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Complexing ability of alkali metal and alkaline earth metal ions with organic phosphinate or phosphates in acetonitrile and binary solvents with protic solvents

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ABSTRACT

In acetonitrile (MeCN), the specific interactions of alkali metal ($M^+ = Li^+$ or Na^+) and alkaline earth metal ions $(M^{2+} = Mg^{2+}, Ca^{2+}, or Ba^{2+})$ with various phosphorus anions, L⁻, *i.e.*, diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate, have been examined by means of UV-visible spectroscopy. The formation of "reverse-coordinated" or coordinated species, M_2L^+ or ML^+ , has been observed in the presence of excess amounts of the metal ions to the anions. Between all the M^+ or M^{2+} ions and 1.0×10^{-3} mol dm⁻³ diphenylphosphinate ion (n-Bu₄N⁺Ph₂PO₂⁻), both the precipitation of the non-charged species (ML or ML₂) and the successive re-dissolution of the precipitates take place. The addition of the alkaline earth metal ions of just the equi-molar to L^{-} causes almost complete dissolution of the precipitates through the soluble ML⁺ coordinated species. As for the diphenylphosphate ion $[n-Bu_4N^+(PhO)_2PO_2^-]$, no apparent interaction can be insisted between the alkali metal ions or Mg^{2+} and 5.0×10^{-4} mol dm⁻³ diphenylphosphate ion, based on just no precipitation occurrence. Only Na⁺ and Ba²⁺ can cause obvious precipitation with 5.0×10^{-4} mol dm⁻³ bis(4-nitrophenyl)phosphate. A good evidence, however, has been provided by the conductometric titration of 5.0×10^{-4} mol dm⁻³ *n*-Bu₄N⁺(PhO)₂PO₂⁻ with LiClO₄ or Mg(ClO₄)₂ in MeCN that the "strong" interaction still operate between L⁻ and Li⁺ or Mg²⁺ regardless of no precipitation (nor the successive re-dissolution). The addition of protic solvents, such as water, MeOH, or EtOH, influences significantly the chemical interaction between the metal ions and the anions in MeCN. The solubility products (K_{sp}) and the "reverse coordination" or coordination constants ($K_2 = [M_2L^+]/([M^+]^2[L^-], K_1 = [ML^+]/([M^{2+}][L^-]))$ have been evaluated for the systems.

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1. Introduction

As one of the sixth most abundant elements in the human body, phosphorus plays an important role in life process. Metal phosphates have been gathering great interest, widespread investigating in biochemical [1] and pharmaceutical fields [2]. Alkali metal and alkaline earth metal ions have very specific functions in biological systems, although alkali metal- or alkaline earth metal-phosphates [3] are less recognized than transition metal-phosphates [4–6] due to their weaker coordination ability. Many studies [7–9] have authenticated that the metal ions can play a structural role on catalyzing the hydrolysis of phosphate diester.

In recent decades, the effects of added salts on the hydrolysis rates of various compounds have been examined in our laboratory [10–16]. The exponential increases in hydrolysis rates of S_N1 substrates (R-X) in binary mixtures between H₂O and many organic solvents containing

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http://dx.doi.org/10.1016/j.molliq.2015.11.053 0167-7322/© 2015 Published by Elsevier B.V. concentrated alkali metal or alkaline earth metal (M^+ or M^{2+}) perchlorates have been explained successfully by the concept of the specific chemical interaction between M^+ or M^{2+} and simple anions. That is, the direct chemical interaction between the metal cations and the leaving-group anions (X^-) can generate favorably the carbocation (R^+) as the reaction intermediate even in "aqueous" solution containing organic solvents.

In low solvating media of relatively high permittivities ($20 < \epsilon_r < 65$), the coordination or "reverse" coordination phenomena of alkali metal (M^+) or alkaline earth metal (M^{2+}) ions with various anions, such as Cl⁻ [17,18], SCN⁻ [19], tropolonates [20,21], sulfonates [22,23,24], and carboxylates [22,25,26], have been examined over past three decades in our group by means of voltammetry, conductometry, UV-visible, and NMR spectroscopy. Where the term of "reverse" coordination represents a species (such as M_2X^+) driven by a single-charged anion (X^-) with two or more of alkali metal ion (M^+) through the chemical interaction above the Coulombic force [27]. We have reported that higher ion-aggregation (over the ion pair formation between ions) takes place not only in low permittivity media ($\epsilon_r < 10$) [28] but also

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Fig. 1. UV spectra of 1.0×10^{-3} mol dm⁻³ diphenylphosphinate ion (L⁻) of *n*-Bu₄N⁺L⁻ (0.1 cm path-length) in MeCN with increasing concentration of LiClO₄.

in the media of relatively high permittivity ($20 < \varepsilon_r < 65$) [29]. We have attributed the higher ion-aggregation to the coordination (of M⁺ or M²⁺) as well as hydrogen bonding forces (of R₃NH⁺) in addition to Coulombic forces [30]. Holmes [31] has examined the hydrogenbonding between imidazole and diphenylphosphate by ¹H NMR, IR, and X-ray technique.

The concept of triple ions in low permittivity media ($\varepsilon_r < 12 \text{ or } 23.2$) has been originated by Fuoss and Kraus [32]. The triple ion formation between an ion pair and a free ion due to the Coulomb force [32,33] should be discussed more. Nevertheless, the triple ion mechanism or theory [34] has been applied in studying on lithium batteries [35], ion-aggregation [36], the color developer of dyes [37,38], and supramolecular construction [39].

In DMF, the higher aggregations of dihydrogenphosphate have been observed [40]. NMR relaxation studies have shown that the sodium ion interacts with the dibutyl phosphate to form ion-aggregates in concentrated aqueous solution of sodium dibutyl phosphate [41]. In the solubility study [23], the specific interaction has been observed between Li^+ and diphenylphosphate [(PhO)₂PO₂⁻], in acetone, but somehow strangely not in acetonitrile.

Acetonitrile (MeCN) is a relatively high permittivity solvent ($\varepsilon_r = 35.94$ [42]) of low donor and acceptor numbers (DN = 14.1, AN = 19.3 [43]), attracting considerable interest in the study of the interplay between ion solvation and association of electrolyte solution [44]. In MeCN, the formation of the precipitates and successive formation of "reverse-coordinated" species has been reported for M⁺ and M²⁺ with nitrophthalates or sulfonates (*p*-toluenesulfonate, 1,5-naphthalenedisulfonate, and 1,3,6-naphethalenetrisulfonate) [22,24].



Fig. 2. Changes in absorbance ($\lambda_{max} = ca. 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of alkali metal ions in MeCN: (\bigcirc) LiClO₄; (\bigcirc) NaClO₄.



Scheme 1. Successive formation of ML and M_2L^+ (M = Li and Na) for the diphenylphosphinate ion in MeCN.

