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J. N. Mathur<sup>a</sup>; P. K. Khopkar<sup>a</sup>

<sup>a</sup> RADIOCHEMISTRY DIVISION BHABHA ATOMIC RESEARCH CENTRE, BOMBAY, INDIA

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## Synergistic Extraction of Trivalent Actinides by Mixtures of 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 and Neutral Oxo Donors

J. N. MATHUR and P. K. KHOPKAR

RADIOCHEMISTRY DIVISION  
BHABHA ATOMIC RESEARCH CENTRE  
BOMBAY 400085, INDIA

### Abstract

The synergistic extraction of trivalent actinides Am, Cm, Bk, and Cf with mixtures of 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) and TBP or TOPO has been investigated in xylene at 30°C. With HPMBP alone, all four trivalent actinides form  $M(\text{PMBP})_3 \cdot \text{HPMBP}$ -type self-adducts. Bk(III) shows an abnormally high extraction with HPMBP alone. With TBP or TOPO(S) as neutral donor, except in the Bk/HPMBP/TBP system where  $\text{Bk}(\text{PMBP})_3 \cdot \text{HPMBP} \cdot \text{TBP}$  was extracted, all metal ions were extracted as  $M(\text{PMBP})_3 \cdot \text{S}$  and  $M(\text{PMBP})_3 \cdot (\text{S})_2$  into the organic phase. The equilibrium constants ( $\beta_1$ ,  $\beta_2$ , and  $K_2$ ) for the organic phase synergistic reactions have been calculated. The  $\beta_1$ ,  $\beta_2$  values for Bk(III)/HPMBP/TOPO system are much lower as compared to the corresponding values for other trivalent actinides. The reasons for this extraordinary behavior of Bk(III) have been discussed. The extraction behavior of the M(III)/HPMBP/S and the M(III)/HTTA/S systems has also been compared.

Mixtures of chelating agents and neutral donors have been used extensively in the synergistic extraction of metal ions. Thenoyltrifluoroacetone (HTTA) has been one of the most favored chelating agents for well-known reasons, and numerous data (1-5) are available on the extraction of trivalent actinides and lanthanides by mixtures of HTTA and neutral donors. 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (HPMBP) is a comparatively new chelating agent and has many uses in solvent extraction since, as compared to HTTA, it can extract metal ions from more acidic solutions. Some data are available on the synergistic extraction of Am(III) (6) and trivalent Am, Cm, Bk, and Cf (7-11) by mixtures of HPMBP and various neutral oxo donors, but the information available on the nature of species

extracted into the organic phase and their equilibrium constant values is rather unsatisfactory. We have therefore initiated a program on the synergistic extraction of trivalent actinides by mixtures of HPMBP and various neutral oxo donors. The present work is concerned with the extraction of these metal ions with HPMBP + TBP and HPMBP + TOPO in xylene.

## EXPERIMENTAL

**Materials.** Tracer solutions of  $^{241}\text{Am}$ ,  $^{244}\text{Cm}$ ,  $^{249}\text{Bk}$ , and Cf (mainly  $^{252}\text{Cf}$ ) were prepared and assayed as described earlier [Am and Cm (12), Bk (4), and Cf (13)]. HPMBP (mp  $92^\circ\text{C}$ ) was kindly supplied in a purified state by Dr M. S. Subramanian of this laboratory. The HPMBP solutions used in this work were always freshly prepared, since it was observed that these solutions are found to deteriorate on keeping, and the distribution coefficient values for all the metal ions are observed to fall continuously with the lapse of time. Tri-*n*-butyl phosphate (TBP) was purified by vacuum distillation after initial treatment with dilute NaOH. Tri-*n*-octylphosphine oxide (TOPO) (Eastman Kodak, mp  $53.5^\circ\text{C}$ ) was used as such. Xylene (B.D.H. Analar) was used as a diluent throughout this work. All other reagents used were of A.R. grade.

**HPMBP Variation Experiments.** One milliliter of the aqueous phase (chloro acetate buffer pH = 2.70,  $\mu = 0.005$  for Am and Cm, HCl pH 2.00 for Bk, and HCl pH 2.42 for Cf) spiked with the tracers of the trivalent actinides were equilibrated with an equal volume of xylene solutions of varying HPMBP concentrations ranging from 0.008 to 0.05 *M*. In the case of synergistic extraction with TBP or TOPO, the aqueous phase was HCl (pH 2.00), the organic phase containing a fixed concentration of the synergist and suitably varying HPMBP concentrations. The equilibrations were carried out in a thermostated bath at  $30 \pm 0.1^\circ\text{C}$  for 1 h (equilibrium was found to be achieved in 40 min) and aliquots of both the phases were pipetted for radioassay after settling the solutions for  $\frac{1}{2}$  h.

**pH Variation Experiments.** One milliliter of the aqueous phase (pH varying from 1.2 to 2.0) spiked with  $^{249}\text{Bk}$  tracer was equilibrated with the same volume of 0.025 *M* HPMBP solution, and aliquots of both phases were taken for radioassay as discussed earlier.

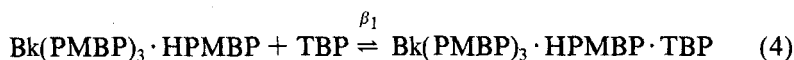
**Synergistic Extraction with HPMBP + TBP (or TOPO).** One milliliter of the aqueous phase (pH 2.00 HCl) spiked with the respective tracers was equilibrated with 1 mL of the organic phase containing HPMBP at a fixed concentration (0.02 *M* for Am, Cm, and Cf and 0.01 *M* for Bk) and varying concentrations of TBP ( $4.94 \times 10^{-3}$  to  $9.26 \times 10^{-3}$  *M*) and TOPO

( $5 \times 10^{-4}$  to  $1 \times 10^{-3}$  M). After settling, the aliquots of both phases were taken for radioassay.

