

Solvent Extraction of Alkaline Earth Metals with Alkylphosphorus Acids*

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Abstract Solvent extraction equilibria of four main alkaline earth metals (magnesium, calcium, strontium and barium) with di(2-ethylhexyl) phosphoric acid (DEHPA), 2-ethylhexyl phosphonic acid mono-(2-ethylhexyl) ester, di(2,4,4-tri-methylpentyl) phosphinic acid and IR spectra of the extracts have been studied. The selectivity order is dependent on the e/r value and hydration energy of the metal ions. The minor shift of the P→O in IR absorption of the alkaline earth metal extracts indicates that the interaction between the metal ions and P→O is much weaker for alkaline earth metals than for transitional metals.

The distribution of the four alkaline earth elements between aqueous solutions and solutions of DEHPA and neutral organophosphorus compounds, tri-*n*-butyl phosphate (TBP) or tri-octyl phosphine oxide (TOPO) in kerosene have been determined at varying ratio of TBP or TOPO to DEHPA and the positive synergism is observed. The synergic effect is explained by using IR spectra of the loaded organic phase.

Keywords solvent extraction, alkaline earth metals, di(2-ethylhexyl) phosphoric acid (DEHPA)

1 INTRODUCTION

Many compounds of alkaline earth metals, such as magnesium, calcium, strontium and barium, are important inorganic chemicals. Precipitation of sulphate, carbonate or occasionally oxalate has been used for separation and purification of these elements in current commercial processes. However, the purity of products by using precipitation is unsatisfactory because of the limited difference in the solubility. Although solvent extraction has been widely used in metallurgical processes for metal separation, it is seldom adopted in alkaline earth metals production. It is reported that a purity of 99.9% magnesium oxide could be achieved by solvent extraction^[1]. There are also some other works^[2-7] related to the extraction of alkaline earth metal ions, mostly for the analytical purposes.

Di(2-ethylhexyl) phosphoric acid (DEHPA), 2-ethylhexyl phosphonic acid mono-(2-ethylhexyl) ester (EHEHPA), and di(2,4,4-tri-methylpentyl) phosphinic acid (DTMPPA) are alkylphosphorus acids which have been widely used in metallurgy. The solvent extraction of alkaline earth elements and the reaction mechanism with the above extractants are systematically investigated in this work.

Synergetic effect is an important phenomenon in solvent extraction, which is usually helpful for increasing the separation ability for elements with similar properties. Synergic extraction of alkaline earth elements has been reported in the system of thenoyltriflu-

oroactone(TTA) and tri-*n*-butyl phosphate(TBP)^[8], TTA and tri-octyl phosphine oxide(TOPO)^[9,10], Versatic acid and crown ethers^[11,12], 1-phenyl-3-methyl-4-benzoylpyrazol-5-one and TOPO^[13]. Another purpose of the present work is to look into the synergism in the solvent extraction system of alkaline earth metal ions with DEHPA and TBP or TOPO.

2 MATERIALS AND METHODS

2.1 Materials

Deionized water was used throughout the experiments. DEHPA, EHEHPA, DTMPPA (Cytec Co.) were purified by the three phase method^[14] and the purity of the refined products is above 98%. DEHPA (Tianjin Chemical Reagent Co.), TBP (Beijing Chemical Reagent Co.) and TOPO (Cytec Co.) for synergic extraction experiments were used as received without further purification. Solutions of alkaline earth metals were prepared by dissolving respective chloride salt in water. All other reagents were of analytical grade.

2.2 Extraction and analysis

Equal volumes (20 ml) of organic and aqueous solutions was shaken for 25 min at room temperature with a mechanical shaker. After phase separation, the metal concentrations in aqueous phase and pH were measured. The alkaline earth metal concentrations were determined colorimetricly with a model 722 spectrophotometer made in Shanghai, China, using chlorophosphonazo as color developing reagent.

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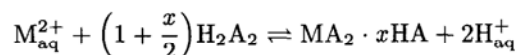
2.3 Infrared spectral

Infrared spectra (IR) of the organic phases were determined with a Model Vector 22 Recording Infrared Spectrophotometer (German Spectroscopic Co.). The organic phases for IR analysis were specially prepared by multi-contact of the organic phase with the respective metal chloride solutions, and heptane was used as diluent for the organic phase.