In the present work, the complexing ability of M^+ or M^{2+} with diphenylphosphinate, diphenylphosphate, and bis(4nitrophenyl)phosphate is examined by means of UV spectroscopy in MeCN, a protophobic and aprotic solvent. The influences of protic solvents, such as water, methanol, or ethanol, are also investigated. The coordination or "reverse" coordination formation constants of anions have been evaluated using UV visible spectroscopic data. The aim of this paper is to try convincing one that alkali metal and alkaline earth metal ions in poor salvation media can exhibit unexpectedly strong coordination ability, not so well as 4d-shell metal ions (such as Ag^+ , Cd^{2+}) in aqueous solution. We would like to recognize that the interaction between phosphates and Mg^{2+} or Ca^{2+} in biochemical systems should be through the real chemical force and not just the electrostatic interaction.

2. Experimental

2.1. Chemicals

Diphenylphosphinic, diphenylphosphate, and bis(4nitrophenyl)phosphate acids were purchased from Aldrich. Tetrabutylammonium diphenylphosphinate (n-Bu₄N⁺ Ph₂PO₂⁻) was prepared as follows: A 1.0 g of diphenylphosphinic acid was dissolved in methanol, and was titrated by n-Bu₄NOH (Wako) in methanol up to an equivalence point. The solution was evaporated to dryness at 50 °C, and the salt was dried *in vacuo* at 120 °C. Tetrabutylammonium diphenylphosphate [n-Bu₄N⁺(PhO)₂PO₂⁻] was prepared from diphenylphosphate acid in a similar way.

Metal perchlorates without hydrate water, LiClO₄, NaClO₄, Mg(ClO₄)₂, and Ba(ClO₄)₂ (all Aldrich), were used as received. Calcium perchlorate tetrahydrates from Aldrich was dried *in vacuo* at 150 °C to obtain anhydrous Ca(ClO₄)₂. Triethylamine (Et₃N), Et₄NClO₄, acetonitrile, acetone (the spectroscopic grade), methanol, and ethanol all from Wako were used as received. The water contents of acetonitrile, methanol, and ethanol are certificated to be less than 0.1, 0.1, and 0.2%, respectively. Water



Fig. 3. UV spectra of 1.0×10^{-3} mol dm⁻³ diphenylphosphinate (0.1 cm path-length) with increasing concentration of Mg(ClO₄)₂ in MeCN.

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Fig. 4. Changes in absorbance ($\lambda_{max} = ca$. 226 nm) of 1.0×10^{-3} mol dm⁻³ diphenylphosphinate ion with increasing concentration of alkaline earth metal ions in MeCN: (\bigcirc) Mg(ClO₄)₂; (\bullet) Ca(ClO₄)₂; (\triangle) Ba(ClO₄)₂; (\bullet) Et₄NClO₄ in addition to 5.0×10^{-4} mol dm⁻³ Mg(ClO₄)₂.

was purified by means of a MilliQ system (Millipore Corp.). The percentage of the solvent in binary solvents is all expressed by the volume fraction [% (v/v)] in the present paper.

2.2. Apparatus and procedure

UV–visible absorption spectra were measured at room temperature using a Shimadzu double-beam spectrophotometer (model UV-2550) in 0.01, 0.05, and 0.1 cm path-length quartz cuvettes. When precipitation occurred, the solution was sonicated for a few minutes in a Branson ultrasonic bath (model Yamato 2510, 42 kHz and 125 W) and the supernatant solution was measured after centrifugation with a Hitachi centrifuge (model CT4D). Sometimes, a long aging time was needed to complete a precipitation reaction. Electrical conductance was measured at 25 \pm 0.02 °C with an Agilent LCR meter model HP4284 at 1 kHz in a conductivity cell with a cell constant of 0.4959 S cm⁻¹.

The evaluation method of solubility products (pK_{sp}) and "reverse" coordination formation constants (K_2 and K_1 for Eqs. (2) and (4), respectively) between metal cations (M^+ , M^{2+}) and "ligand" ainons (L^-) have been proposed in the previous paper [22].

(a) Alkali Metal ions

$$\mathsf{ML} \leftrightarrows \mathsf{M}^+ + \mathsf{L}^-, \mathsf{K}_{\mathsf{sp}} = [\mathsf{M}^+][\mathsf{L}^-],\tag{1}$$

$$2 M^{+} + L^{-} \leftrightarrows M_{2}L^{+}, K_{2} = [M_{2}L^{+}] / ([M^{+}]^{2}[L^{-}]).$$
⁽²⁾

(b) Alkaline earth metal ions

$$\mathsf{ML} \leftrightarrows \mathsf{M}^{+} + 2 \, \mathsf{L}^{-}, \mathsf{K}_{\mathsf{sp}} = \left[\mathsf{M}^{2+}\right] [\mathsf{L}^{-}]^{2},\tag{3}$$



Scheme 2. Successive formation of ML_2 and ML^+ (M = Mg, Ca, and Ba) for the diphenylphosphinate ion in MeCN.

Table 1

Precipitation and re-dissolution reactions of the diphenylphosphinate ion $(n-Bu_4N^+L^-)$ with alkali metal or alkaline earth metal perchlorates in MeCN.

<i>n</i> -Bu ₄ N ⁺ salt	Equilibrium constants ^a	Li+	Na ⁺	${\rm Mg}^{2+}$	Ca ²⁺	Ba ²⁺
Diphenylphosphinate ion $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$	(pK_{sp}) $(pK_{sp})^{b}$	▲ 8.28 8.38	▲ 8.06 8.16	▲ 11.89 12.20	▲ 11.35 11.66	▲ 10.43 10.74
	$\log K_2$, $\log K_1$	5.88	5.20	4.36	4.11	3.63

Explanatory notes: Solid circles and triangles represent the complete and partial precipitation, respectively. The complete precipitation means here that the absorbance of a "ligand" anion (L^-) reaches < 1/10 of the initial value at an equivalence or any amount of a metal ion. Open circles and triangles represent complete and partial re-dissolution of precipitation, respectively. The mark "No" indicates no precipitation or no re-dissolution.

^a Solubility products (K_{sp}) and "reverse" coordination constants (K_2 , K_1), *cf.* the Experimental section in this paper.

^b Thermodynamic solubility products (K_{sp}) corrected with the activity coefficients of ions. The mean activity coefficients of ions are evaluated from the limiting Debye–Hückel equation, log $\gamma_{\pm} = -A|Z_{+}Z_{-}|\mu^{1/2}$, cf. Ref. [46].

$$\mathbf{M}^{2+} + \mathbf{L}^{-} \leftrightarrows \mathbf{M}\mathbf{L}^{+}, \mathbf{K}_{1} = [\mathbf{M}\mathbf{L}^{+}] / \left(\left[\mathbf{M}^{2+} \right] [\mathbf{L}^{-}] \right).$$

$$\tag{4}$$

3. Results and discussion

3.1. The diphenylphosphinate ion (L^{-})

3.1.1. Specific interaction between the diphenylphosphinate ion (L⁻) and M^+ or $M^{2\,+}$

The diphenylphosphinate ion (Ph₂PO₂⁻: L⁻) of *n*-Bu₄N⁺ L⁻ (1.0 × 10⁻³ mol dm⁻³) in acetonitrile (MeCN) gives a broad peak around 226 nm (ε /cm⁻¹ mol⁻¹ dm³ = *ca*. 1.35 × 10⁴) but the aromatic band around 265 nm is very weak (Fig. 1). When LiClO₄ is added to the solution, the L⁻ absorbance gradually decreases with increasing concentration of LiClO₄, and reaches its minimum value of 0.099 at an equivalence of Li⁺ (1.0 × 10⁻³ mol dm⁻³), accompanying white precipitates. However, the further addition of LiClO₄ causes the precipitates to re-dissolve partially at 0.10 mol dm⁻³ Li⁺ and completely at 0.50 mol dm⁻³ Li⁺ or more. The peak absorbance of the solution recovers fully the initial value, showing a slight blue shift ($\lambda_{max} = 223.5$ nm).