**Calculation of the Equilibrium Constants.** The organic phase substitution and addition reactions of  $M(\text{PMBP})_3 \cdot \text{HPMBP}$  with TBP and TOPO can in general be represented by



except for  $\text{Bk(III)}/\text{HPMBP}/\text{TBP}$  system where it could be represented (as discussed later) as



The equilibrium constants ( $\beta_1$ ,  $\beta_2$ , and  $K_2$ ) for the first three organic phase reactions (1)–(3) have been calculated by using the equation

$$\frac{D - D_{\text{PMBP}}}{[\text{S}]_{\text{org}}} = K_{\text{syn1}} \frac{[\text{HPMBP}]_{\text{org}}^3}{[\text{H}^+]_{\text{aq}}^3} + K_{\text{syn2}} \frac{[\text{HPMBP}]_{\text{org}}^3}{[\text{H}^+]_{\text{aq}}^3} [\text{S}]_{\text{org}} \quad (5)$$

as described earlier (14). In Eq. (5),  $D$  and  $D_{\text{PMBP}}$  are the distribution coefficients of the trivalent actinides in the synergistic extraction and extraction by HPMBP alone, respectively.  $K_{\text{syn1}}$  and  $K_{\text{syn2}}$  are the two phase equilibrium constants for the uptake of  $M(\text{PMBP})_3\text{S}$  and  $M(\text{PMBP})_3(\text{S})_2$ , respectively, in the organic phase. The plots of  $(D - D_{\text{PMBP}})/[\text{S}]_{\text{org}}$  vs  $[\text{S}]_{\text{org}}$  for all the trivalent actinides–HPMBP–TBP or TOPO systems (except  $\text{Bk}/\text{HPMBP}/\text{TBP}$  system) gave straight lines whose intercepts and slopes are equal to

$$c = K_{\text{syn1}} \frac{[\text{HPMBP}]_{\text{org}}^3}{[\text{H}^+]_{\text{aq}}^3} \quad (6)$$

and

$$m = K_{\text{syn}_2} \frac{[\text{HPMBP}]_{\text{org}}^3}{[\text{H}^+]_{\text{aq}}^3} \quad (7)$$

Knowing the concentrations of HPMBP in the organic phase and the pH of the aqueous phase, the organic phase equilibrium constants  $\beta_1$  and  $\beta_2$  were evaluated using the relations

$$\beta_1 = K_{\text{syn}_1}/K_{\text{PMBP}} \quad (8)$$

and

$$\beta_2 = K_{\text{syn}_2}/K_{\text{PMBP}} \quad (9)$$

where  $K_{\text{PMBP}}$  is the equilibrium constant of the reaction



The  $K_{\text{PMBP}}$  values in the case of Am and Cm were determined from the  $D_{\text{PMBP}}$  values at pH  $\sim 2.6$  (HCl) by measuring accurately the equilibrium pH with an Orion pH-meter (accuracy  $\pm 0.01$ ). In the case of Bk(III) and Cf(III), the  $K_{\text{PMBP}}$  values were evaluated from the  $D_{\text{PMBP}}$  data at pH 2.00 and pH 2.42, respectively.

In the Bk/HPMBP/TBP system the synergistic species formed is  $\text{Bk}(\text{PMBP})_3 \cdot \text{HPMBP} \cdot \text{TBP}$  whose equilibrium constant  $\beta_1$  was calculated by a least squares fit of  $\log [D - D_{\text{PMBP}}]$  vs  $\log [\text{TBP}]_{\text{org}}$  using

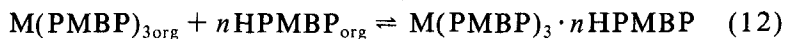
$$\log [D - D_{\text{PMBP}}] = \log K_{\text{syn}_1} + 4 \log [\text{HPMBP}]_{\text{org}} + 3\text{pH} + \log [\text{S}]_{\text{org}} \quad (11)$$

which gave a straight line with slope = 1.0 and intercept  $c = \log K_{\text{syn}_1} + 4 \log [\text{HPMBP}]_{\text{org}} + 3\text{pH}$ . Knowing the concentration of HPMBP in the organic phase and pH of the aqueous solution, the value of  $K_{\text{syn}_1}$  is evaluated and the value of  $\beta_1$  was evaluated from the relation  $\beta_1 = K_{\text{syn}_1}/K_{\text{PMBP}}$ .

The equilibrium constant values mentioned here refer only to the concentration quotients which have been calculated on the assumption that the activity coefficients of the species involved do not change significantly under the experimental conditions employed.