3 RESULTS AND DISCUSSION

3.1 Extraction mechanism of alkylphosphorus acids

Figure 1 shows the pH dependence of extraction of alkaline earth metals from their respective chloride solutions with $0.1 \text{ mol}\cdot\text{L}^{-1}$ alkylphosphorus acids in kerosene. The slope is close to 2, therefore, the reaction is postulated as the following



and the extraction constant, K_{ex} , can be expressed as

$$K_{\text{ex}} = [\text{MA}_2 \cdot x\text{HA}][\text{H}_{\text{aq}}^+]^2 / [M_{\text{aq}}^{2+}][\text{H}_2\text{A}_2]^{(1+x/2)}$$

The distribution ratio D is given by

$$D = [\text{MA}_2 \cdot x\text{HA}] / [M_{\text{aq}}^{2+}]$$

Therefore, the extraction constant can be expressed as

$$K_{\text{ex}} = D[\text{H}_{\text{aq}}^+]^2 / [\text{H}_2\text{A}_2]^{(1+x/2)}$$

$$\lg D = \lg K_{\text{ex}} + 2\text{pH} + \left(1 + \frac{x}{2}\right) \lg [\text{H}_2\text{A}_2]$$

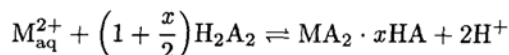
A good linear relationship between $\lg D$ and pH exists at lower pH, but not in higher pH range.

The order of alkaline earth metal extraction varies a little from one alkylphosphorus extractant to another as follows

DEHPA	Ca > Sr > Mg > Ba
EHEHPA	Ca > Sr > Mg > Ba
DTMPPA	Ca > Mg > Sr > Ba

For the same main group elements, the stability of the metal extracts mostly depends on the energy of static electric interaction between the metal cations and the organo-phosphate anions, because of the same outer electronic structure and no ligand field stabilization energy. For alkaline earth metal ions, the interaction between the metal ion and the extractant is essentially electrostatic. Therefore, an ion with a smaller ionic radius produces greater ionic potential e/r , resulting a higher extraction equilibrium constant.

However, the formation of extraction complexes is a process of replacement of hydration water molecules by extractant molecules or ions, and the free energy of the extraction reaction



is determined by both the hydration energy of M^{2+} and the stability of MA_2 . The hydration energy of Mg^{2+} is $-1921 \text{ kJ}\cdot\text{mol}^{-1}$, which is much more negative than Ca^{2+} ($-1577 \text{ kJ}\cdot\text{mol}^{-1}$), Sr^{2+} ($-1443 \text{ kJ}\cdot\text{mol}^{-1}$) and Ba^{2+} ($-1303 \text{ kJ}\cdot\text{mol}^{-1}$).

It explains that although Mg^{2+} has the highest e/r , the exceptional high hydration energy renders its extractability being weaker than Ca^{2+} or even Sr^{2+} . It is interesting to notice that the extractability of

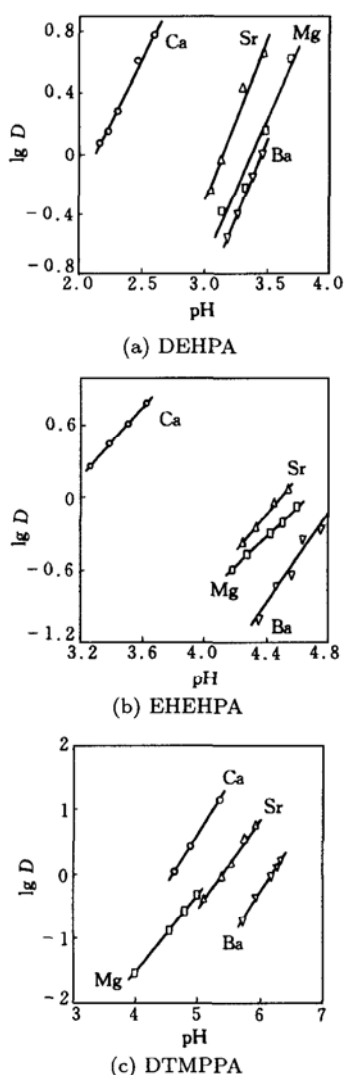


Figure 1 pH dependency of the extraction of alkaline earth metals with $0.1 \text{ mol}\cdot\text{L}^{-1}$ alkylphosphorus acids in kerosene

