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Charge Transfer Interaction of Trivalent Lanthanides and Actinides with β-Diketones

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The charge transfer (C.T.) interaction between metal ions and ligands is of great interest and has often been exploited in developing colorimetric estimation methods for various metal ions. β-diketones are known to be good donors in C.T. of the type ligand → metal (L → M). The C.T. in Fe(III) thenoyl trifluoroacetone (HTTA) [1], Ce(IV)–HTTA [2] and Pu(IV)–HTTA [3] is of this type. The importance of C.T. interaction lies in the extraction of Eu(III) by HTTA and its synergistic mixture with a long chain quaternary amine has been demonstrated [4]. However, no C.T. of the type M → L has yet been observed in the case of trivalent lanthanides and actinides with β-diketones [5]. The present study deals with the C.T. interaction of the type M → L for Ce(III) with different β-diketones and the results have been correlated with the extraction data of various trivalent lanthanides and actinides, especially Bk.

Experimental

The tracer solutions of ^{249}Bk, Cf (mainly ^{252}Cf) ^{141}Ce, ^{147}Pm and ^{170}Tm were prepared and assayed as described earlier [6]. HTTA (Merck's Pro-Analysi), benzoyltrifluoroacetone (HBTFA) (Peninsular Chem. Research Inc.), 1-phenyl-3-methyl-4-benzoyl pyrazolone-5 (HPMBP) (m.p. 92 °C, prepared in this laboratory) and the other chemicals used were of A.R. grade.

The experimental details of determining the distribution coefficients of different metal ion-β-diketone systems were as given in Ref. [7]. The absorption spectral studies were carried out using a Cary Model 14 spectrophotometer by well established procedures [2].

Results and Discussion

Figure 1 gives the absorption spectra of Ce(III) and Ce(IV) in HTTA–xylene systems. Here Ce was maintained as Ce(III) in the organic phase by adding adequate amounts of the reducing agent, tert-butyl hydroquinone. The presence of Ce(III) in the organic phase was confirmed by back extraction studies where all the Ce could be extracted back by 1 M HCl. It was also observed that in the absence of the reducing agent in the organic phase the Ce extracted with HTTA and HBTFA was completely converted into the Ce(IV) form. However, with HPMBP no difference was observed in the Ce(III) spectra in the presence or in the absence of the reducing agent. As seen from Fig. 1 the ε at 500 nm for Ce(IV) is much higher than that for Ce(III). The C.T. thus observed between Ce and HTTA (in the virtual absence of any Ce(IV)) is of the M → L type. This type of interaction has not yet been reported for trivalent lanthanides or actinides, although it is known in the case of transition metal ions–acetylacetone systems [5]. Figure 2 shows the absorption

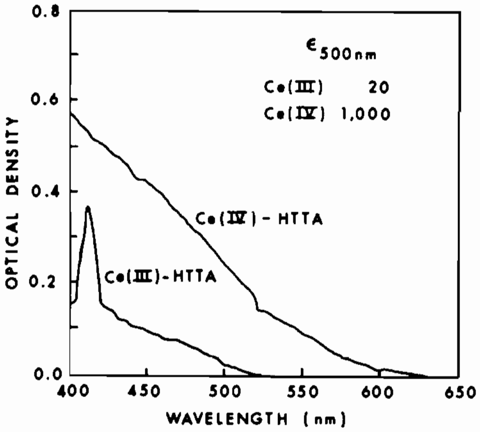

Fig. 1. Absorption spectra of Ce(III) and Ce(IV) extracted by HTTA in xylene.

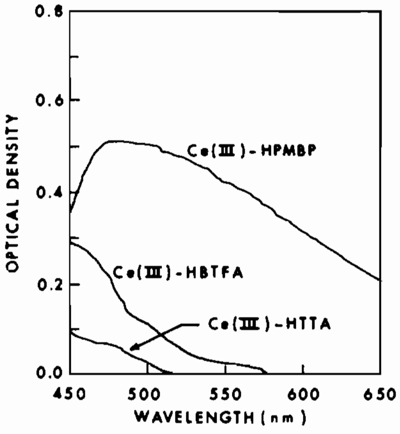

Fig. 2. Absorption spectra of Ce(III) extracted by HTTA, HBTFA and HPMBP in xylene.

