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Highly Acidic Extractant, 4-Benzoyl-3-phenyl-5-isoxazolone: The Synergistic Extraction of Alkaline Earth and Alkali Metals Combined with Trioctylphosphine Oxide or Bis(diphenylphosphinyl)methane

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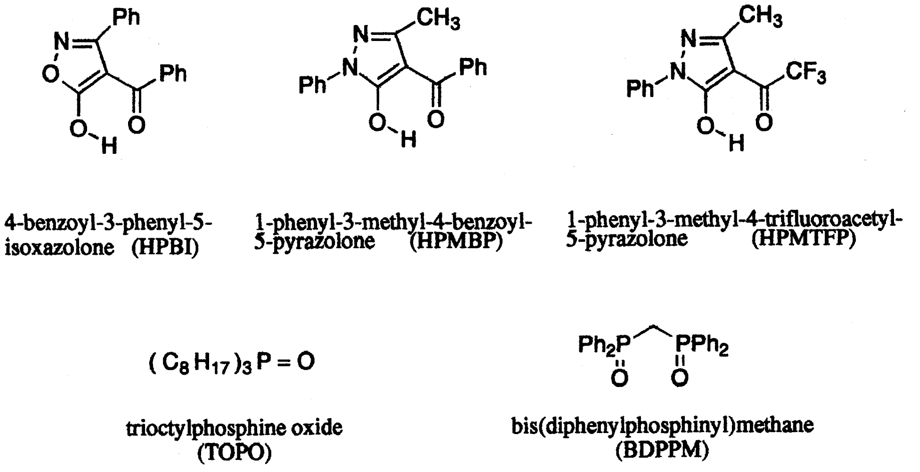
The synergistic extraction of alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) and alkali metals (Li^+ and Na^+) with a highly acidic extractant, 4-benzoyl-3-phenyl-5-isoxazolone (HPBI), combined with a synergist, trioctylphosphine oxide (TOPO) or bis(diphenylphosphinyl)methane (BDPPM), has been examined. The results were compared with those of the analogous extractants, 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HPMBP) and 3-methyl-1-phenyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP) which are also highly acidic extractants derived from heterocyclic compounds. Owing to the strong acidity of HPBI ($pK_a=1.23$), alkaline earths were extracted quantitatively from a very low pH region. Especially, alkaline earths were readily extracted at pH 2—3 with the bidentate phosphine oxide, BDPPM, as a synergist. The extraction of Li^+ and Na^+ with HPBI and TOPO was inferior to that with HPMBP and HPMTFP, though their acidity is weaker. In contrast to the excellent extractability of HPBI, its separation was poor. The extractability and separability are discussed in terms of the molecular structure, particularly the distance of the two donating oxygens.

The liquid–liquid extraction of lanthanides using 3-phenyl-4-benzoyl-5-isoxazolone (HPBI), a recently emerging strongly acidic extractant derived from heterocyclic 5-isoxazolone,[1,2] in the presence or absence of TOPO, has been reported in our previous paper.[3] The results obtained have proved the superiority of HPBI over other extractants. With a very strong acidity ($pK_a=1.23$) compared to those of typical β-diketones, 1,1,1-trifluoro-3-(2-thenoyl)acetone (HTTA, $pK_a=6.23$)[4] and the well-known acylpyrazolones, HPMBP ($pK_a=3.92$) and HPMTFP ($pK_a=2.56$),[5] HPBI can extract lanthanides into chloroform quantitatively at pHs below 3 (Chart 1). The extractability is much improved in the presence of a synergist such as TOPO. However, it is not convenient to use HPBI as a separator for this group of metals, as can be noticed through the modest values of separation factors. It has been found in our recent work[6] that improved extraction with a strongly



4-benzoyl-3-phenyl-5-isoxazolone (HPBI)

1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (HPMBP)

1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (HPMTFP)

$(C_8H_{17})_3P=O$

trioctylphosphine oxide (TOPO)

bis(diphenylphosphinyl)methane (BDPPM)

Chart 1.

acidic extractant is usually accompanied by poor selectivity. There is a close relationship between the distance of the two donating oxygen atoms in the structure of β-diketone, which has a significant effect on the acidity of the extractant, and the separability. The synergistic extraction of alkaline earth (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) and alkali metals (Li^+ and Na^+) with HPBI combined with a synergist, TOPO or BDPPM, has been studied to examine the extraction power of HPBI for those metal ions, which are usually known to be hard to extract quantitatively because of the low stability of the complexes and the remaining water molecules in the chelate.