($[\text{HA}] = 0.1 \text{ mol}\cdot\text{L}^{-1}$, $[\text{M}] = 8 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, O/A=1)

strontium relative to magnesium is inconsistent for the three organophosphorus acids. For the alkylphosphoric acid and alkylphosphonic acid, strontium is extracted at a lower pH value than that of magnesium; the opposite is true for the alkylphosphinic acid. The extraction of Mg^{2+} by DTMPPA is even at a lower pH than that of Ca^{2+} [15]. This phenomenon is consistent with the fact that DTMPPA has the highest electron density in its oxygen atom among those organophosphorus acids[16]. Therefore, it is expected to have a strongest interaction with Mg^{2+} .

Different solvation number of extractant molecules for the same element in similar diluents was obtained with these organophosphorus acids. McDowell and Coleman[3,17] reported different Ca^{2+} and Sr^{2+} complexes in benzene at various sodium nitrate concentrations in the aqueous phase. At $4 \text{ mol}\cdot\text{L}^{-1}$ $NaNO_3$ they found complexes $SrA_2\cdot 4HA$, $CaA_2\cdot 2HA$ ($< 0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA) and $CaA_2\cdot 4HA$ ($> 0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA); at $0.5 \text{ mol}\cdot\text{L}^{-1}$ $NaNO_3$ the complexes $MA_2\cdot 2HA$ ($< 0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA) and $MA_2\cdot 4HA$ ($> 0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA) both for Ca^{2+} and Sr^{2+} (the existence of the complex $CaA_2\cdot 2HA$ was also considered when the slope of the extractant plot was 2.3). Furthermore, the results gathered in Table 1 show that in the case of Mg^{2+} , Ca^{2+} and Sr^{2+} , the composition of the complexes prevailing in the organic phase is influenced by diluents. The solvation numbers of the synergic extracts of the present work are going to be discussed in a latter section of this paper.

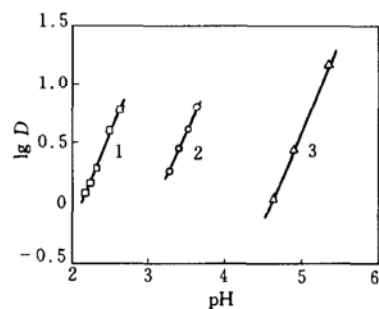
Table 1 The composition of complexes $MA_2\cdot xHA$ in the organic phase

Diluent	Extractant	Mg^{2+}	Ca^{2+}	Sr^{2+}	Reference
heptane	DEHPA		2, 3	3	[18]
cyclohexane	DEHPA		3	3, 4	[18]
butyl ether	DEHPA		4	3	[18]
CCl_4	DEHPA		3	4	[18]
toluene	DEHPA		3	4	[18]
xylene	DEHPA		3		[3]
benzene	DEHPA			4	[19]
kerosene	DEHPA	3			[2]
kerosene	DEHPA	2, 4	4		[5]
kerosene	EHEHPA		2, 3		[7]
kerosene	EHEHPA		2	2	[7]
octane	EHEHPA			3 or 4	[20]

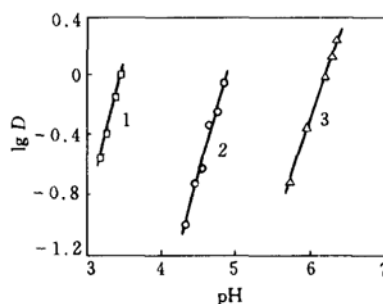
The extraction ability of alkylphosphorus extractants decreases in the following order as shown in Fig. 2,



It is obviously that the extractive ability decreases with the decreasing acidity of the alkylphosphorus acids.



(a) Ca



(b) Ba

Figure 2 pH dependency of the extraction of calcium and barium with three alkylphosphorus acids in kerosene

($[HA]=0.1 \text{ mol}\cdot\text{L}^{-1}$, $[M]=8 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$, $O/A=1$)
1—DEHPA; 2—EHEHPA; 3—DTMPPA

3.2 Synergic extraction of alkaline earth metals by DEHPA

The variation of the distribution ratio of strontium with the concentration of TBP and TOPO extracted with $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA+TBP or $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA +TOPO in kerosene is illustrated in Fig. 3. The distribution ratio increases almost linearly with the concentration increase of TBP or TOPO, and after passing a maximum, it decreases with the increase of the neutral components.

