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The Synergistic Extraction of Alkaline Earth Metals with 4-Benzoyl-3-methyl-1-phenyl-5-pyrazolone and Bis(diphenylphosphinyl)methane

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The bidentate neutral ligand, bis(diphenylphosphinyl)methane, was synthesized and applied to the synergistic extraction of alkaline earth metals into benzene with 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone. This bidentate ligand was found to be much more powerful than the monodentate neutral ligand such as trioctylphosphine oxide.

In the liquid-liquid extraction of β-diketonates, it is well known that the presence of a Lewis base such as trioctylphosphine oxide (TOPO) enhances the extraction owing to the adduct formation between the metal chelate and the Lewis base. The synergistic effects on the extraction with a monodentate neutral ligand have been widely investigated.1) The synergistic extraction with a bidentate ligand should be of interest, for it would be expected that peculiar adduct formation between the bidentate neutral ligand and the metal β-diketonate might result in more enhanced extraction and/or improved separation. Among the various kinds of neutral ligands, substituted phosphine oxide is one of the most powerful and versatile reagents. An attempt has been made to synthesize the bidentate phosphine oxide derivative and to apply this reagent to the synergistic extraction of alkaline earth metals. The results are discussed comparing with those in the TOPO system.2)

Bis(diphenylphosphino)methane was synthesized according to the literature.3) Bis(diphenylphosphinyl)methane (BDPPM) was synthesized by the oxidation of bis(diphenylphosphino)methane with hydrogen peroxide.4,5)

The extraction procedures are almost the same as described previously.2) An aliquot of a benzene phase containing 0.05 mol dm^{-3} of 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HPMBP) and 0.01 mol dm^{-3} of BDPPM was equilibrated with the equal volume of an aqueous phase containing a required amount of metal ion and 0.01 mol dm^{-3} of sodium acetate. After the two phases were separated, pH of the aqueous phase was measured and taken as the equilibrated value. The concentrations of the alkaline earth metal ions in the aqueous phase were determined by inductively coupled plasma emission spectrometry. Their concentrations in the organic phase were measured in the same way after back extracted into dilute hydrochloric acid solution.

When a Lewis base is present in the extraction system, the extraction equilibrium and the synergistic extraction constant ($K_{ex,s}$) can be expressed as follows.

$$M^{2+} + 2HA_o + sL_o \rightleftharpoons MA_2L_{s,o} + 2H^+ \qquad (1)$$

$$K_{ex,s} = [MA_2L_s]_o[H^+]^2/[M^{2+}][HA]_o^2[L]_o^s$$
$$= D[H^+]^2/[HA]_o^2[L]_o^s \qquad (2)$$

In these equations, M, HA, L, and D denote the metal ion, HPMBP, BDPPM and the distribution ratio of metal ions, respectively. Subscript o indicate the species in the organic phase.

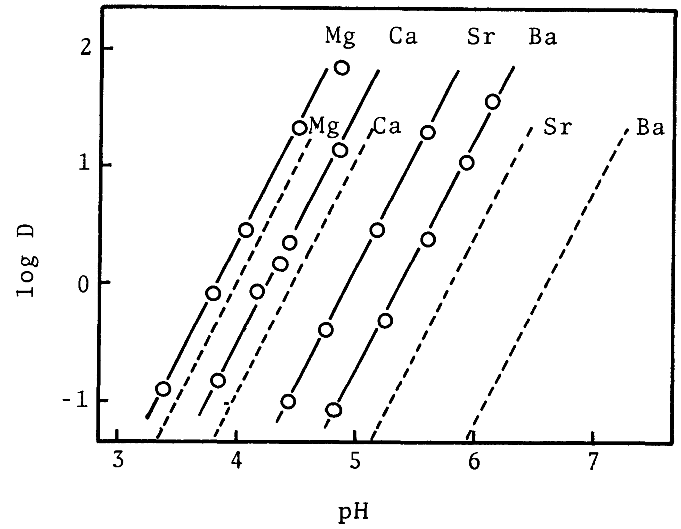

Fig. 1. Extraction of alkaline earth metals.
BDPPM or TOPO 0.01 mol dm^{-3},
HPMBP 0.05 mol dm^{-3} in benzene.
(———) HPMBP/BDPPM system,
(-----) HPMBP/TOPO system.

Figure 1 shows the extraction of alkaline earth metals into benzene as a function of pH. The solid lines indicate the extractions with HPMBP and BDPPM, and the dotted lines indicate those with HPMBP and TOPO. As seen in the figure, quantitative extractions can be achieved with HPMBP and BDPPM, and it was found that the extraction were made at a lower pH region. As compared with the HPMBP/TOPO system, magnesium and calcium are extracted at a slightly lower pH region, whereas strontium and barium are extracted at a much lower pH region. For instance, in the extraction of barium, the $pH_{1/2}$ value, at which half of metal is extracted, is 6.58 for HPMBP/TOPO system and 5.36 for HPMBP/BDPPM system, that is, the $pH_{1/2}$ value is shifted to a lower pH by about 1.2.