The addition of an equivalence of NaClO₄ to the L⁻ ion also causes precipitation similarly, but the re-dissolution of the precipitates of NaL is not completed even in the presence of an excess amount of Na⁺ (*cf.* Fig. 2). Scheme 1 indicates the manner of the ML (M = Li and Na) precipitation and the successive re-dissolution of ML through M_2L^+ .

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Fig. 5. Changes in absorbance $(\lambda_{max} = ca. 226 \text{ nm})$ of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of LiClO₄ in MeCN-H₂O mixtures: $(\bigcirc) 0$; (\blacklozenge) 1.0; (\triangle) 2.0; (\bigstar) 5.0% (ν/ν) of H₂O.

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Table 2

Precipitation and re-dissolution reactions of the diphenylphosphinate ion with alkali metal ions in binary mixtures of MeCN-H₂O or MeCN-MeOH.

Metal ion ^a	Equilibrium constants ^b				
MeCN-H ₂ O [H ₂ O% (v/v)]		1.0	2.0	5.0	7.0
				No	
	(pK_{sp})	7.20	6.68	_	
Li ⁺	(pK_{sp})	7.30	6.78	-	
		0	0	No	
	$\log K_2$	4.93	4.98	_	
		A	A	A	No
	(pK_{sp})	6.64	3.54	3.11	_
Na ⁺	(pK_{sp})	6.74	3.64	3.21	_
		0	0	No	No
	$\log K_2$	4.15	_	-	-
MeCN-MeOH					
[MeOH% (v	/v)]	2.0	5.0	10	
				No	
	(pK_{sp})	7.30	6.83	-	
Li ⁺	(pK_{sp})	7.40	6.93	-	
		0	0	No	
	$\log K_2$	5.02	5.21	_	
		A	A	No	
	(pK_{sp})	6.75	4.09	—	
Na ⁺	(pK_{sp})	6.85	4.19	_	
		0	0	No	
	log K ₂	3.45	-	-	

For the Explanatory notes, cf. Table 1.

^a MClO₁.

^b Solubility products (K_{sp}) and "reverse" coordination constants (K_2) , *f*. the Experimental section.

Fig. 3 shows the UV spectral changes of L⁻ $(1.0 \times 10^{-3} \text{ mol dm}^{-3})$ with increasing concentration of Mg(ClO₄)₂ in MeCN. The absorbance suddenly decreases to reach its minimum in the presence of an equivalence of Mg(ClO₄)₂ $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$. However, even 7.0×10^{-4} or 1.0×10^{-3} mol dm⁻³ Mg²⁺ causes the re-dissolution of the precipitates and also a drastic increase in the intensity of the absorbance band recovers completely the initial value, (showing a blue shift to 223 nm), which should indicate the formation of the coordinated species, MgL⁺.

We would like to confirm concisely that the increase in the ionic strength is not the main factor for the recovering of the absorbance in the presence of higher Mg(ClO₄)₂ concentrations. The ionic strength of the MgL₂-precipitated-solution (the supernatant contains 1.0×10^{-3} mol dm⁻³ *n*-Bu₄NClO₄) has been increased up to 0.1 by

0.5

Fig. 6. Changes in absorbance ($\lambda_{max} = ca. 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of LiClO₄ in MeCN–MeOH mixtures: (\bigcirc) 0; (\bullet) 2.0; (\blacktriangle) 5.0; (\bigstar) 10% (ν/ν) of MeOH.

Et₄NClO₄. As is shown in Fig. 4, however, the absorbance value of L^- remains constant without the re-dissolution of precipitation.

The coordination behavior of Ca^{2+} with L^{-} is very similar to that of Mg^{2+} (*cf.* Fig. 4). The precipitation takes place in the presence of 5.0×10^{-4} mol dm⁻³ $Ca(ClO_4)_2$, then the re-dissolution occurs suddenly with 1.0×10^{-3} mol dm⁻³ Ca^{2+} . Strange to say, the precipitation of BaL₂ occurs only to a smaller extent than that of MgL₂ and CaL₂. Scheme 2 shows the precipitation of ML₂ (M = Mg, Ca, and Ba) and the successive re-dissolution of ML₂ through ML⁺. The equilibrium constants of the reactions between M⁺ or M²⁺ and the diphenylphosphinate ion (L⁻) in MeCN are listed in Table 1. The "reverse coordination" or coordination constants indicate the interaction increases in the order of Na⁺ < Li⁺ and Ba²⁺ < Ca²⁺ < Mg²⁺. In the previous paper [25], the sudden formation of ML₂ for the benzoate ion in MeCN, and furthermore the $C_6H_5CO_2Ca^+$ ion has been detected, indeed, by the electrospray ionization mass spectroscopy [24].

3.1.2. The influences of added water and methanol on the interaction between M^+ or M^{2+} and the diphenylphosphinate ion (L^-)

We have urged that the properties of "residual water" (the water remains after drying) in non-aqueous solvents are much different from those of the bulk water and that the presence of such "minor" water can be often ignored [27]. However, additional water or protic solvents in MeCN may cause strong influences on the reactions between alkali metal or alkaline earth metal ions and the diphenylphosphinate ion (L^-) because of the stronger salvation toward both the metal and $L^$ ions by the additional water.

Fig. 5 shows the influences of added water on the precipitation and the successive re-dissolution of lithium diphenylphosphinate (LiL) in MeCN. The added water of a small content disturbs the precipitation of LiL, and the absorbance minimum increases from 0.099 in 0.0% H₂O to 0.343 and 0.586 in 1.0 and 2.0% H₂O, respectively. The solubility products (pK_{sp}) are evaluated to be 8.28, 7.20, and 6.68 in 0.0, 1.0, and 2.0% H₂O, respectively (*cf.* Tables 1 and 2). The re-dissolution of precipitates seems to be promoted apparently by the additional H₂O. At 0.10 mol dm⁻³ LiClO₄, the absorbance increases as 0.602, 0.733, and 1.36 for 0.0, 1.0, and 2.0% H₂O, respectively. The precipitation and redissolution reactions are completely inhibited in 5.0% H₂O.