Complexes between TBP or TOPO and DEHPA, and also the extracts of DEHPA metal ions are formed through hydrogen bonds, which was suggested by Sato[21] and others[22,23]. This explanation was supported by infrared spectra. The adducts of TBP or TOPO with DEHPA metal ion extracts, which may form through replacement of coordinated water, therefore increasing the lipophilicity and the molar volume of the extracts, exhibit a positive synergic effect.

On the other hand, with the increase of the neutral organophosphorus compounds, the formation of the adducts between the TBP or TOPO and DEHPA will be gradually dominating, the donor center in DEHPA is blocked to some extent in the adducts, and the activity of the reagent is weakened. The competition between two effects, the positive synergism and the

weakened activity, results in the appearance of a maximum in the curve of the distribution ratio against the ratio of TBP (TOPO) to DEHPA (Fig. 3).

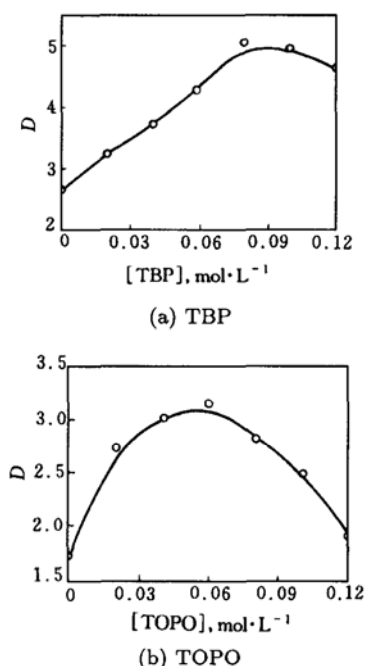
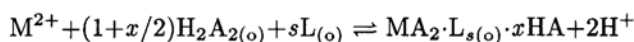


Figure 3 Variation of distribution ratio of strontium with the concentration of TBP and TOPO when extracted with $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA in kerosene ($[M]=1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, pH 3.45, O/A=1)

Similar data were obtained for magnesium, calcium and barium. These indicate that both TBP and TOPO have positive synergic effects on the extraction of alkaline earth metal ions within a certain range of TBP/DEHPA or TOPO/DEHPA ratio. However, the linear relationship of $\lg D$ vs. $\lg c_{\text{TBP}}$ or $\lg c_{\text{TOPO}}$ is kept until approaching the peak concentration (Fig. 4). Therefore, the extraction equilibrium and the extraction constant K_{ex} for the linear part can be expressed as



$$\lg K_{\text{ex}} = \lg D - 2\text{pH} - \lg[\text{H}_2\text{A}_2]_{(\text{o})} - \frac{x}{2}\lg[\text{H}_2\text{A}_2]_{(\text{o})} - s\lg[\text{L}]_{(\text{o})}$$

$$\lg D - 2\text{pH} - \lg[\text{H}_2\text{A}_2]_{(\text{o})} = \frac{x}{2}\lg[\text{H}_2\text{A}_2]_{(\text{o})} + \lg K_{\text{ex}} + s\lg[\text{L}]_{(\text{o})}$$

The number of L in the mixed complex, denoted as s , can be determined from the slope of the line of $\lg D$ vs. $\lg[\text{L}]$ at constant pH and $[\text{H}_2\text{A}_2]$. And the number of HA, denoted as n , can be determined from the slope of the line of $\lg D - 2\text{pH} - \lg[\text{H}_2\text{A}_2]$ vs. $\lg[\text{H}_2\text{A}_2]$ at constant $[\text{L}]$. The compositions of the complexes and extraction constants for $\text{MA}_2 \cdot \text{L}_{s(\text{o})} \cdot x\text{HA}$ determined for the four alkaline earth elements are listed in Table 2.