## RESULTS AND DISCUSSION

The traditional "slope analysis method" based on the variation of  $D$ , the distribution coefficient values with relevant experimental variables, has been used to arrive at the stoichiometry of the formation of the extractable complexes and then to calculate the equilibrium constants of the species formed in the organic phase. Figure 1 shows the plots of  $\log D$  vs  $\log [\text{HPMBP}]$  for the trivalent actinides Am, Cm, Bk, and Cf. In the case of Am(III) and Cm(III), straight lines with a slope of 3.7 have been observed. This slight departure from the slope of 4.0 may be due to the chloroacetate buffer ( $\mu = 0.005$ ) being used as the aqueous phase (in order to obtain measurable  $D$  values) for these two metal ions. With Bk(III) and Cf(III), where the aqueous phase was HCl, a clear-cut slope of 4 has been observed. However, in the case of Cf(III) when chloroacetate buffer was used as the aqueous phase (broken line in Fig. 1), two straight lines, one with a slope of 3 at lower HPMBP concentrations and another with a slope of 4 at higher HPMBP concentrations, were obtained. At lower HPMBP concentrations the slope of 3 for HPMBP can be explained on the basis of the probable extraction of the species  $\text{Cf}(\text{PMBP})_2(\text{ClAc}) \cdot \text{HPMBP}$ . On the basis of the fourth power dependence of HPMBP concentration and the inverse third power dependence on the  $\text{H}^+$  concentration (Fig. 2) of the extraction of trivalent actinides by HPMBP, the species extracted into the organic phase can be represented by  $\text{M}(\text{PMBP})_3 \cdot \text{HPMBP}$ . Formation of such self-adduct species has already been shown by Dyrssen (15) during the extraction of Sr(II) with 8-hydroxyquinoline, and by Newman and Klotz (16), Navratil (17), Chmutova et al. (9) and Freiser et al. (18) in the extraction of trivalent actinides or lanthanides by HTTA, HPMBP, or 8-hydroxyquinoline. As suggested by Freiser et al. (18) in the formation of self-adducts of the type



the value of  $n$ , the extra HPMBP attached to the self-adduct, can be obtained by plotting  $\log D - 3\text{pH} - 3 \log [\text{HPMBP}]_{\text{org}}$  (instead of  $\log D$ ) vs  $\log [\text{HPMBP}]_{\text{org}}$ , where the slope of this derived plot will be equal to  $n$  and not to  $3 + n$ . In Fig. 3 such plots have been drawn for trivalent Am, Cm ( $n = 0.8$ ) and Bk, Cf ( $n = 1.0$ ). This shows that in all these systems the extracted species is always  $\text{M}(\text{PMBP})_3 \cdot \text{HPMBP}$ , a self-adduct. In the synergistic extraction of these metal ions with HPMBP and TBP or TOPO, two types of reactions, namely substitution (Reactions 1 and 2) and addition (Reaction 4), are possible. These are discussed in the following text.

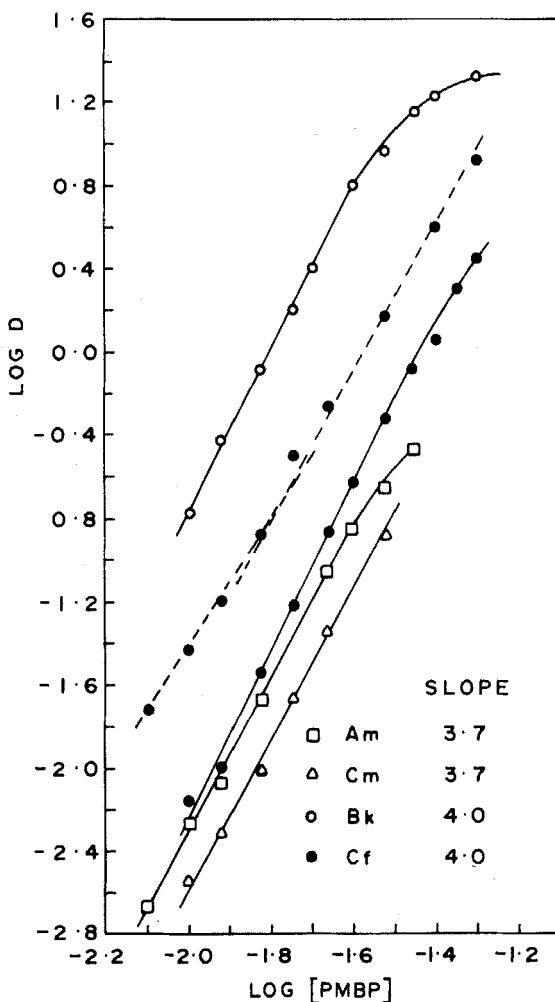


FIG. 1. Variation of distribution coefficient of trivalent actinides as a function of HPMBP concentration.

Figures 4 and 5 show the plots of  $\log D$  vs  $\log [\text{HPMBP}]$  at fixed TBP and TOPO concentrations, respectively. It appears from these figures that in all these systems (except Bk/HPMBP/TBP) there are only three HPMBP moieties attached to the trivalent metal ions in the presence of the neutral donors TBP or TOPO. The mechanism represented by Reactions (1) and (2) is applicable in all such systems where the extra HPMBP molecule attached

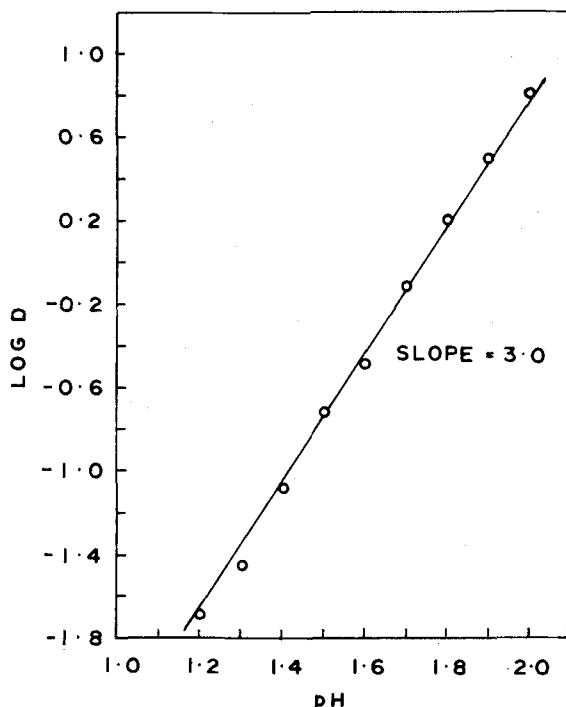


FIG. 2. Distribution of Bk(III) in the presence of HPMBP as a function of pH.