Experimental

Chemicals and Apparatus. HPBI was synthesized from 3-phenyl-5-isoxazolone and benzoic anhydride in the presence of sodium benzoate in dioxane by the method of Kortes and Störiko.[7] The procedure of preparation in detail and analytical data can be found in our previous paper.[3] BDPPM was synthesized as described in the literature.[8,9] Analytical data have been given in the literature.[9] TOPO was purchased from Dojindo and used without purification. Metal solutions were prepared from standard solutions provided by Wako Pure Chemicals Industries. Other chemicals were of analytical reagent grade. Water was demineralized and distilled.

Metal ion concentrations were measured with a Japan Jarrell Ash Model ICAP-500 inductively coupled argon plasma atomic emission spectrometer. In case of alkali metal ions, flame emission measurements were made with a Hitachi Polarized Zeeman Atomic Absorption Spectrophotometer, model 180-80. pH measurements were done with a Hitachi-Horiba F-8L pH meter with a glass electrode.

A semi-empirical MNDO/H calculation was done on fully optimized molecular geometries on a Cray Y-MP2E/264 computer using MNDO93.

Solvent Extraction Procedure. A 10-mL sample of an aqueous phase containing 1×10^{-4} M (1 M=1 mol dm^{-3}) metal ion, 0.1 M sodium perchlorate, and 0.01 M acetic acid as a buffer component was adjusted to the desired pH with hydrochloric acid or sodium hydroxide solution. Sodium perchlorate was excluded in case of alkali ions and when BDPPM is used to avoid a precipitation reaction.[10] For the extraction of alkali metal ions, cesium hydroxide was used instead. The aqueous phase was mechanically shaken with an equal volume of benzene containing the required amount of HPBI together with TOPO or BDPPM in a 30-mL centrifuge tube for one hour at 25 °C. Preliminary experiments showed that a shaking time of one hour is long enough for equilibration. After centrifugation, the pH of the aqueous phase was measured and taken as an equilibrium value. The metal concentration in the aqueous phase was measured by inductively coupled argon plasma atomic emission spectrometry or flame spectrophotometry. That in the organic phase was measured in the same way after back-extraction by stripping with 1 M hydrochloric acid solution. The sum of the metal concentrations in two phases agreed well with the initial concentrations.

Results and Discussion

Extraction of Alkaline Earths in the Presence of TOPO. The distribution of alkaline earths with the combination of HPBI and TOPO as a function of pH is shown in Fig. 1. Without any synergistic reagent like TOPO, the extraction was negligible. In the presence of TOPO, Mg, Ca, and Sr can be readily extracted. As can be seen, log D, which is the distribution ratio of alkaline earth ions, increases linearly with pH and then the curves tend to bend towards the right.

$$D=[M^{2+}]_o/[M^{2+}] \quad (1)$$

The subscript o denotes the species in the organic phase. The slopes of the linear part of the curves are all very close to 2, indicating that two hydrogen ions are released during the formation of the complex.

In Fig. 2, the $\log D-2\text{pH}$ vs. $\log[\text{HPBI}]_o$ dependence of Sr, represented by a straight line with slope 2, indicates that two molecules of HPBI have reacted with one molecule of metal ion to form the $M(PBI)_2(TOPO)_s$ type of chelate and there is no formation of a self-adduct complex type $M(PBI)_2(HPBI)_j(TOPO)_s$. Similar results have been obtained for the remaining metal ions. As can be seen in Fig. 3, log D also increases with the concentration of TOPO in the organic phase. All these plots have slopes varying from 1 to 2 as the TOPO concentration becomes larger whatever the alkaline earth ion is. This means the composition of the extracted species depends on the TOPO concentra-