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TABLE I. Distribution Coefficient (Kd) of Trivalent Actinides and Lanthanides with Different β-Diketones in Xylene.

M^{3+}	Distribution Coefficient (Kd)		
	HPMBP[a]	HBTFA[b]	HTTA[c]
Bk	3.96	4.28	0.32
Cf	5.13×10^{-3}	4.63×10^{-2}	2.09×10^{-2}
Ce	1.36×10^{-2}	1.29×10^{-2}	3.02×10^{-3}
Pm	6.57×10^{-4}	5.91×10^{-3}	1.15×10^{-2}
Tm	2.30×10^{-3}	0.11	4.78×10^{-2}

[a] [HPMBP] = 0.02 M, Aqueous phase pH 2.0 (HCl). [b] [HBTFA] = 0.4 M. [c] [HTTA] = 0.14 M; Aqueous phase for both, pH 2.70 (Chloroacetate buffer, $\mu = 0.005$).

TABLE II. Molar Extraction Coefficients of Ce(III) (at 500 nm) and Separation Factors between Ce(III), Pm(III); Ce(III), Tm(III) and Bk(III), Cf(III) with Different β-Diketones in Xylene.

β-diketone	ε, Ce(III)	Separation factors between		
		Ce, Pm	Ce, Tm	Bk, Cf
HPMBP	1208	20.7	5.9	772
HBTFA	68[a]	2.2	0.11	92.5
HTTA	20[a]	0.26	0.06	14.7

[a] Tert-butylhydroquinone added in the organic phase (0.05 M).

spectra of Ce(III) extracted into various β-diketone xylene systems where the wavelength of the lowest energy charge transfer as well as the value of ϵ_{500} (Table II) are seen to increase in the order HPMBP > HBTFA > HTTA. This order indicates the relative tendency of the β-diketones to accept an electron from Ce(III) in C.T. interaction.

Table I gives the distribution coefficient values (Kd) of Bk(III), Cf(III), Ce(III), Pm(III) and Tm(III) in HPMBP, HBTFA and HTTA in xylene. For Ce(III) experiments wherein ^{141}Ce was used on a tracer scale it was confirmed from back extraction experiments with 1 M HCl that Ce is extracted as Ce(III) with all the β-diketones used. This was in contrast to the extraction behaviour of Ce when used in miligram scale experiments as described above. The difference between the extraction behaviour of tracer and macro quantities has also been observed with Pu(III) [8]. Among the lanthanides the Kd of Pm(III) and Tm(III) with these β-diketones follow the order Tm > Pm which is the expected order due to the lanthanide contraction. However, the Kd of Ce(III) is nearly an order of magnitude higher in the case of HPMBP and HBTFA. Also the Kd of Bk(III) is much higher than that of Cf(III) for all these β-diketones. The high Kd values of Bk(III) and Ce(III) compared to the other trivalent actinides and lanthanides respectively may be explained on the basis of the C.T. effect. It is quite conceivable that the bond between Ce(III) or Bk(III) and the various β-diketonates is stabilised by a quasi covalent interaction involved in C.T. leading in turn to the comparatively higher Kd values observed. This effect is more apparent from the separation factors (S.F.) between Ce(III)–Pm(III) and Ce(III)–Tm(III) (Table II) which follow the order HPMBP > HBTFA > HTTA. The S.F. between Ce(III)–Pm(III) and Ce(III)–Tm(III) and the ϵ_{500} of Ce(III)–β-diketones follow the same pattern as obtained for the S.F. between Bk(III)–Cf(III) (Table II, last column). With the closeness of the redox potentials of Ce(IV)–(III) and Bk(IV)–(III) couples it looks likely that the high S.F. between Bk(III)–Cf(III) could possibly arise due to the M → L type of C.T. interaction between Bk(III) and these β-diketones as has been shown above for the similar Ce(III) systems, though this could not be demonstrated experimentally due to the non-availability of miligram amounts of Bk.

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