as an un-ionized chelating agent to the chelate  $M(\text{PMBP})_3$  is replaced by the neutral donors. In the system Bk/HPMBP/TBP, the mechanism represented by Reaction (4) is applicable because only in this case, even in the presence of TBP, is a slope of 4 obtained for HPMBP variation (Fig. 4). It appears that the attachment of the extra HPMBP to Bk(III) is much stronger than its attachment to other trivalent actinides. In the case of TOPO, which is much more basic than TBP, as the neutral donor, the extra HPMBP is also replaced from the Bk(III) self-adduct  $\text{Bk}(\text{PMBP})_3 \cdot \text{HPMBP}$ .

Figures 6 and 7 show the plots of  $\log [D - D_{\text{PMBP}}]$  vs  $\log [\text{TBP}]$  and  $\log [\text{TOPO}]$ , respectively, at fixed HPMBP concentrations. In the Bk/HPMBP/TBP system (Fig. 6) a straight line with slope = 1.0 is obtained. At higher TBP concentrations a negative slope is observed. In the case of all other trivalent actinides HPMBP/TBP or TOPO systems, slopes ranging from 1.3 to 1.9 have been observed which indicate the presence of more than one synergistic species in the organic phase. Figures 8 and 9 are the plots of  $(D - D_{\text{PMBP}})/[\text{S}]_{\text{org}}$  vs  $[\text{S}]_{\text{org}}$  where S is TBP and TOPO, respectively, for all



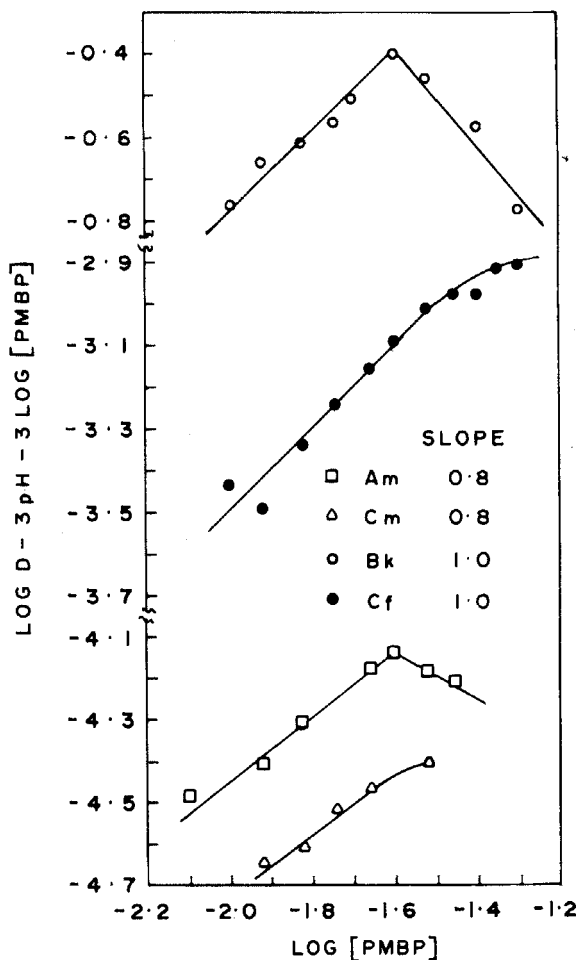


FIG. 3. Derived plots of  $\log D - 3 \text{ pH} - 3 \log [\text{HPMBP}]$  vs  $\log [\text{HPMBP}]$  of the trivalent actinides.

the trivalent actinides. In all the trivalent actinide synergist system (except Bk/HPMBP/TBP), straight lines are obtained in such plots, and from the intercept ( $c$ ) and slope ( $m$ ) of these straight lines the organic phase equilibrium constants  $\beta_1$  and  $\beta_2$  can be calculated using Eqs. (8) and (9). In the case of the Bk/HPMBP/TBP system a straight line almost parallel to the  $x$ -axis is obtained (Fig. 8) which, in conjunction with the results from Fig. 6, shows that only one TBP is attached to the Bk-HPMBP chelate.

Table 1 gives the  $K_{\text{syn}1}$  and  $K_{\text{syn}2}$  values for trivalent Am, Cm, Bk, and Cf

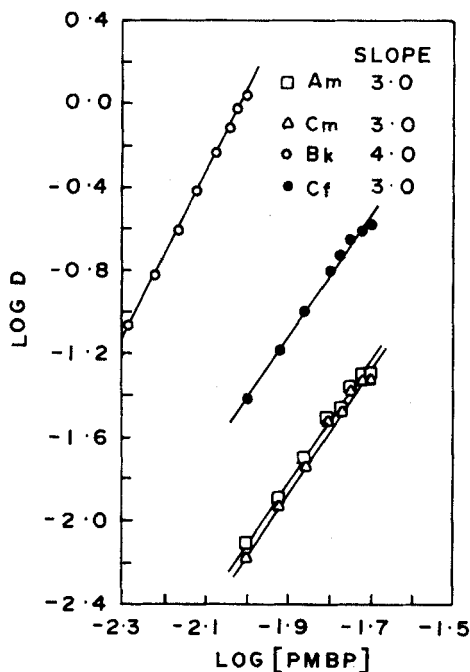


FIG. 4. Variation of distribution coefficient of trivalent actinides as a function of HPMBP concentration at fixed TBP concentration.