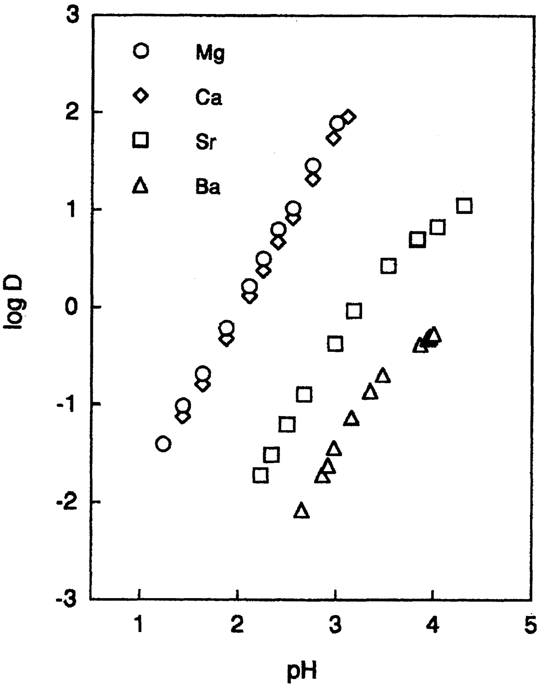


Fig. 1. Extraction of alkaline earths into benzene with HPBI and TOPO. $[\text{HPBI}]_o=0.05$ M, $[\text{TOPO}]_o=0.01$ M in benzene, $[\text{NaClO}_4]=0.1$ M.

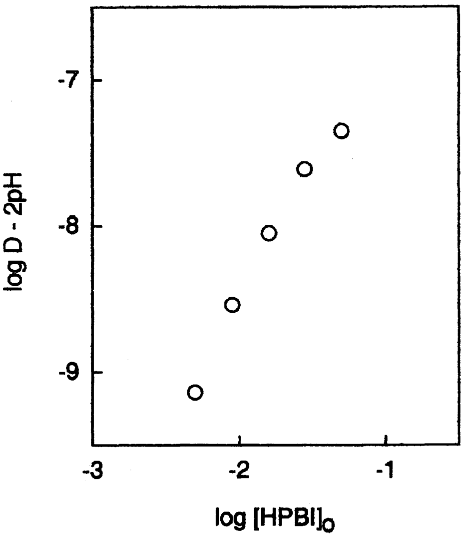


Fig. 2. Plots for log $D-2$pH vs. log $[\mathrm{HPBI}]_o$ in the synergistic extraction of alkaline earths with HPBI and TOPO.

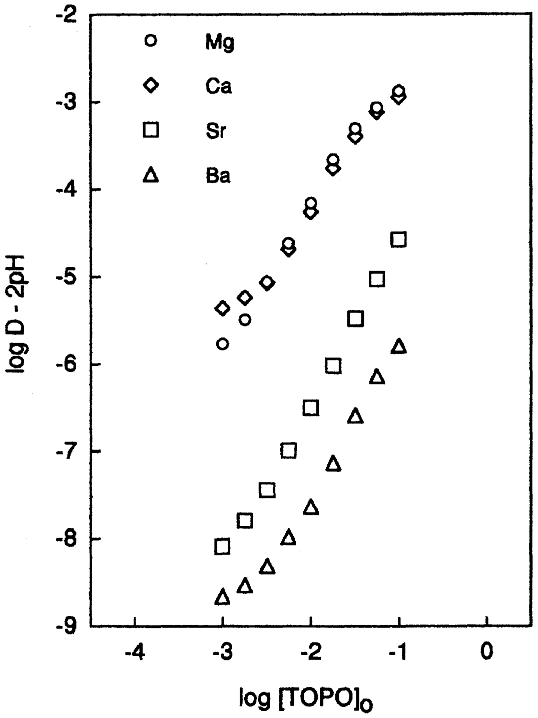


Fig. 3. Plots for $\log D-2\mathrm{pH}$ vs. $\log [\mathrm{TOPO}]_o$ in the synergistic extraction of alkaline earths with HPBI and TOPO.

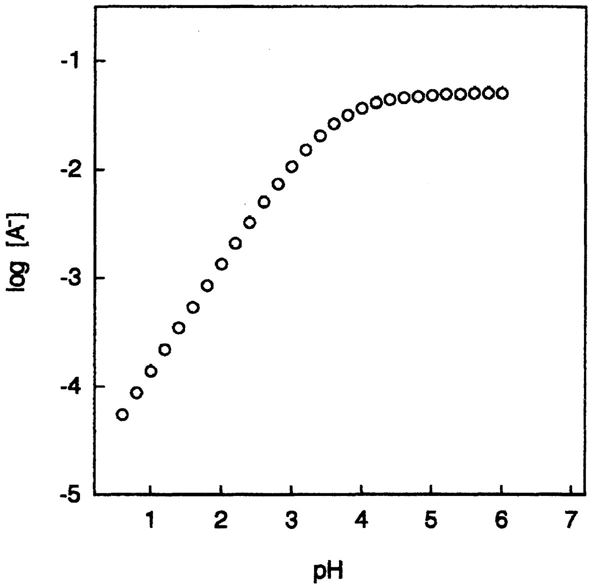


Fig. 4. The concentration of A^- as a function of pH calculated on the basis of Eq. 6. $[\mathrm{HA}]_i=0.05$ M.

