]. Therefore, for easy comparison, the $\log K'$ values of elements were standardized to those of Ce by subtracting $\log K'_{\mathrm{Ce}}$ for every system, and these values are marked by an asterisk ($\log K'^{*}$).

The relative $\log K'^{*}$ values (i.e. $\log K' - \log K'_{\mathrm{Ce}}$) of various systems are plotted in Fig. 4. The solid line in Fig. 4, which corresponds to the fitted line of observed $\log K_{3\ \mathrm{Anhyd}} + \log K_{\mathrm{sol}\upsilon\ \mathrm{Anhyd}}$ of Fig. 3, shows good agreement with the points of lighter series in hydrate melt

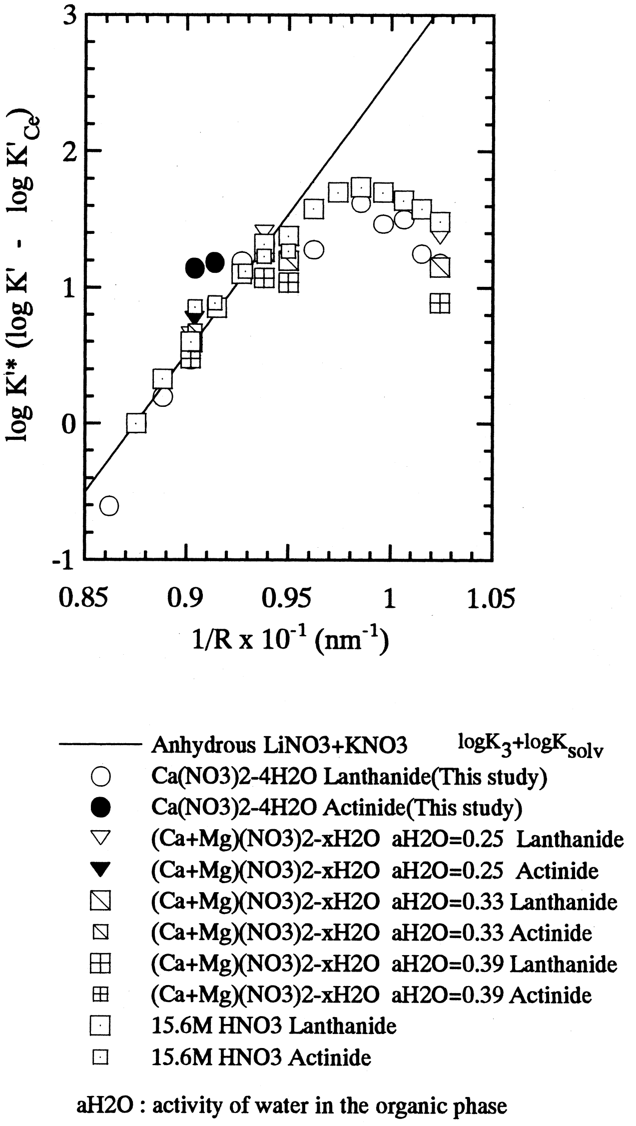


Fig. 4. Relative comparison of the dependence of equilibrium constants for various systems.

systems. This suggests that, in hydrate melt systems, TBP solvation on lighter series and the inter-phase transfer of their complexes occur almost like those in anhydrous systems. On the contrary, the heavier series show increasing deviations from the line, suggesting an increasing hydration effect on heavier elements. On the reasonable assumption that log $K^*_{3\,\mathrm{HM}}$ and log $K^*_{\mathrm{solv}\ \mathrm{M}^{3+}}$ approximately agree with the corresponding values for an anhydrous system (log $K^*_{3\,\mathrm{Anhyd}}$ and log $K^*_{\mathrm{solv\ Anhyd}}$), the difference between the line and the points of hydrate melt systems is expected to represent the gradation of log $K^*_{\mathrm{hyd}\ \mathrm{M}^{3+}}$ along $1/R$ (Fig. 5). It is obvious that, in hydrate melt systems, the hydration effect steeply increases at $1/R=\sim0.95$. Because the ordinate of Fig. 5 is the logarithm of the equilibrium constant and is the same dimensions as the free energy change of the equilibrium, the curves are expected to reflect the relative difference in the magnitude of hydration energies. Therefore, we can conclude that, in hydrate melt systems, there is a smaller contribution of hydration for the lighter series of actinides and lanthanides, but there occurs a steep increase of hydration after the mid-series around $1/R=0.95$. Considering that the standard free energy change of the hydration of fully hydrated aquo-ions of trivalent f-elements varies rather smoothly with increasing atomic number [9], the observed irregular variation of the hydration effect in hydrate melt systems is attributed to water-deficiency and the very large ionic strength of the system. Consequently, we point out the possible presence of a drastic change of the hydration mechanism in the middle of the f-series in hydrate melt systems.

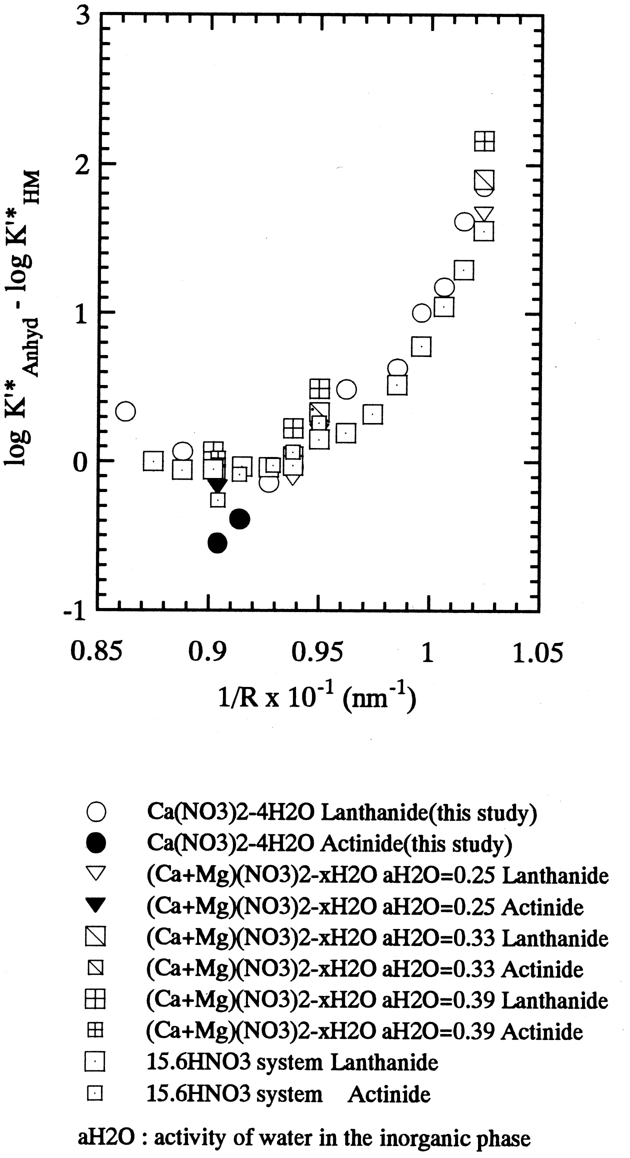


Fig. 5. Dependence of the relative hydration effect over the f-series.

5. Conclusion

The distribution equilibria of trivalent actinides and lanthanides were determined experimentally, and their systematics was studied. By comparison with the systematics of the anhydrous melt system, it was found that a sudden change in hydration occurs in the middle of the f-series in hydrate melt systems.

Acknowledgements

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