TABLE I

Two Phase Equilibrium Constants of Trivalent Actinides in  
HPMBP-Neutral Oxo Donors-Xylene Systems at 30°C

M(III)	$\log K_{\text{syn}1}$	$\log K_{\text{syn}2}$	$\log K_{\text{PMBP}}$
<i>HPMBP + TBP</i>			
Am	$-0.62 \pm 0.06$	$1.87 \pm 0.02$	$-2.73 \pm 0.04$
Cm	$-0.46 \pm 0.06$	$1.87 \pm 0.04$	$-2.64 \pm 0.04$
Bk	$4.43 \pm 0.16$	—	$1.23 \pm 0.03$
Cf	$0.52 \pm 0.02$	$2.32 \pm 0.04$	$-1.49 \pm 0.01$
<i>HPMBP + TOPO</i>			
Am	$1.89 \pm 0.08$	$5.56 \pm 0.02$	
Cm	$2.17 \pm 0.09$	$5.81 \pm 0.03$	
Bk	$3.33 \pm 0.02$	$6.16 \pm 0.04$	
Cf	$3.02 \pm 0.05$	$6.23 \pm 0.04$	

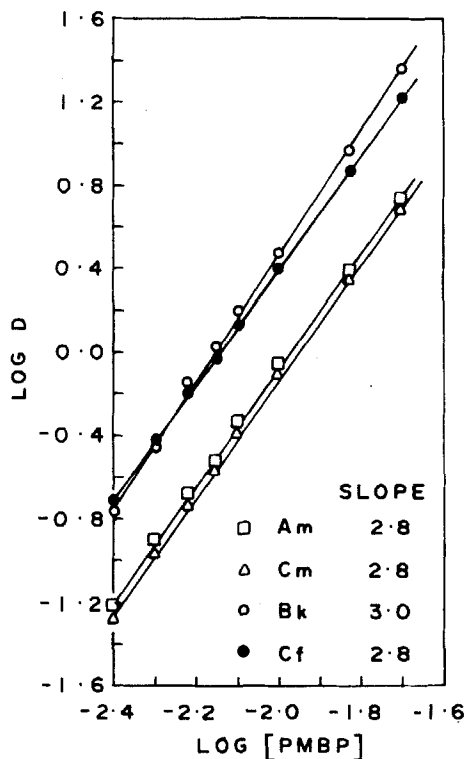


FIG. 5. Variation of distribution coefficient of trivalent actinides as a function of HPMBP concentration at fixed TOPO concentration.

with TBP and TOPO as the neutral donors along with the  $K_{\text{PMBP}}$  values of these trivalent actinides. The stability constants of the organic phase substitution or additions reactions ( $\beta_1$ ,  $\beta_2$ , and  $K_2$ ) of the trivalent actinides-HPMBP chelates with TBP and TOPO are given in Table 2. Bacher and Keller (6) have studied the synergistic extraction of Am(III) by mixtures of HPMBP and various neutral donors (MIBK, TBP, TOPO, AND TPPO) in chloroform. Their organic phase equilibrium constant values for TBP as synergist,  $\log \beta_1 = 0.77$  and  $\log \beta_2 = 2.0$ , are much lower compared to these values as presented in Table 2 of this paper. Similarly, the values for TOPO as synergist quoted by Keller et al.,  $\log \beta_1 = 0.9$  and  $\log \beta_2 = 7.6$ , are different than the present values. These differences between the values reported by Keller et al. and those reported by us could be due to the solvent  $\text{CHCl}_3$  used by them, in which the adduct stability constants are known to be lower. Chmutova et al. (7-10) have studied the synergistic extraction of

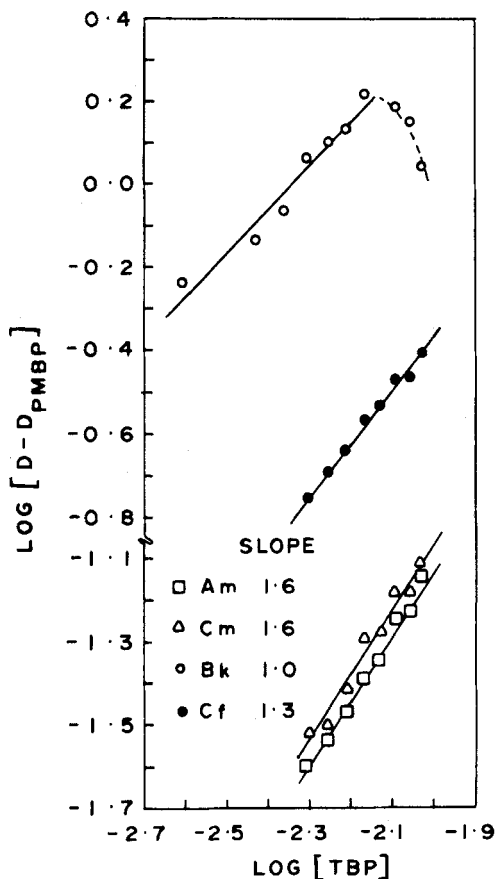


FIG. 6. Variation of distribution coefficient of trivalent actinides as a function of TBP concentration at fixed HPMBP concentration.