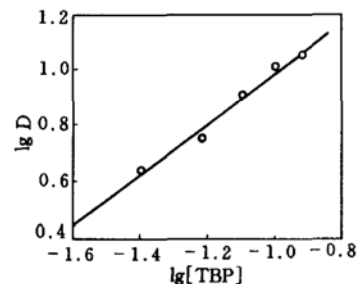


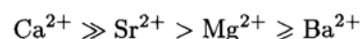
Figure 4 Effect of TBP concentration on barium extraction with $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA ($[M]=1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, pH 3.45, O/A=1)

Data in Table 2 show that CaA_2 is a better acceptor than SrA_2 and BaA_2 for the donors TOPO and TBP. The difference may therefore reflect a greater hydration tendency for SrA_2 and weaker solvation tendency of SrA_2 for $\text{L}^{[7]}$, leading to a lower value of the distribution equilibrium constant. As for magnesium, the number of coordinated TBP and TOPO is only 0.5 rather than an integer, which may be related to the stability of $\text{MgA}_2 \cdot \text{L} \cdot 4\text{HA}$, ($\text{MgA}_2 \cdot \text{L} \cdot 4\text{HA}$ and $\text{MgA}_2 \cdot 4\text{HA}$ may coexist in the equilibrium organic phase), caused by the too small ionic radius of magnesium. It was also reported that when the non-integer solvation number appeared, there might exist two or more extracts^[24].

Table 2 The composition of the organic complexes and extraction constants

	L	s	x	$\lg K_{\text{ex}}$
Mg	TBP	0.5	4	-2.19
	TOPO	0.5	4	-2.85
Ca	TBP	2	4	2.64
	TOPO	3	3	2.42
Sr	TBP	1	4	-0.12
	TOPO	1	4	-1.75
Ba	TBP	1	4	-1.21
	TOPO	1	4	-1.84

The synergic effect of TBP and TOPO for different alkaline earth metal ions is shown in Fig. 5. The extraction order for the DEHPA+TBP and DEHPA+TOPO system below the peak concentration is similar:



Both TBP and TOPO greatly enhance the extraction of calcium, especially TOPO.

Therefore, Ca^{2+} can be easily separated from the other three ions by using the synergic mixture.

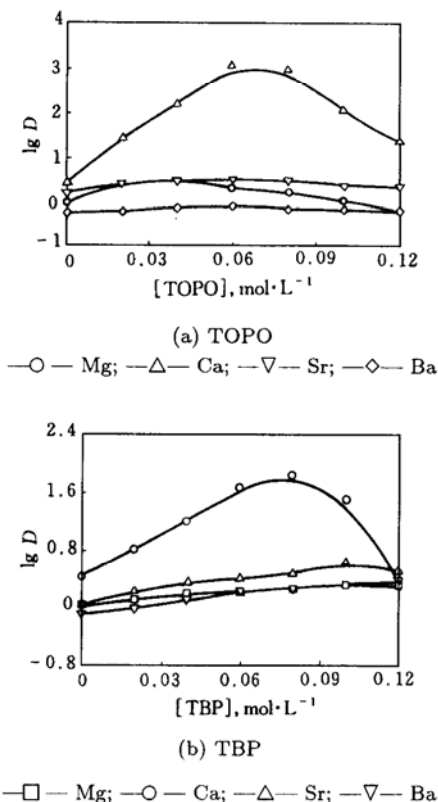


Figure 5 Logarithm distribution ratio of alkaline-earth metal ions versus TBP and TOPO concentration when extracted with $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA at pH 3.45

Acidic synergic coefficient R_{HA} is defined as the ratio of D_{synergic} to D_{HA} , which reflects the increase of the distribution ratio with the added neutral compound related to the original acidic extractants^[25]

$$R_{\text{HA}} = D_{\text{synergic}}/D_{\text{HA}}$$

The maximum R_{HA} for alkaline earth metals are listed in Table 3. Calcium ions enjoy the maximum R_{HA} in both TBP-DEHPA and TOPO-DEHPA systems. For Mg^{2+} and Ca^{2+} , TOPO shows a stronger effect, but for Sr^{2+} and Ba^{2+} , TOPO is weaker.

Table 3 The acidic synergic coefficient R_{HA} at pH 3.45

	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
TBP	1.86	30.47	1.97	2.38
TOPO	2.85	458.85	1.85	1.47

The extraction series at a concentration of $1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ of metals with $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA+ $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBP is the following (see Fig. 6):

$$\text{Ca} > \text{Sr} > \text{Ba} > \text{Mg}$$

$$\text{pH}_{1/2} \quad 1.95 \quad 2.98 \quad 3.18 \quad 3.32$$

while $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA system reported earlier is as follows [see Fig. 1(a)]:

$$\text{Ca} > \text{Sr} > \text{Mg} > \text{Ba}$$

$$\text{pH}_{1/2} \quad 2.14 \quad 3.15 \quad 3.39 \quad 3.46$$

The extraction order of magnesium and barium in DEHPA+TBP system differs from that in DEHPA system. The difference between the systems may offer a beneficial possibility for different separation purpose.