tion, $M(PBI)_2(TOPO)$ at the low TOPO concentration and $M(PBI)_2(TOPO)_2$ at the high one. The maximum number of coordinated TOPO molecules is thus 2 for all the examined alkaline earth ions. Some deviation from the straight lines was seen at the high $[\mathrm{HA}]_o$ in Fig. 2 and also at the high $[\mathrm{TOPO}]_o$ in Fig. 3 for magnesium and calcium. This deviation might be attributed to the association of HPBI and TOPO in the organic phase, which reduces the effective concentration of both HPBI and TOPO.[11]

From the results obtained for the extraction system (HPBI/alkaline earths/TOPO), the overall extraction equilibrium and the synergistic extraction constant can be readily written as follows:

$$M^{2+}+2\mathrm{HPBI}_o+2\mathrm{TOPO}_o \rightleftharpoons M(\mathrm{PBI})_2(\mathrm{TOPO})_{2,o}+2H^+ \quad (2)$$

$$K_{\mathrm{ex,s}} = [M(\mathrm{PBI})_2(\mathrm{TOPO})_2]_o[H^+]^2/[M^{2+}][\mathrm{HPBI}]_o^2[\mathrm{TOPO}]_o^2 \quad (3)$$

Putting the expression of the distribution ratio D in Eq. 1 into Eq. 3, we obtain

$$K_{\mathrm{ex,s}} = D[H^+]^2/[\mathrm{HPBI}]_o^2[\mathrm{TOPO}]_o^2 \quad (4)$$

Consequently,

$$\log K_{\mathrm{ex,s}} = \log D - 2\mathrm{pH} - 2\log [\mathrm{HPBI}]_o - 2\log [\mathrm{TOPO}]_o \quad (5)$$

Based on Eq. 5 and the $\mathrm{pH}_{1/2}$ values, at which half of the metal ion is extracted, read from Fig. 1, the synergistic extraction constants, $K_{\mathrm{ex,s}}$, of alkaline earths have been calculated and are displayed in Table 1.

The extractant dissolved in the organic phase is distributed to the aqueous phase and releases hydrogen to form the anionic species (A^-) followed by complexation with metal ions. The concentration of A^- can be obtained by the following equation.[5]

$$[A^-] = \frac{[\mathrm{HA}]_i}{1+[H^+](1+P_{\mathrm{HA}})K_a{}^{-1}}, \quad (6)$$

where $[\mathrm{HA}]_i$ stands for the initial concentration of HPBI in the benzene phase, P_{HA} the partition constant defined as $[\mathrm{HA}]_o/[\mathrm{HA}]$, and K_a the acid dissociation constant. The concentration of A^- is calculated using the

Table 1. Extraction Constants for Alkaline Earths and Li with HPBI, HPMBP, and HPMTFP in the Presence of TOPO

	HPBI			HPMBP[a)]		HPMTFP[a)]	
	$s^{b)}$	$pH_{1/2}{}^{c)}$	$\log K_{ex,s}$	s	$\log K_{ex,s}$	s	$\log K_{ex,s}$
Ba^{2+}	2	$(3.82)^{d)}$	−1.03	3	−4.56	3	−0.04
Sr^{2+}	2	$(3.25)^{d)}$	0.10	2	−5.02	3	1.30
Ca^{2+}	2	2.04	2.52	2	−2.27	2	1.48
Mg^{2+}	2	1.98	2.64	2	−1.44	2	1.86
Li^{+}	2	$(3.68)^{d,e)}$	−0.38	2	$-2.68^{f)}$	2	$-0.48^{f)}$

a) Taken from Ref. 12. b) The number of TOPO molecule in the extracted species. c) $[HPBI]_o=5\times10^{-2}$ M, $[TOPO]_o=1\times10^{-2}$ M in benzene. d) Obtained by extrapolating the linear part the extraction curves in Figs. 1 and 6. e) $[HPBI]_o=5\times10^{-2}$ M, $[TOPO]_o=1\times10^{-1}$ M in benzene. f) Taken from Ref. 16.