Am(III), Cm(III), Bk(III), and Cf(III) by mixtures of HPMBP + TBP or TOPO in benzene from  $\text{HNO}_3$  solutions. The adducts formed in the organic phase are  $\text{M}(\text{PMBP})_3 \cdot (\text{TOPO})_2$ ,  $\text{M}(\text{PMBP})_2(\text{NO}_3)(\text{TOPO})_2$ , and  $\text{M}(\text{PMBP})_3 \cdot (\text{TBP})_2$ . They do not encounter the formation of the first adduct, namely  $\text{M}(\text{PMBP})_3 \cdot \text{S}$ , probably because at the higher concentrations of HPMBP, TBP, and TOPO used by these authors, the formation of the first adduct is masked. These authors further report (21) that the synergic coefficient increased in the following order:  $\text{Cf(III)} < \text{Bk(III)} < \text{Cm(III)} < \text{Am(III)}$ . However, in the present work Bk(III) is an exception from this monotonic order with both TBP and TOPO as the neutral donors. The

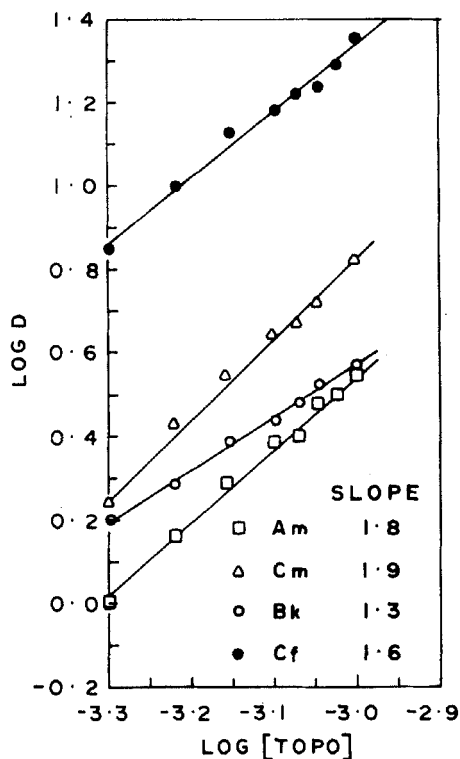


FIG. 7. Variation of distribution coefficient of trivalent actinides as a function of TOPO concentration at fixed HPMBP concentration.

TABLE 2

Equilibrium Constants for the Organic Phase Synergistic Reaction of Trivalent Actinides-HPMBP Chelate with Neutral Oxo Donors

M(III)	$\log \beta_1$	$\log \beta_2$	$\log K_2$
<i>HPMBP + TBP</i>			
Am	$2.11 \pm 0.07$	$4.61 \pm 0.03$	$2.49 \pm 0.06$
Cm	$2.18 \pm 0.07$	$4.51 \pm 0.06$	$2.33 \pm 0.07$
Bk	$3.20 \pm 0.16$	—	—
Cf	$2.02 \pm 0.02$	$3.81 \pm 0.05$	$1.79 \pm 0.05$
<i>HPMBP + TOPO</i>			
Am	$4.62 \pm 0.08$	$8.29 \pm 0.03$	$3.67 \pm 0.08$
Cm	$4.81 \pm 0.10$	$8.45 \pm 0.04$	$3.64 \pm 0.09$
Bk	$2.10 \pm 0.04$	$4.93 \pm 0.05$	$2.83 \pm 0.05$
Cf	$4.51 \pm 0.05$	$7.72 \pm 0.05$	$3.21 \pm 0.07$

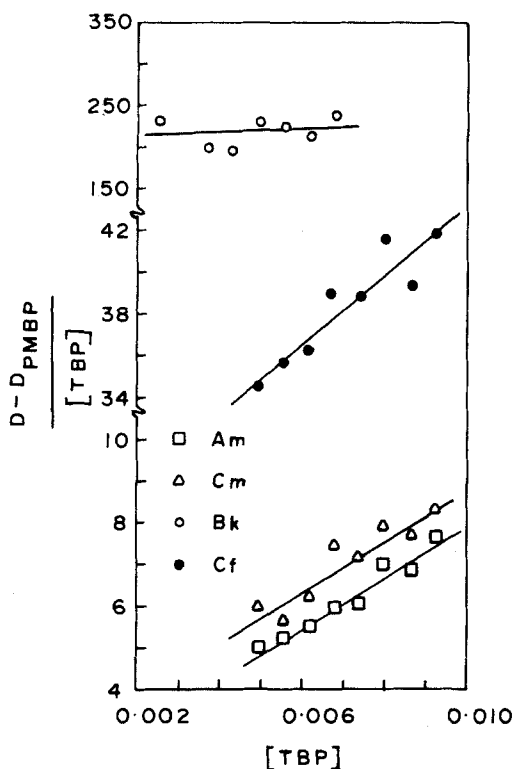


FIG. 8. Variation of  $(D - D_{\text{PMBP}})/[\text{TBP}]_{\text{org}}$  vs  $[\text{TBP}]_{\text{org}}$  for the trivalent actinides.

comparatively higher  $\beta_1$  value in the Bk/HPMBP/TBP system studied by us is evidently due to the nonreplacement of HPMBP in the synergistically extracted species, namely  $\text{Bk}(\text{PMBP})_3 \cdot \text{HPMBP} \cdot \text{TBP}$ . Navratil (17) and Tomilova et al. (19) have studied the synergistic extraction of a few trivalent lanthanides with HPMBP and various neutral donors. The formation of either the first, the second, or both the synergistic species has been observed in these systems.