The influences of MeOH on the interaction between Li⁺ and L⁻ in MeCN are very similar but smaller than those of H₂O (Fig. 6). In 2.0% MeOH and 1.0% H₂O, solubility products (pK_{sp}) are observed to be 7.30 and 7.20, respectively, and "reverse" coordination constants (log K_2) are 5.02 and 4.93 (*cf.* Table 2). In 10% MeOH, no apparent precipitation or re-dissolution reactions are observed between Li⁺ and L⁻. We can easily notice that the useful solvation parameters for the added protic solvents of >0.5% H₂O and MeOH in MeCN should be those (DN_{bulk} = 40.3 and 31.3) given by Marcus [45] and not the originally given by Gutmann (DN = 18.0 and 19) [43] for H₂O and MeOH, respectively.

The influences of added water and methanol have been also examined on the interaction between Na⁺ and L⁻. It is worth noticing that the added water or methanol gives larger influences on the interaction between Na⁺ and L⁻ than that for Li⁺. In 5.0% MeOH, for instance, the precipitation of NaL occurs only slightly ($pK_{sp} = 4.09$), while that of LiL still takes place to a relatively large extent ($pK_{sp} = 6.83$, *cf.* Table 2). In the reactions with sulfonate anions [22,24], however, the metal ions of larger size or lower charge density have been less affected by the added H₂O and MeOH.

Fig. 7(a) shows the influences of added water (1.0–5.0%) on the precipitation and the successive re-dissolution of CaL₂. Without H₂O, as shown Fig. 4, the distinct precipitation takes place at an equivalence of Ca²⁺. In the presence of 1.0 and 2.0% H₂O, no remarkable influences are observed in the precipitation and re-dissolution reactions, that is, the pK_{sp} values for 0.0, 1.0, and 2.0% H₂O are given to be 11.35, 11.31, and 10.96 and log $K_1 = 4.11, 4.11$, and 3.93, respectively (*cf.* Tables 1



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Fig. 7. (a). Changes in absorbance ($\lambda_{max} = ca. 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of Ca(ClO₄)₂ in MeCN-H₂O mixtures: (\bigcirc) 0; (\bigcirc) 1.0; (\triangle) 2.0; (\triangle) 4.0; (\square) 5.0% (ν/ν) of H₂O. (b). Changes in absorbance ($\lambda_{max} = ca. 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of Ca(ClO₄)₂ in MeCN-MeOH mixtures: (\bigcirc) 0; (\triangle) 5.0; (\triangle) 10; (\triangle) 15% (ν/ν) of MeOH.

and 3). The absorbance minimum increases to 0.611 in 4.0% H₂O, and finally it almost disappears in 5.0% H₂O. The influences of MeOH on the coordination reaction between Ca^{2+} and L^{-} are smaller than H₂O [Fig. 7(b)]. With increasing contents of MeOH, the precipitation reaction takes place to lesser extent. Precipitation may take place in 10% MeOH,

Table 3

Precipitation and re-dissolution reactions of the diphenylphosphinate ion with alkaline earth metal ions in binary mixtures of MeCN-H₂O or MeCN-MeOH.

Metal ion ^a	Equilibrium constants ^b							
MeCN-H [H ₂ O% (1	H ₂ Ο ν/ν)]	0.5	1	2	3	4	5	10
								No
	(pK_{sp})	12.40	12.14	11.89			_	_
Mg ²⁺	(pK_{sp})	12.71	12.45	12.19			-	_
		0	0	0			0	No
	$\log K_1$	4.43	4.08	3.87		_	_	_
	/		A	A		A	No	
C-2+	(pK_{sp})		11.31	10.96		10.05	_	
Cd ⁻	(pK_{sp})		0	0		10.32	No	
	log V		411	2 02		2 40	INO	
	log K ₁		4.11	J.95		5.45	No	
	(nK)		10.79	10.89	9.96		_	
Ba^{2+}	$(\mathbf{p}K_{sp})$		11 10	11 19	10 25			
Du	(Prisp)		0	0	0		No	
	$\log K_1$		3.89	3.96	_		-	
MeCN-M	ЛеОН							
[MeOI	H% (v/v)]	2.0	5.0	10	15	20	25	30
								No
	(pK_{sp})			12.47	11.35	10.72	9.77	_
Mg ²⁺	(pK_{sp})			12.79	11.67	11.04	10.09	—
				0	0	0	0	No
	$\log K_1$			4.20	4.00	3.84	_	_
	/		A	A	No			
C 2⊥	(pK_{sp})		9.72	9.42	_			
Ca ²	(pK_{sp})		10.03	9.74	— No			
	log K		_	_	_			
	8.1							No
	$(\mathbf{p}K_{sp})$	10.94	10.96	10.73	10.41	10.00		_
Ba^{2+}	(nK_{m})	11.25	11.27	11.05	10.73	10.32		_
	(PriSD)							
	(Prisp)	0	0	0	0	0		No

For the Explanatory notes, cf. Table 1.

^a $M(ClO_4)_2$.

^b Solubility products (K_{sp}) and "reverse" coordination constants (K_1), *cf*. the Experimental section.

but it is almost inhibited in 15% MeOH. The higher solubility of CaL and the sudden increase of absorbance with increasing Ca²⁺ [(0.5-1.0) × 10^{-3} mol dm⁻³] in 5.0% MeOH kept us from evaluating appropriate K_1 values [*cf.* Fig. 7(b)].

The added water (0–10%) has influenced in a different way for Mg^{2+} with L⁻. When 0.50% H₂O is added to MeCN, the dissolution of MgL at 1.0×10^{-3} mol dm⁻³ Mg²⁺ (without added water, Fig. 4) is obstructed remarkably and the absorbance of L⁻ recovers its original value at as high as 1.0×10^{-2} mol dm⁻³ Mg²⁺. The addition of 10% H₂O causes no precipitation between Mg²⁺ and L⁻. Compared with H₂O, methanol causes much smaller influences on the interaction between Mg²⁺ and L⁻. The precipitation and re-dissolution reactions disappear in 30% MeOH.

The influences of added water (1.0-5.0%) have been examined also for BaL₂. With the addition of 1.0% H₂O, very interestingly, the absorbance minimum value (at an equivalence) decreases from 0.451 to 0.346. In 5.0% H₂O, the precipitation and re-dissolution reactions are not observed. In general, the water influences on the interaction of Ba²⁺ and L⁻ are similar to those on Ca²⁺ and L⁻.

The influences of added MeOH on the behavior of precipitation and the successive re-dissolution of BaL_2 are rather complicated. When MeCN contains 10% MeOH, the log K_{sp} is evaluated to be 10.73. This value is still very close to that in 5.0% MeOH ($pK_{sp} = 10.96$, *cf.* Table 3). The precipitation takes place in 20% MeOH, but finally, neither precipitation nor re-dissolution appears in 30% MeOH.



Fig. 8. Changes in absorbance ($\lambda = ca$. 206 nm) of 5.0×10^{-3} mol dm⁻³ diphenylphosphate ion (0.05 cm path-length) with increasing LiClO₄ and NaClO₄ concentrations in MeCN (triangles) and acetone (circles). The open and solid symbols represent LiClO₄ and NaClO₄, respectively.