P_{HA} value of $10^{2.33}$ reported in the literature[3)] and illustrated in Fig. 4 as a function of pH. Log $[A^-]$ increases linearly as the pH increases by pH 3 and is asymptotic to the value of −1.30, the initial concentration (0.05 M) at the higher pH region. This is the reason why the extraction curves for Sr and Ba deviate from straight lines with a slope of 2 over pH 3. When $\log D$ was plotted against $\log [A^-]$ instead of pH, all the plots were found to fall on the straight lines with a slope of 2. The straight lines of slope of 2 in the $\log D$ vs. $\log [A^-]$ plots also indicate that the formation of other metal species such as MA^+ are negligible.

Table 1 gives the $pH_{1/2}$ and $\log K_{ex,s}$ values for HPBI and TOPO together with those for HPMBP and HPMTFP[12)] for comparison. In all cases, the employed solvent was benzene. From the data, it can be easily noticed that the synergistic extraction constants, $K_{ex,s}$, for HPBI are the largest among the three extractants. This can be explained by the stronger acidity of HPBI than HPMBP and HPMTFP. The strong acidity is caused partly by the high electron-withdrawing effect of the heterocyclic isoxazole ring, which contains both the π-electron conjugation system and highly electronegative elements, O and N. Moreover, it is worth paying attention to the distance between the two donating oxygen atoms in the enol form of the extractants. The effect of the O–O distance on the acidity had been examined in our previous paper.[6)] The O–O distances calculated by MNDO/H are 2.90, 2.65, 2.66, and 2.50 Å for HPBI, HPMBP, HPMTFP, and HTTA, respectively. The large O–O distance of HPBI weakens the intramolecular hydrogen bond and consequently leads to its strong acidity owing to the easy leaving of hydrogen from the ligand molecule.

The plots of $\log K_{ex,s}$ vs. pK_a of the extractants do not give straight lines as in the case of rare earth metals[3)] but a curved one, as shown in Fig. 5. When the composition is the same, that is, the number of TOPO molecules in the extracted species is the same, then it is possible to compare the extractability. In fact, unlike the extraction constant of lanthanides, the synergistic extraction constant is the product of two factors, the extraction constant, K_{ex}, and the adduct formation constant, β_s.

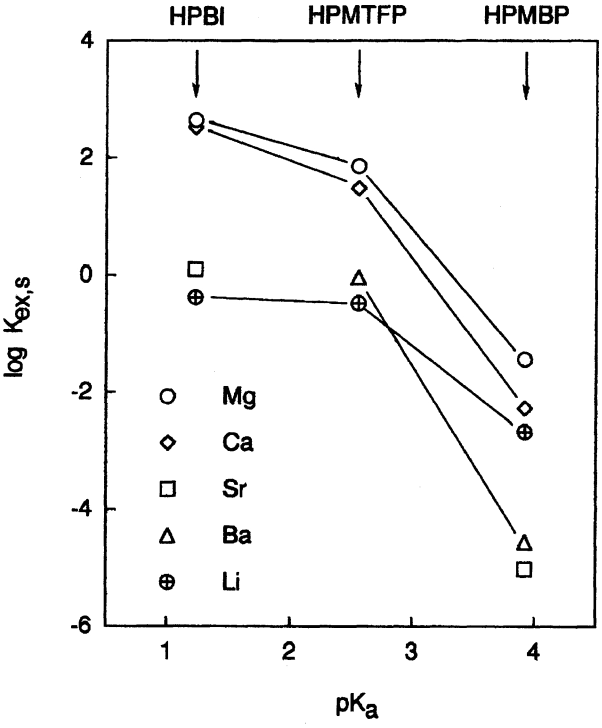


Fig. 5. Plots for $\log K_{ex,s}$ vs. pK_a in the synergistic extraction of alkaline earths and lithium with HPBI, HPMTFP, or HPMBP combined with TOPO.