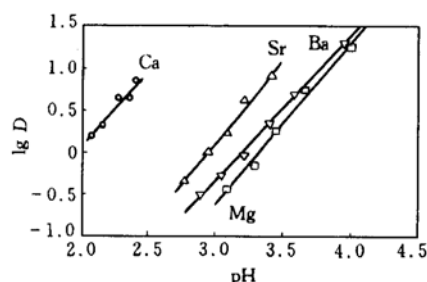


Figure 6 pH dependency of alkaline earth metal ions extracted by $0.1 \text{ mol}\cdot\text{L}^{-1}$ DEHPA + $0.1 \text{ mol}\cdot\text{L}^{-1}$ TBP ($[M] = 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$, $O/A=1$)

3.3 Infra-red spectra of the extracts of alkylphosphorus acids

The IR spectra and the main peaks of these alkylphosphorus acids are given in Table 4 and Fig. 7. Replacement of alkoxy groups by alkyl groups in the organophosphorus acids results in a shift of the absorption band of P→O group to a lower wave number.

Table 4 IR Spectra of DEHPA, EHEHPA and DTMPPA

	P→O stretching band	OH bending band	P-O-C stretching band
DEHPA	1230	1690	1033
EHEHPA	1197	1684	1036, 984
DTMPPA	1172	1685	—

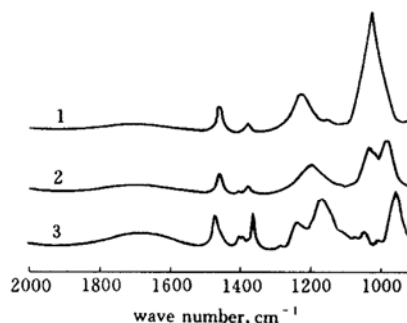


Figure 7 IR spectra of alkylphosphorus acids 1—DEHPA; 2—EHEHPA; 3—DTMPPA

The IR spectra of magnesium, calcium, strontium and barium extracts are shown in Fig. 8. The

saturated organic phases were prepared by multi-extraction of the organic phase with the respective metal chloride solutions.

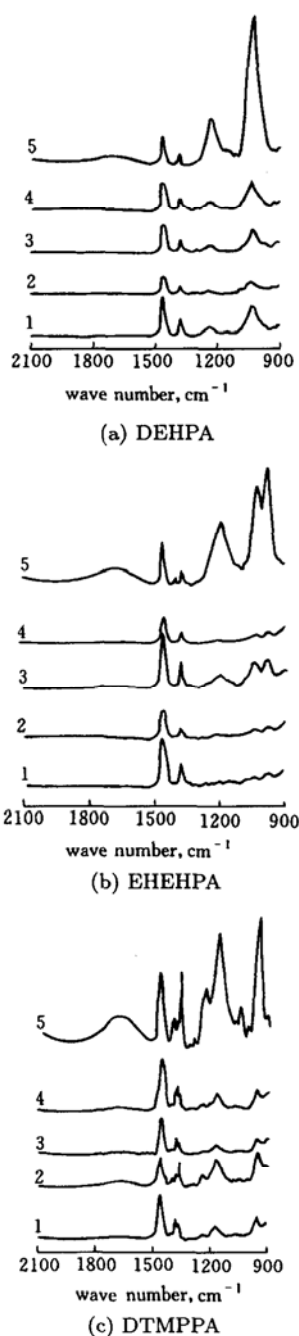


Figure 8 IR spectra of metal extracts with $0.1 \text{ mol}\cdot\text{L}^{-1}$ alkylphosphorus acids in heptane
1—Mg; 2—Ca; 3—Sr; 4—Ba; 5—extractant

Compared with that of the acids, the absorption of OH bending band of all the metal extracts decreases or even nearly disappears because of the displacement of H^+ by M^{2+} . Accordingly, the intensity of the P→O absorption is also decreased, but comparing with the extracts of the transition metals, there is much less shift for the wave number of P→O absorption band.