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6 Table 4

Precipitation and re-dissolution reactions on the diphenylphosphate ion (L^-) or Et₃N-HL with alkali metal or alkaline earth metal perchlorates in MeCN.

Mixed solution	Equilibrium constants ^a	Li+	Na ⁺	${\rm Mg}^{2+}$	Ca ²⁺	Ba ²⁺
Diphenylphosphate $(5.0 \times 10^{-3} \text{ mol } \text{dm}^{-3} \text{ L}^{-} \text{ for}$	(pK_{sp})	▲ b	▲ 5.56	No 	▲ 13.07 13.29	• 13.57 13.79
$(5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ L}^{-1} \text{ for})$	(prosp)	0	0	No	0	0
alkaline earth metal ions)	log K ₂ , log K ₁	_0	3.73	_	4.72	3.61
						•
	(pK_{sp})				12.71	13.78
Et ₃ N-HL	(pK_{sp})				12.93	14.00
$(5.0 \times 10^{-4} \text{ mol } dm^{-3})$					0	0
	log K ₁				4.50	3.85

For the Explanatory notes, cf. Table 1.

^a Solubility products (K_{sp}) and "reverse" coordination constants (K_2, K_1) , *cf.* the Experimental section.

^b The pK_{sp} and $\log K_2$ values are not evaluated because the precipitation of LiL in MeCN is not enough, *cf.* Fig. 8.

3.2. Diphenylphosphate (L^{-} and HL)

3.2.1. Specific interaction between M^+ or M^{2+} and the diphenylphosphate ion (L^-) or the mixture of diphenylphosphate (HL) with Et_3N

Diphenylphosphate [(PhO)₂PO₂H, phosphoric acid diphenyl ester] in the group of week acids is fairly strong in water ($pK_a = ca. 1.5$) [23]. The UV absorption spectrum of tetrabutylammonium diphenylphosphate [n-Bu₄N⁺ (PhO)₂PO₂⁻] exhibits a band at around 206 nm in MeCN.

In MeCN, no apparent interaction could be detected between Li⁺ or Na⁺ and 5.0×10^{-4} mol dm⁻³ diphenylphosphate (L⁻). However, in a higher L⁻ concentration solution, 5.0×10^{-3} mol dm⁻³, the precipitation of LiL or NaL takes place (Fig. 8). The pK_{sp} and log K₂ values can be evaluated for Na⁺ but not for Li⁺ and L⁻ (*cf.* Table 4). Further details will be discussed for the interaction between Li⁺ and L⁻ along with between Mg²⁺ and L⁻ (*vide infra*).

In acetone, the precipitation of LiL occurs to a larger extent than that of NaL. The Li⁺ ion may have a stronger tendency than Na⁺ to associate with L⁻ in acetone ($\varepsilon_r = 20.56$) [42]. The pK_{sp} and log K₂ values have been evaluated from 5.0×10^{-3} diphenylphosphate ion (Fig. 8) to be 6.28 and 4.07, respectively, for Li⁺ and also 5.20 and 4.29 for Na⁺. By means of polarography on DME, coincidently, we [23] have reported (rather larger) overall formation constants of LiX₂⁻ and Li₂X⁺ to be $10^{6.5}$ and $10^{7.1}$, respectively, in acetone, where X = (PhO)₂PO₂.



Fig. 10. UV spectra of 5.0×10^{-4} mol dm⁻³ diphenylphosphate ion (0.1 cm path-length) with increasing concentration of Ba(ClO₄)₂ in MeCN.

Fig. 9(a) shows the absorbance ($\lambda = ca.$ 206 nm) of 5.0×10^{-4} mol dm⁻³ diphenylphosphate ion (L⁻) with increasing concentration of alkaline earth metal ions in MeCN. Almost no absorbance changes appear by the addition of Mg²⁺, *i.e.*, no apparent interaction between L^- and Mg^{2+} . With increasing concentration of $Ca(ClO_4)_2$, however, the absorbance firstly decreases and reaches its minimum at an equivalence of $Ca(ClO_4)_2$ (2.5 × 10⁻⁴ mol dm⁻³), then the equi-molar $Ca(ClO_4)_2$ (5.0 × 10⁻⁴ mol dm⁻³) causes suddenly the re-dissolution of precipitates and also the drastic increase in absorbance, the pK_{sp} and log K₁ are listed as 13.07 and 4.72 in Table 4. Almost complete precipitation is caused by an equivalence of $Ba(ClO_4)_2$, and the precipitation continues up to 1.0×10^{-2} mol dm⁻³ Ba²⁺. The precipitates of BaL₂ partially re-dissolve at 0.10 mol dm⁻³ Ba²⁺, and finally the absorbance recovers the original value at 0.20–1.0 mol $dm^{-3} Ba^{2+}$. The UV spectral changes of $n-Bu_4N^+$ L⁻ in the presence of increasing Ba(ClO₄)₂ concentrations are shown in Fig. 10. Scheme 3 shows the (reverse) coordinated species of ML^+ (M = Ca, Ba), *i.e.*, the 1:1 complex formation from the ML₂ precipitate.

Fig. 9(b) shows the changes in absorbance ($\lambda = ca. 206 \text{ nm}$) of 5.0×10^{-4} mol dm⁻³ diphenylphosphate (HL) containing an equivalent amount of Et₃N with increasing of alkaline earth metal ions in MeCN. Comparing Fig. 9(a) with 9(b), it is obvious that the alkaline earth metal ions react with both (n-Bu₄N⁺) L⁻ and Et₃N-HL (or Et₃NH⁺-L⁻) in a very similar way. Strictly speaking, the proper interactions (without any obstruction) should be observed only with (n-Bu₄N⁺) L⁻ and not with Et₃N-HL (or Et₃NH⁺-L⁻). However, in the



Fig. 9. (a). Changes in absorbance ($\lambda = ca. 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate ion with increasing of alkaline earth metal ions in MeCN: (\bigcirc) Mg(ClO₄)₂; (\bullet) Ca(ClO₄)₂; (\bullet)

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Scheme 3. Successive formation of $ML_2\ (M=Ca$ and Ba) and ML^+ for the diphenylphosphate ion (L^-) in MeCN.

following sections, we examine the metal ion reaction with Et₃N-HL for experimental simplicity. It may be worth mentioning that the hydrogen bonding interaction (in addition to the Coulombic interaction) between R₃NH⁺ and (PhO)₂PO₂⁻ is much stronger than the mere Coulombic interaction between R₄N⁺ and (PhO)₂PO₂⁻ in several protophobic aprotic solvents, such as MeCN, benzonitrile, nitrobenzene, and propylene carbonate, according to the conductometric data [23]. Nevertheless, *n*-Bu₄N⁺ L⁻ and Et₃N-HL give similar pK_{sp} and log K₁ values for Ca²⁺ and Ba²⁺ in MeCN (*cf.* Table 4).