$$K_{ex} = [M(PBI)_2]_o[H^+]^2/[M^{2+}][HPBI]_o^2 \tag{7}$$

$$\beta_s = [M(PBI)_2(TOPO)_s]_o/[M(PBI)_2]_o[TOPO]_o^s \tag{8}$$

$$K_{ex,s} = K_{ex} \cdot \beta_s. \tag{9}$$

According to our study in the extraction of lanthanides with acylpyrazolones[13)] or acylisoxazolone,[3)] the extractability represented by $\log K_{ex}$ increases almost linearly as pK_a decreases. In the synergistic extraction, the adduct formation reaction represented by β_s also increases as pK_a decreases. As a result, the extraction of metals can be greatly improved by using extractants of strong acidity together with appropriate synergists. The strong acidity of HPBI could be considered to arise from two origins as mentioned above; the heterocyclic isoxazolone ring including electronegative elements and the weak intramolecular hydrogen bond brought by the long O–O distance. An electron-withdrawing substituent such as the trifluoromethyl group in HPMTFP also strengthens the acidity. Among the origins, the effects of the heterocyclic ring and the electron-withdrawing substituent are similar: The electron density on the donating oxygens is reduced and the negative charge after releasing hydrogen is delocalized, resulting in a strong acidity. On the contrary, the effect of the long O–O distance does not affect the electron state on the donating oxygens. In the synergistic extraction of lanthanides with HPBI[3)] or acylpyrazolones[14,15)] combined with TOPO, it was found that the adduct formation constants for HPMTFP are larger than those for HPMBP and HPBI, the constants of which are similar regardless of their acidity. This indicates that the role of the strong acidity brought by the long O–O distance on the adduct formation reaction seems quite different from that by the heterocyclic and the substituent effects, that is, the strong acidity caused by the long O–O distance does not increase the adduct formation reaction as much. It would be possible to interpret the curved plots in Fig. 5 through the different role of the origins of the strong acidity.

In spite of the superior extraction by HPBI of alkaline earths, the separation of HPBI is evidently poor as compared to HPMBP and HPMTFP. A similar combination, the superior extraction and poor selectivity or the poor extraction and superior separation, could be seen in the extraction of lanthanides.[3,6)] The O–O distance affects not only the acidity but also the selectivity. Since the electron density decreases as the ionic radius increases, the stability of the alkaline earth is usually in the order, Mg>Ca>Sr>Ba, which is also the order in the solvent extraction of alkaline earths. It can be considered that more energy is required to complex a metal ion with a smaller ionic radius than a metal ion with a larger one. The O–O distance of the anionic form (A^-) of HPBI is longer than those of other β-diketones including HPMBP and HPMTFP. HPBI needs to pay even more energy to arrange its conformation to fit the complex structure of a smaller metal cation, which should lead to a poor ion size selectivity. Although we need to take into account the adduct formation reaction on evaluating separation in the synergistic extraction, the tendency that the superior extraction by an extractant with a long O–O distance is accompanied by a poor separation is also applicable to this synergistic extraction system.

Extraction of Lithium and Sodium in the Presence of TOPO. Similarly, without any synergist like TOPO, alkali metals were totally unextractable with HPBI. In the presence of 0.1 M TOPO, 50% of lithium can be extracted at pH 4.5—5 into benzene, but the extraction of sodium was very low as shown in Fig. 6. The slope of the curve of log D vs. pH of Li was found to be 1 at the linear portion, that of log $D-$pH vs. log $[\mathrm{HPBI}]_o$ was also very close to 1, but that of log $D-$pH vs. $[\mathrm{TOPO}]_o$ had the maximum value equal to 2. We can deduce that the composition of the extracted species is $\mathrm{Li(PBI)(TOPO)_2}$.

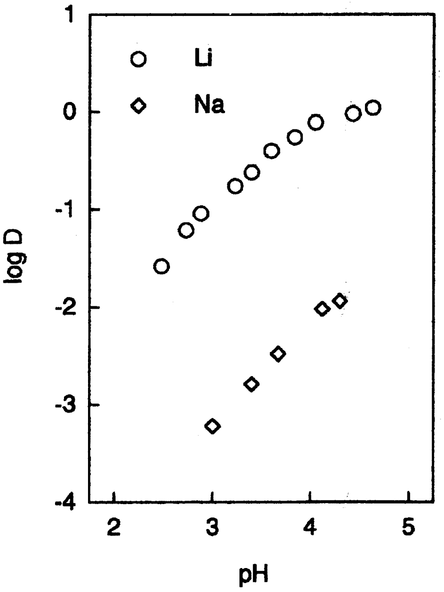


Fig. 6. Extraction of lithium and sodium into benzene with HPBI and TOPO. $[\mathrm{HPBI}]_o$=0.05 M, $[\mathrm{TOPO}]_o$= 0.1 M in benzene.