Figure 10 gives the plots of  $\log \beta_1$ ,  $\log \beta_2$  (both with TOPO as synergist), and  $K_{\text{PMBP}}$  vs atomic number of the trivalent actinides Am, Cm, Bk, and Cf obtained in the present work. The general trend of decreasing  $\beta_1$  or  $\beta_2$  values with increasing atomic number is observed here, with the exception of Bk(III). This should normally be the order since with decreasing ionic radii (or increasing atomic number of the trivalent actinides), the  $\text{M(III)}\text{--HPMBP}$  chelate stability will increase and hence the stability of the adducts should follow the decreasing trend. The increasing trend for the chelate stability  $\text{M(III)}\text{--HPMBP}$  can also be seen from the  $K_{\text{PMBP}}$  values plotted in the same

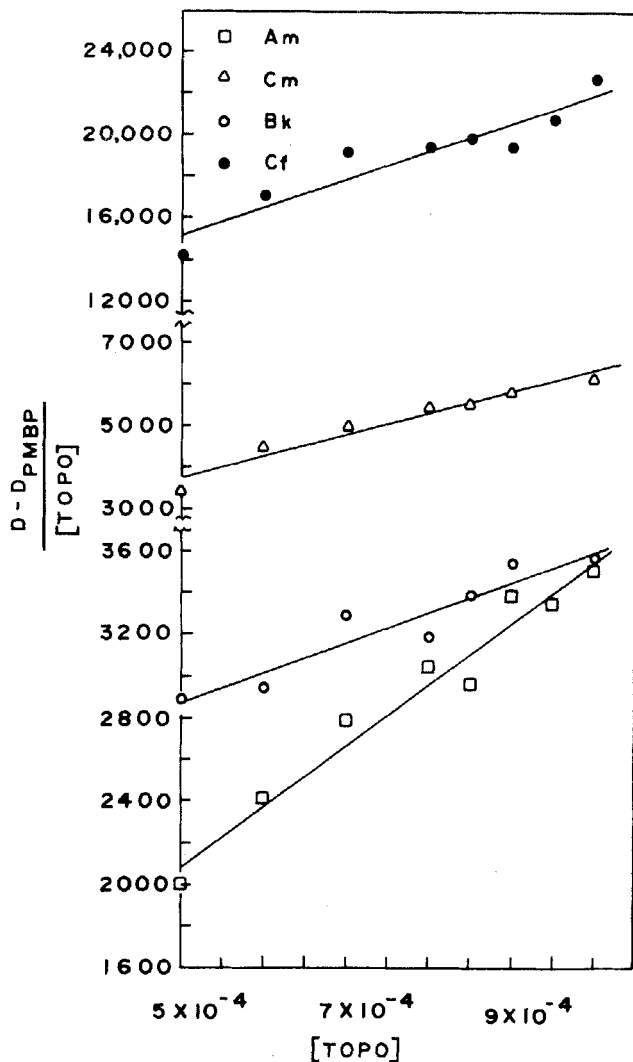


FIG. 9. Variation of  $(D - D_{\text{PMBP}})/[\text{TOPO}]_{\text{org}}$  vs  $[\text{TOPO}]_{\text{org}}$  for the trivalent actinides.

figure. In the Bk/HPMBP/TOPO system the  $\beta_1$  and  $\beta_2$  values are nearly 2 to 3 orders of magnitude lower than those for the other trivalent actinides studied here (Table 2). At the same time, the  $K_{\text{PMBP}}$  for Bk(III) is much higher (nearly 3 orders of magnitude) as compared to this value for Am, Cm, and Cf. As seen from our earlier work on the trivalent actinides-HTTA-

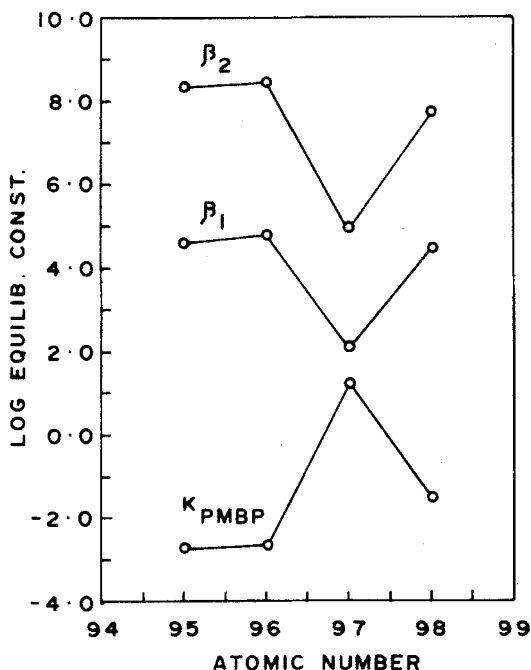


FIG. 10. Variation of equilibrium constant values ( $\beta_1$ ,  $\beta_2$ ,  $K_{\text{PMBP}}$ ) of the trivalent actinides-HPMBP-TOPO system with respect to the atomic number of the trivalent actinides.