By means of the present method utilizing the successive reactions of precipitation and re-dissolution, no interaction between a metal ion and L^- can be indicated unless the precipitation reaction occurs properly. Nevertheless, we may predict the log K_2 of ~4.2 for Li⁺ and log K_1 of ~5.0 for Mg²⁺ with the L⁻ ion in MeCN, judging from the log K_2 and log K_1 values for the interaction between M⁺ or M²⁺ and the analogous compound (diphenylphosphinate, Ph₂PO₂⁻), given in Table 1.

The specific interaction between Li^+ or Mg^{2\,+} and 5.0 \times 10^{-4} mol dm⁻³ L⁻ in MeCN cannot be obviously detected from the UV spectral changes, as described above. Without observing distinct phenomena of precipitation and the successive re-dissolution, we cannot insist that \hat{Li}^+ or Mg^{2+} keeps still the strong interaction with L^- . However, conductometric titrations of 5.0 \times 10⁻⁴ mol dm⁻³ tetrabutylammonium diphenylphosphate $[n-Bu_4N^+ (PhO)_2PO_2^-]$ with $LiClO_4$ and $Mg(ClO_4)_2$ have supplied us with the good evidence for the interaction. The deviation point has been given at an equivalence point for LiClO₄ (5.0 \times 10⁻⁴ mol dm⁻³) or for Mg(ClO₄)₂ $(2.5 \times 10^{-4} \text{ mol dm}^{-3})$, as shown in Fig. 11 (a) or Fig. 11 (b), respectively, indicating that the chemical interaction operates actually between Li⁺ or Mg²⁺ and 5.0×10^{-4} mol dm⁻³ L⁻. It may be worth mentioning again that the both systems give no precipitation indeed. The solubility of non-charged species for Li⁺ and Mg²⁺ with L⁻ must be too high to form precipitates under those conditions.



Fig. 12. Absorbance ($\lambda = ca$. 206 nm) of 5.0×10^{-4} mol dm⁻³ diphenylphosphate containing 5.0×10^{-4} mol dm⁻³ Et₃N in the presence of Ba(ClO₄)₂ in MeCN-H₂O mixtures: (\bigcirc) 0; (\bigcirc) 1.0; (\triangle) 2.0; (\triangle) 3.0; (\square) 5.0; (\blacksquare) 10% (ν/ν) of H₂O.

At an equivalence point $(5.0 \times 10^{-4} \text{ mol dm}^{-3})$ in the titration curve with LiClO₄, the observed specific conductance ($k/S \text{ cm}^{-1}$) of 0.1425 × 10⁻³ equals 285 of the molar conductivity ($\Lambda/S \text{ cm}^2 \text{ mol}^{-1}$). In the solution, we can expect the presence of two pairs of $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Li}^+(\text{PhO})_2\text{PO}_2^-$ and n-Bu₄N⁺ClO₄⁻.

The observed Λ value (ca. 118) of Li⁺ (PhO)₂PO₂⁻ at the equivalence point has been found to be smaller than the calculated Λ one (130.6) for the independent Li⁺ and (PhO)₂PO₂⁻. The Λ_{clcd} [Li⁺(-PhO)₂PO₂⁻] = Λ_0 [*n*-Bu₄N⁺(PhO)₂PO₂⁻](123.0) + Λ_0 (LiClO₄) (174.8) [29] - Λ_0 (*n*-Bu₄N⁺ClO₄)(167.2) [29] = 130.6. By the way, the Λ_0 value of *n*-Bu₄N⁺(PhO)₂PO₂⁻ has not directly been measured yet, therefore, the values is estimated by the calculation from Λ_0 [Et₄N⁺(-PhO)₂PO₂⁻] (149.1) [23] and the difference (26.1) between Et₄N⁺ and *n*-Bu₄N⁺ [17]. We should note that any tetraalkylammonium and perchlorate ions have no chemical interaction except for the Coulombic force, that is, R₄N⁺X⁻ or Li⁺ClO₄⁻ is a strong electrolyte in higher permittivity media such as MeCN. For instance, the association constants of *n*-Bu₄NClO₄, LiClO₄, and Et₄N⁺(PhO)₂PO₂⁻ have been reported to be $K_a = 0, 13.6$ [29], and *ca.* 4.0 [23], respectively.

It is worth mentioning once more that the balance (*ca.* 118) between 285 and 167.2, attributed to the molar conductivity of $\text{Li}^+(\text{PhO})_2\text{PO}_2^-$, seems to be enough smaller than the sum value (130.6) of independent Λ_0 values of Li^+ and (PhO)_2PO_2^-. Therefore, we can predict the "strong"



Fig. 11. (a). Conductometric titration curve of 5.0×10^{-4} mol dm⁻³ diphenylphosphate ion [n-Bu₄N⁺(PhO)₂PO₂⁻] with increasing concentration of LiClO₄ in MeCN. (b). Conductometric titration curve of 5.0×10^{-4} mol dm⁻³ diphenylphosphate ion [n-Bu₄N⁺(PhO)₂PO₂⁻] with increasing concentration of Mg(ClO₄)₂ in MeCN.

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Fig. 13. (a). Absorbance ($\lambda = ca. 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ Et}_3 \text{N}$ in the presence of Ba(ClO₄)₂ in MeCN–MeOH mixtures: (\bigcirc) 0; (\bigcirc) 10; (\triangle) 15; (\triangle) 20% (ν/ν) of MeOH. (b). Changes in absorbance ($\lambda = ca. 206 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ Et₃N in the presence of Ba(ClO₄)₂ in MeCN–EtOH mixtures: (\bigcirc) 0; (\triangle) 10; (\triangle) 20; (\square) 30; (\blacksquare) 30% (ν/ν) of EtOH.

interaction between (PhO)₂PO₂⁻ and Li⁺ in MeCN, even without observing precipitates. The observed specific conductance of 0.129 \times 10⁻³ from the titration with Mg(ClO₄)₂ may also support the "strong" interaction between Mg²⁺ and L⁻ under no precipitation conditions.

3.2.2. The influences of added H₂O, MeOH, and EtOH on the interaction between M^+ or M^{2+} and the mixture of HL with Et₃N

Fig. 12 shows the influences of added H_2O on precipitation and the successive re-dissolution reactions of BaL_2 in MeCN. The precipitation

is obviously restrained but the re-dissolution is promoted apparently by the added H₂O. The (reverse) coordination constants (log K_1) are given as "pseudo" values to be 4.25, 3.95, and 3.08 in 1.0, 2.0, and 3.0% H₂O, respectively. These values may be valid just relatively. In 5.0% H₂O, the absorbance decrease (*i.e.*, precipitation) occurs slightly at 2.5 × 10⁻⁴ and 5.0 × 10⁻⁴ mol dm⁻³ Ba²⁺. The 10% H₂O addition causes no apparent precipitation or re-dissolution reactions between Ba²⁺ and L⁻.



Fig. 15. Changes in absorbance ($\lambda_{max} = ca$. 290 nm) of 5.0 × 10⁻⁴ mol dm⁻³ bis(4-nitrophenyl)phosphate containing 5.0 × 10⁻⁴ mol dm⁻³ Et₃N with increasing of alkali metal ions: (\bigcirc) LiClO₄; (\bigcirc) NaClO₄.