The overall synergistic extraction equilibrium of Li can be written as

$$\mathrm{Li^+ + HPBI_o + 2TOPO_o \rightleftharpoons Li(PBI)(TOPO)_{2,o} + H^+} \quad (10)$$

and

$$\log K_{\mathrm{ex,s}} = \log D - \mathrm{pH} - \log\,[\mathrm{HPBI}]_o - 2\log\,[\mathrm{TOPO}]_o \quad (11)$$

The calculated $K_{\mathrm{ex,s}}$ for Li has also been displayed in Table 1.

HPBI was found to be a poor extractant for Li and Na. Although the extraction constant is comparable to that of HPMTFP, 98% of Li is extracted into benzene with HPMTFP under the same conditions.[16)] The poor extraction of Li could be referred to the low stability in the adduct formation reaction as mentioned in the synergistic extraction of alkaline earths. It could be also attributed to unstable complexation owing to the exceedingly small ionic radius of Li. Finally, owing to the low stabilities in complexation and adduct formation, the extraction was done over pH 3, where A^- does not increase linearly and neither does the extraction. The relationship between log $K_{\mathrm{ex,s}}$ and pK_a of the extractants is illustrated in Fig. 5. Paying attention to the separability, HPBI is inferior to HPMBP and HPMTFP. The separation factor defined by $D_{\mathrm{Li}}/D_{\mathrm{Na}}$ read from Fig. 4 is about 200, but they are reported to be 1590 and 1450 for HPMBP and HPMTFP,[16)] respectively. The poor separation is also attributable to the long O–O distance of HPBI.

Extraction of Alkaline Earths in the Presence of BDPPM. Bis(diphenylphosphinyl)methane (BDPPM), a bidentate neutral phosphine oxide in which two diphenylphosphinyl groups are connected by a methylene group, has been proved to be one of the most powerful synergists,[9,15,17—19] for it has two P=O groups, a very strong Lewis base, and forms with the metal chelate a stable six-membered ring. When monodentate TOPO is replaced by BDPPM, the extraction of alkaline earths using HPBI has been much increased, as can be clearly seen in Fig. 7. A quantitative extraction of alkaline earths with HPBI has been done with a fairly good efficiency (almost 100% for all the metal ions) at more acidic pH (2—3). In a similar way to the case of TOPO, analyzing all the related plots allows us to express the overall extraction equilibrium as follows:

$$M^{2+}+2HPBI_o+sBDPPM_o \rightleftharpoons M(PBI)_2(BDPPM)_{s,o}+2H^+ \quad (12)$$

and

$$\log K_{ex,s} = \log D - 2pH - 2\log [HPBI]_o - s\log [BDPPM]_o \quad (13)$$

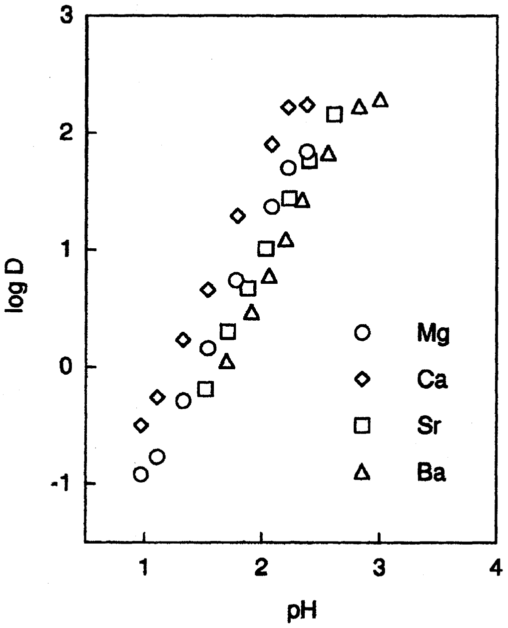


Fig. 7. Extraction of alkaline earths into benzene with HPBI and BDPPM. $[HPBI]_o$=0.05 M, $[BDPPM]_o$= 0.01 M in benzene.