In order to clarify the composition of the extracted species, the dependence of BDPPM concentration on the extraction of alkaline earth metals were examined keeping the HPMBP concentration and pH of the aqueous phase at constant. As can be seen in Fig. 2, the distribution curves are asymptotic to straight lines. The slope of the straight line indicates the number of the BDPPM molecule which attaches to the metal-acylpyrazolonate. The slope is found to be almost 1 for magnesium and 2 for calcium, strontium and barium, respectively.

The extraction constants calculated by means of Eq. 2 and $pH_{1/2}$ values are summarized in Table 1 together with those for the HPMBP/TOPO system.[2)] The distribution of the chelates were scarcely influenced by 0.1 mol dm^{-3} of sodium perchlorate which was added in the aqueous phase to keep the ionic strength 0.1 in the HPMBP/TOPO system. On the other hand, the presence of sodium perchlorate, even when the concentration was below 0.01 mol dm^{-3}, has remarkably affected the extraction in the HPMBP/BDPPM system. The extraction parameters for the HPMBP/BDPPM system in the present work have been determined in the absence of sodium perchlorate. No influence caused by such anions as chloride or acetate

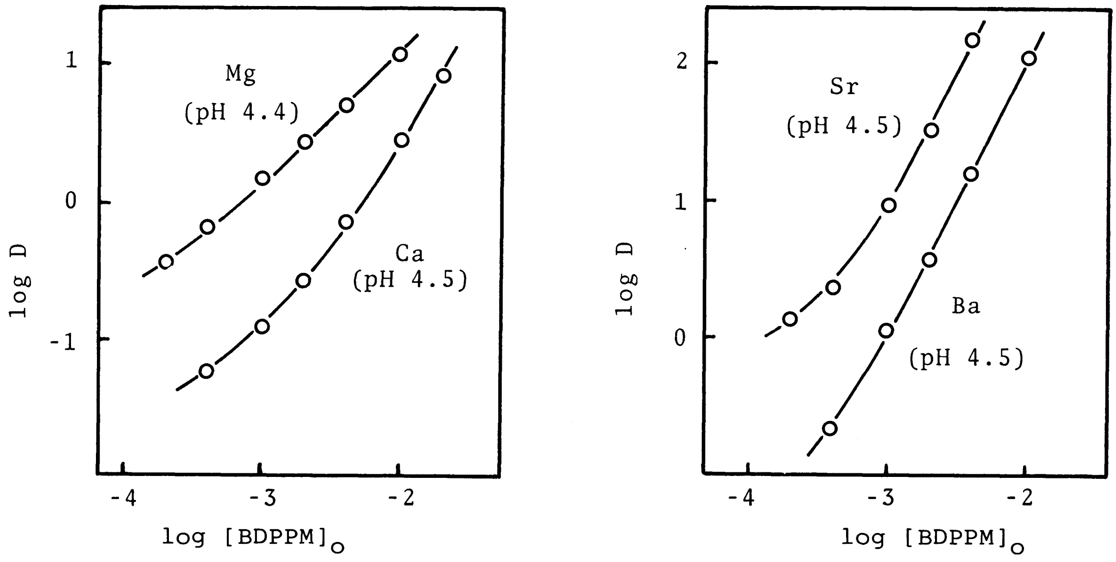

Fig. 2. Influence of the BDPPM concentration on the extraction of alkaline earth metals. The HPMBP concentration (0.05 mol dm^{-3}) and the pH of the aqueous phase were kept at constant.

Table 1. Extraction parameters for MA_2L_s

Neutral ligand		Mg	Ca	Sr	Ba
BDPPM	$pH_{1/2}$[a]	3.84	4.26	4.93	5.36
	log $K_{ex,s}$	-3.08	-1.92	-3.26	-4.11
	s	1	2	2	2
TOPO[b]	$pH_{1/2}$[a]	4.02	4.44	5.81	6.58
	log $K_{ex,s}$	-1.44	-2.27	-5.02	-4.56
	s	2	2	2	3

a) Organic phase: $[HPMBP]_o$=0.05 mol dm^{-3} and $[BDPPM]_o$=$[TOPO]_o$=0.01 mol dm^{-3} in benzene. b) Values are taken from Ref. 2.

were observed. The detailed investigation on the effect of sodium perchlorate in the HPMBP/BDPPM system is now under examination.

As can be seen in the table, BDPPM is found to be a more powerful ligand than TOPO especially for strontium and barium. When BDPPM attaches to the metal-acylpyrazolonate, it is expected to form a six-membered ring, which is known to be a very stable structure. A relatively large space is required for BDPPM to attach to the metal chelate, for the BDPPM molecule is bulky as compared with TOPO. This should be the reason why only one molecule of BDPPM attaches to the magnesium chelate while two molecules of BDPPM attach to calcium, strontium and barium chelate.

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