Influences of the concentration on the 1:1 mixture of Et₃N and diphenylphosphate (Et₃N-HL) on the precipitation and re-dissolution reactions for $Ba(ClO_4)_2$ in MeCN–MeOH.

Mixed solution	Equilibrium	MeCN–MeOH [MeOH% (v/v)]					
wixed solution	constants ^a	10	15	20	20 30		
Et ₃ N-HL				No			
$(5.0 \times 10^{-4} \text{ mol } \text{dm}^{-3})$	(pK_{sp})	12.74	(10.94)	-			
	(pK_{sp})	12.96	(11.16)	-			
		0	0	No			
	$\log K_1$	3.90	(3.78)	-			
Et ₃ N-HL			A		A	No	
$(5.0 \times 10^{-3} \text{ mol } \text{dm}^{-3})$	(pK_{sp})		11.26	8.97	8.52	-	
	(pK_{sp})		11.97	9.68	9.24	-	
			0	0	0	No	
	$\log K_1$		3.35	3.06	2.68	-	

For the Explanatory notes, cf. Table 1.

^a Solubility products (K_{sp}) and "reverse" coordination constants (K_1), *cf*. the Experimental section.



Fig. 14. UV spectra of 5.0×10^{-4} mol dm⁻³ bis(4-nitrophenyl)phosphate (0.1 cm pathlength) containing 5.0×10^{-4} mol dm⁻³ Et₃N with increasing concentration of NaClO₄ in MeCN.

Table 5

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Scheme 4. The partial ionization of bis(4-nitrophenyl)phosphate by the addition of Et₃N in MeCN.



Scheme 5. Successive formation of BaL_2 and BaL^+ for the bis(4-nitrophenyl)phosphate ion (L^-) in MeCN.

Both MeOH (DN_{bulk} = 31.3 [45]) and EtOH (DN_{bulk} = 27.8 [45]) are protic solvents of higher donicities. Not only MeOH but also EtOH may inhibit the precipitation between Ba²⁺ and L⁻, and the influences may increase in the order of EtOH < MeOH < H₂O [*cf.* Fig. 13 (a) and (b)]. With increasing contents of MeOH and EtOH, the precipitation reactions become incomplete. The slight precipitation occurs in 15% MeOH or 30% EtOH, and the interaction is totally hidden by 20% MeOH and 50% EtOH.

Table 5 lists the equilibrium constants of the reactions between Ba²⁺ and the (1:1) Et₃N-HL (5.0×10^{-3} and 5.0×10^{-3} mol dm⁻³) mixture in MeCN–MeOH. Even in 15–30% MeOH, the precipitation and "reverse" coordination can take place between 5.0×10^{-3} mol dm⁻³ Et₃N-HL and Ba²⁺ to a relatively large extent. The (reverse) coordination constants of 5.0×10^{-3} mol dm⁻³ Et₃N-HL have been given as "pseudo" values to be log $K_1 = 3.35$, 3.06, and 2.68 in 15, 20, and 30% MeOH, respectively. The above results indicate clearly that, by performing experiments with higher concentrations (*e.g.*, a ten-fold) of L⁻, we have still the chance to obtain equilibrium constants even though no precipitation takes place for a metal ion with a lower L⁻ concentration. Table 5 may convince us that the equilibrium values evaluated from different L⁻ (Et₃N-HL) concentrations are well consistent.

3.3. Bis(4-nitrophenyl)phosphate (HL)

3.3.1. Specific interaction between M^+ or M^{2+} and the mixture of HL with Et_3N

Fig. 14 shows the UV spectral changes of 5.0×10^{-4} mol dm⁻³ bis(4-nitrophenyl)phosphate (HL) containing an equivalent amount of Et₃N (5.0×10^{-4} mol dm⁻³), as the function of NaClO₄ concentration. The UV spectrum of Et₃N-HL shows two distinct absorption bands at around 218 nm and 295 nm (ϵ/cm^{-1} mol⁻¹ dm³ = *ca.* 2.0 × 10⁴). With increasing concentration of NaClO₄, if we may pay attention to



Fig. 17. Changes in absorbance ($\lambda_{max} = ca. 290 \text{ nm}$) of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate containing $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ Et₃N with increasing of alkaline earth metal ions in MeCN: (\bigcirc) Mg(ClO₄)₂; (\bigoplus) Ca(ClO₄)₂; (\triangle) Ba(ClO₄).

the band at around 295 nm, it decreases gradually and reaches its minimum of 0.067 at 1.0×10^{-2} mol dm⁻³ NaClO₄, accompanying white precipitates (*cf.* Eq. (5)). Then, the band absorbance begins to increase with the addition of more than 1.0×10^{-2} mol dm⁻³ Na⁺, and recovers almost the original value at 1.0 mol dm^{-3} Na⁺ (*cf.* Eq. (6)). Meanwhile, the band shows a remarkable blue shift to 287 nm, suggesting the formation of a "reverse-coordinated" species of Na₂L⁺. The evaluated values of pK_{sp} and log K₂ between Na⁺ and L⁻ in MeCN are 6.70 and 3.75, respectively. However, no apparent interaction is detected between Li⁺ and L⁻ based on the almost constant absorbance values of the Et₃N-HL mixture (Fig. 15), except for the blue shifts with increasing Li⁺ concentrations.

$$Et_3N-HL + Na^+ \leftrightarrows Na^+L^- + Et_3NH^+, \tag{5}$$

$$Na^{+}L^{-} + Na^{+} \leftrightarrows Na_{2}L^{+}.$$
(6)

The UV spectral changes of 5.0×10^{-4} mol dm⁻³ Et₃N-HL, as the function of $Ba(ClO_4)_2$ concentration, are shown in Fig. 16. The absorption band at around 290-295 nm almost disappears on the addition of an equivalence of Ba²⁺ (2.5×10^{-4} mol dm⁻³), accompanying white precipitates. The absorbance begins to increase with the further addition Ba²⁺, forming the (reverse) coordinated species of BaL⁺. The "pseudo" values of pK_{sp} and $\log K_1$ between Ba⁺ and L⁻ in MeCN are obtained to be 13.68 and 4.81. The partial ionization of HL and the coordination reaction are illustrated by Schemes 4 and 5. According to Fig. 17, a slight precipitation reaction may take place between bis(4nitrophenyl)phosphate and Mg²⁺ or Ca²⁺. Only Na⁺ and Ba²⁺ cause observable interactions with L⁻ through the remarkable precipitation and re-dissolution reactions. However, we never believe that the bis(4-nitrophenyl)phosphate ion cannot interact with Li⁺, Mg²⁺, or Ca²⁺ in MeCN. The solubilities of the non-charged species for Li⁺, Mg^{2+} , and Ca^{2+} should be just too high to form precipitates in the solvent. Needless to mention, the chemical interaction operates actually between Li⁺, Mg²⁺, or Ca²⁺ and 5.0×10^{-4} mol dm⁻³ L⁻.