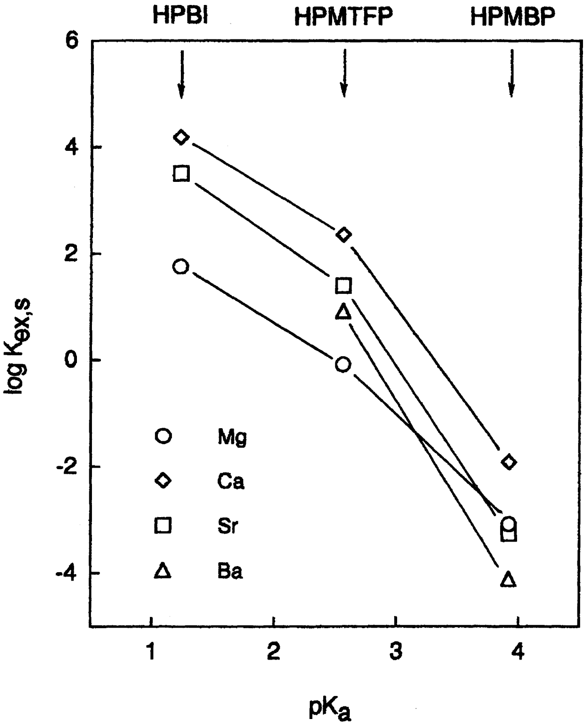


Fig. 8. Plots for $\log K_{ex,s}$ vs. pK_a in the synergistic extraction of alkaline earths with HPBI, HPMTFP, or HPMBP combined with BDPPM.

The results obtained are summarized in Table 2, together with those of HPMBP and HPMTFP for comparison.

As shown in Table 2, the number of BDPPM molecules that coordinate to the extracted species increases with the ion size of the metals. Mg was extracted as $Mg(PBI)_2(BDPPM)$, and Ca and Sr as $Ca(PBI)_2(BDPPM)_2$ and $Sr(PBI)_2(BDPPM)_2$, and Ba with the largest ion size among them as $Ba(PBI)_2(BDPPM)_3$. Of course BDPPM was acting as a bidentate neutral ligand as can be confirmed by the large enhancement in the extraction of alkaline earths, the capacity of admitting adduct-forming reagent depends largely on the metal ion size. This explains the rather large steric hindrance suffered by Ca and Sr owing to their smaller ionic radii than Ba when two BDPPM molecules are admitted, which also led to a reversion in the extraction order of Ca and Mg, as can be seen in Fig. 7. The latter has accepted only one

Table 2. Extraction Constants of Alkaline Earths with HPBI, HPMBP, and HPMTFP in the Presence of BDPPM

	HPBI			HPMBP[a]		HPMTFP[a]	
	s	$pH_{1/2}$	$\log K_{ex,s}$	*s*	$\log K_{ex,s}$	*s*	$\log K_{ex,s}$
Ba^{2+}	3	1.67	5.26	2	−4.11	2	0.92
Sr^{2+}	2	1.55	3.51	2	−3.26	2	1.40
Ca^{2+}	2	1.22	4.19	2	−1.92	2	2.36
Mg^{2+}	1	1.42	1.76	1	−3.08	1	−0.08

a) Taken from Ref. 17.

BDPPM molecule in the adduct.

The plots of $\log K_{\mathrm{ex,s}}$ vs. $\mathrm{p}K_\mathrm{a}$ of the extractants in Fig. 8 does not give straight lines like the case for TOPO in Fig. 5. The discussions about the relation between the adduct formation and $\mathrm{p}K_\mathrm{a}$ that comes from differing origins is again applicable to the present BDPPM system. The effect of BDPPM on enhancing the extraction also depends on the ion size. The enhancement increases as the ion size increases. MNDO/H calculation was made for BDPPM keeping the two P=O moiety on the same plane. The obtained distance between the two donating oxygens is 3.22 Å. It is much larger than that of β-diketone type extractants including acylisoxazolone and acylpyrazolone. This large O–O distance favors metals with a large ionic radius in a similar manner as mentioned for HPBI. As a result, the separation among alkaline earths with HPBI and BDPPM is very poor, while they are quantitatively extractable at extremely low pH.

Conclusions

It has been explicitly demonstrated that the ligand structure, particularly the O–O distance, is decisive in both the extractability and separability. The combination of the extractant and the bidentate synergist with a large O–O distance brought about an excellent extraction and a poor separation simultaneously. The implications of these results should be significant in designing extraction–separation systems of high efficiency and selectivity.

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