neutral oxo donor systems (4, 5), the  $\log K_{\text{TTA}}$  for Bk(III) ( $-6.12$ ) is about one log unit higher than the corresponding value for Cf(III) ( $-7.29$ ) but the overall effect observed on the synergistic constants ( $\beta_1$ ,  $\beta_2$ ) are not as significant as they are in the HPMBP systems. The higher  $K_{\text{PMBP}}$  value for Bk(III) as compared to that for other trivalent actinides and the consequent low  $\beta_1$ ,  $\beta_2$  values for the TOPO adducts could have been easily explained on the assumption that Bk(III) is to some extent oxidized to Bk(IV) in the organic phase. However, the observed inverse third-power dependence on  $[\text{H}^+]_{\text{aq}}$  and the fourth-power dependence on  $[\text{HPMBP}]_{\text{org}}$  in the extraction of Bk(III) by HPMBP alone indicates the complete absence of oxidation of Bk(III) in the organic phase. Similar conclusions can be arrived at about the synergistic extraction of Bk(III).

Data in Table 3 on the extraction of trivalent actinides and lanthanides by HPMBP under identical experimental conditions indicate that Ce(III) also, like Bk(III), forms a stronger chelate compared to the HPMBP chelates of neighboring trivalent metal ions. Absence of any oxidation of Ce(III) in the organic phase was demonstrated by the observed lack of extraction of Ce



TABLE 3

Distribution Coefficient Values of Trivalent Actinides and Lanthanides  
in 0.02 *M* HPMBP/Xylene at pH 2.0 (HCl)

M(III)	Distribution coefficient, <i>D</i>	M(III)	Distribution coefficient, <i>D</i>
Am	$2.92 \times 10^{-4}$	La	$3.33 \times 10^{-5}$
Cm	$3.67 \times 10^{-4}$	Ce	$1.37 \times 10^{-2}$
Bk	3.96	Pm	$6.57 \times 10^{-4}$
Cf	$5.13 \times 10^{-3}$	Eu	$1.30 \times 10^{-3}$
		Tm	$2.30 \times 10^{-3}$

from 0.5 *M* HNO<sub>3</sub> solutions by HPMBP. The couples Ce(III)–(IV) and Bk(III)–(IV) have very close redox potentials of –1.60 and –1.54, respectively. It appears very probable that the higher stability of Ce(III) and Bk(III)–HPMBP (and other  $\beta$ -diketones like HTTA) chelates could conceivably arise through charge-transfer-type interactions of the metal ions with the  $\beta$ -diketonate moieties, though the exact mechanism of such an interaction is far from clear. This view is further strengthened by the fact that the order of extraction of the trivalent actinides increases with their atomic number when other extractants like dinonylnaphthalene sulfonic acid and di-2-ethylhexyl phosphoric acid are used as extractants which do not have a tendency (like the  $\beta$ -diketones) to donate an electron in charge-transfer interactions.

In all the synergistic systems studied here, the equilibrium constant values for the adducts of all the metal ions were higher with TOPO as compared to the corresponding adducts with TBP, which is also the order of basicity of these neutral oxo donors.

When the equilibrium constant values for the trivalent actinides–HPMBP–TBP (or TOPO) systems are compared with the corresponding values for the HTTA–TBP (or TOPO) systems (4, 5) (both in xylene), those with HPMBP are much lower (2–3 log units). A similar effect has been observed by Zolotov and Gavrilova (20) in the extraction of Zn(II) by mixtures of HPMBP + TBP and HTTA + TBP in carbon tetrachloride where the log  $\beta_1$  value for Zn(PMBP)<sub>2</sub>·TBP is 2.49 but for the analogous compound with HTTA it is 4.34. Normally a very distinct correlation between  $pK_{HA}$  of  $\beta$ -diketones and adduct stability constants has been observed, i.e., the stronger the chelating agent is as an acid (lower  $pK_{HA}$ ), the more stable an adduct it forms. In the case of the HPMBP–HTTA pair ( $pK_{Ha}$ , HPMBP = 4.11 and HTTA = 6.23 at 25°C,  $\mu = 0.1$ ), there is no such dependence, the reason

for which may perhaps be the substantial difference between the structure of these two  $\beta$ -diketones as suggested by Zolotov et al. (20). In HPMBP, one of the C=O groups is fixed in the pyrazolone group (cyclic type) and in HTTA both the C=O groups are of the noncyclic type.

The low adduct stabilities obtained in the HPMBP systems in the present work could also result from the nature of the chelate species extracted; namely,  $M(\text{PMBP})_3 \cdot \text{HPMBP}$ , which can be described as a self-adduct. The relatively hydrophobic HPMBP molecule exerts a strong synergistic effect, resulting in high  $K_{\text{PMBP}}$  values (Table 1) which are 5–7 orders of magnitude higher than the corresponding values for the HTTA chelates (4, 5) in spite of the higher acidity of HPMBP. The synergistic reactions with TBP and TOPO (except in the Bk/HPMBP/TBP system) are in fact replacement reactions taking place due to the higher basicities of TBP and TOPO compared to HPMBP. The  $\beta_1$ ,  $\beta_2$  values obtained reflect only the difference in the strength of the two adduct systems (HPMBP and TBP/TOPO). It can therefore be inferred that the equilibrium constants ( $\log \beta_1$ ) of a "normal" synergistic reaction between  $M(\text{PMBP})_3$  and TBP/TOPO would be in the range of 7–10 log units. With such a high stability of the adduct, the residual positive charge on the metal ion in  $M(\text{PMBP})_3$  would be very effectively neutralized, resulting in the comparatively low values of stability of the second adduct ( $\log K_2$ ) as observed from Table 2.

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