However, when alkaline earth metals extracted into the alkylphosphorus acids, the P→O absorption band only shifts 3 or 5 cm^{-1} . It was reported that no shift in the spectra of magnesium and calcium ligands with DEHPA, EHEHPA and other alkylphosphorus acid was observed, and it explained that in order to satisfy the largest coordination number, alkylphosphorus acid coordinated as dimer anions^[26]. It was also reported that for the sodium DEHPA extract, the P→O absorption band also had minor shift compared with that of the original alkylphosphorus acid^[27] and believed that the interaction of sodium ion and DEHPA was only an electrovalent bonding with P-O^- ^[28]. The similar minor shift of the P→O absorption in the case of alkaline earth element extracts also reveals the weak interaction between the metal ion and the P→O group. This indicates the structure difference between the extracts of the main group metal ions and that of the transition metal ions with alkylphosphorus acids.

3.4 IR spectra of the synergic extracts by DEHPA for alkaline earth metals

IR spectra of the mixed solutions of DEHPA and TBP with a molar ratio of 1:1 in heptane exhibit a shift of P→O stretching band of DEHPA from 1230 cm^{-1} to a higher frequency 1235 cm^{-1} and that of TBP from 1272 cm^{-1} to 1265 cm^{-1} . This implies that there should be an interaction between the phosphoryl oxygen of TBP and DEHPA through hydrogen bonding, which may cause the break of the hydrogen bonding between DEHPA dimers.

As shown in Fig. 9, there is little shift of the main peaks of IR spectra throughout the extracts from magnesium to barium with the mixture of DEHPA and TBP. This indicates that after extraction, the hydrogen bonding between TBP and DEHPA remains, suggesting that TBP coordinated into the complex through hydrogen bonding with DEHPA. Considering the data in Table 2, it may be inferred that the complexes are $\text{CaA}_2\cdot 4\text{HA}\cdot 2\text{TBP}$, $\text{SrA}_2\cdot 4\text{HA}\cdot \text{TBP}$ and $\text{BaA}_2\cdot 4\text{HA}\cdot \text{TBP}$, respectively.

Similarly, the IR spectra of the mixed solutions of DEHPA and TOPO with a molar ratio of 1 : 1 in heptane exhibit a shift of P→O stretching band of DEHPA at 1230 cm^{-1} to a higher frequency 1245 cm^{-1} and TOPO at 1185 cm^{-1} to a lower frequency 1154 cm^{-1} (actually a wide peak at 1135 cm^{-1} combined with the asymmetric peak of POO^-). Similar result was also reported by Sato *et al.*^[29] that the IR spectra of the mixed solutions of DEHPA and TOPO in kerosene exhibit a shift of P→O from 1230 cm^{-1} to 1245 cm^{-1} and TOPO from 1185 cm^{-1} to 1160 cm^{-1} with an increasing molar ratio of $[\text{TOPO}]/[\text{DEHPA}]$ of 0.5, 1 and 2.

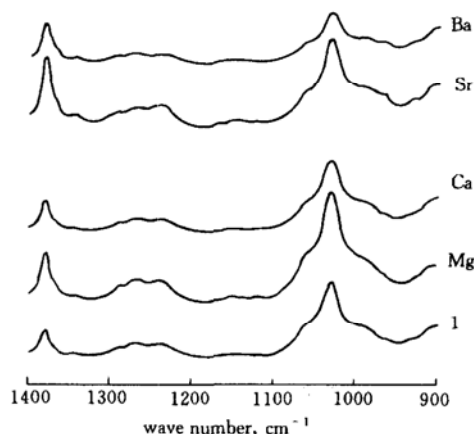


Figure 9 IR spectra of extracts of alkaline earth metal ions with DEHPA and TBP in heptane
1—0.1 mol·L⁻¹ DEHPA+ 0.1 mol·L⁻¹ TBP

The IR spectra of strontium and barium DEHPA+TOPO extracts are similar to that of DEHPA+TBP, which implies that TOPO coordinated to the complex in the same way as TBP. However, the IR spectra of calcium extract are exceptional. Probably TOPO is combined with calcium ions directly through a coordination bond to the metal ion because of its higher e/r , and it is noteworthy that the solvation number of TOPO in calcium extract complex is 3 as shown in Table 2.

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NOMENCLATURE

D	distribution ratio
e/r	ion potential
HA	organic acid
K_{ex}	equilibrium constant
L	neutral organophosphorus compound
M	metal
O/A	volume ration between organic phase and aqueous phase
$pH_{1/2}$	pH value when $D = 1$

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