Fig. 18. Absorbance $(\lambda_{max} = ca. 290 \text{ nm})$ of $5.0 \times 10^{-4} \text{ mol } dm^{-3} \text{ bis}(4-nitrophenyl)phosphate (0.1 cm path-length) containing <math>5.0 \times 10^{-4} \text{ mol } dm^{-3} \text{ Et}_3 \text{N}$ in the presence of NaClO₄ in MeCN-H₂O mixtures: (\bigcirc) 0; ($\textcircled{\bullet}$) 1.0; (\triangle) 2.0 (\bigstar) 3.0% (v/v) of H₂O.

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Fig. 19. Absorbance ($\lambda_{max} = ca$. 290 nm) of 5.0 \times 10⁻⁴ mol dm⁻³ bis(4-nitrophenyl)phosphate containing 5.0 \times 10⁻⁴ mol dm⁻³ Et₃N in the presence of Ba(ClO₄)₂ in MeCN-H₂O mixtures: (○) 0; (●) 0.50; (△) 1.0 (▲) 2.0% (v/v) of H₂O.

3.3.2. The influences of added H_2O and MeOH on the interaction between Na^+ or Ba^{2+} and the mixture of HL with Et_3N

Fig. 18 shows the influences of added H₂O on the precipitation and the successive re-dissolution of NaL. With increasing contents of H₂O, the solubility of NaL increases distinctly. The pK_{sp} values are 6.70, 5.80, and 4.63 in 0.0, 1.0, and 2.0% H₂O, respectively. In 3.0% H₂O, no precipitation reaction is observed. Similarly, no apparent interaction can be detected also in 10% MeOH.

Fig. 19 shows the influences of added H₂O on the precipitation and the successive re-dissolution of BaL₂. The added 0.5% H₂O affects obviously both precipitation and re-dissolution between Ba²⁺ and the anion, despite the absorbance minimum appears at an equivalence of Ba²⁺. Slight precipitation takes place in 1.0% H₂O. The "pseudo" solubility products (pK_{sp}) are 13.68, 12.36 and 10.72 in 0.0, 0.50, and 1.0% H₂O, respectively. The interaction is totally obscured by 2.0% H₂O. Compared with water, MeOH affects weakly the precipitation and re-dissolution. The interaction is totally hidden by 5.0% MeOH. The remarkable influences on Ba²⁺ of low contents of protic solvents should be caused by the stronger solvation toward the bis(4-nitrophenyl)phosphate ion.

4. Conclusion

The coordination ability of alkali metal (M⁺) and alkaline earth metal (M^{2+}) ions with diphenylphosphinate, diphenylphosphate, and bis(4-nitrophenyl)phosphate ions has been confirmed not only in sole MeCN but also in the binary solvents with H₂O, MeOH, and EtOH. The precipitation and the successive re-dissolution reactions have been observed between every M^+ or M^{2+} and 1.0 \times 10^{-3} mol dm^{-3} diphenylphosphinate. The "reverse coordination" or coordination constants suggest that the chemical interaction should increase in the order of Na^+ < Li^+ and Ba^{2+} < Ca^{2+} < Mg^{2+} . With $5.0\times 10^{-4}\mbox{ mol }dm^{-3}$ diphenylphosphate, however, only \mbox{Ca}^{2+} and Ba^{2+} (the strength order of $Ba^{2+} < Ca^{2+}$) can cause the obvious precipitation in MeCN. Nevertheless, we are confident that all the phosphinate and phosphonate ions should interact with the alkali metal and alkaline earth metal ions through the chemical (coordination) force above the Coulombic force in poor solvating media. The results in the present study may give an important clue to recognize the kinetic mechanism in hydrolysis reactions under "non-aqueous solvent conditions" or in biological systems, based on the direct interaction between "indifferent" metal ions and the anion species released from substrates.

References

- [1] L.S.B. Upadhyay, N. Verma, Biosens. Bioelectron. 68 (2015) 61.
- L. Ronconi, P.J. Sadler, Coord. Chem. Rev. 251 (2007) 1633
- D. Loca, M. Sokolova, J. Locs, A. Smirnova, Z. Irbe, Mater. Sci. Eng. C 49 (2015) 106. [3] Y. Zhang, A. Clearfield, Inorg. Chem. 31 (1992) 2821.
- Z. Rohlik, P. Holzhauser, J. Kotek, J. Rudovsky, I. Nemec, P. Hermann, I. Lukes, J. [5]
- Organomet. Chem. 691 (2006) 240.
- M. Mitra, R. Ghosh, Inorg. Chem. Commun. 24 (2012) 95.
- F.M. Menger, L.H. Gan, E. Johnson, D.H. Durstt, J. Am. Chem. Soc. 109 (1987) 2800.
- P. Jurek, A.E. Martell, Inorg. Chim. Acta 287 (1999) 47. [8]
- J. Xie, B. Jiang, X. Kou, C. Hu, X. Zeng, Transit. Met. Chem. 28 (2003) 782.
- L.C. Manege, T. Ueda, M. Hojo, Bull. Chem. Soc. Jpn. 71 (1998) 589 [10]
- [11] L.C. Manege, T. Ueda, M. Hojo, M. Fujio, J. Chem. Soc. Perkin Trans. 2 (1998) 1961.
- [12] M. Hojo, T. Ueda, S. Inoue, Y. Kawahara, J. Chem. Soc. Perkin Trans. 2 (2000) 1735.
- [13] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, D. Fujimura, Bull. Chem. Soc. Jpn. 79 (2006) 751.
- [14] M. Hojo, T. Ueda, E. Ueno, T. Hamasaki, T. Nakano, Bull. Chem. Soc. Jpn. 83 (2010) 401.
- [15] M. Hojo, S. Aoki, Bull. Chem. Soc. Jpn. 85 (2012) 1023
- L.D. Bayissa, Y. Ohmae, M. Hojo, J. Mol. Liq. 199 (2014) 294. Ì16Ì
- M. Hojo, T. Takiguchi, M. Hagiwara, H. Nagai, Y. Imai, J. Phys. Chem. 93 (1989) 955. [17]
- M. Hojo, H. Nagai, M. Hagiwara, Y. Imai, Anal. Chem. 59 (1987) 1770. [18]
- M. Hojo, Y. Miyauchi, A. Tanio, Y. Imai, J. Chem. Soc. Faraday Trans. 24 (1991) 3847. [19]
- 1021 M. Hojo, T. Ueda, T. Inoue, M. Ike, J. Phys. Chem. B 117 (2007) 1759.
- M. Hojo, H. Hasegawa, H. Yoneda, J. Chem. Soc. Perkin Trans. 2 (1994) 1855. [21]
- M. Hojo, S. Ohta, K. Ayabe, K. Okamura, K. Kobiro, Z. Chen, J. Mol. Liq. 177 (2013) [22] 145.
- [23] M. Hojo, H. Hasegawa, Y. Miyauchi, H. Moriyama, H. Yoneda, S. Arisawa, Electrochim. Acta 39 (1994) 629.
- X. Chen, K. Ayabe, M. Hojo, Z. Chen, M. Kobayashi, J. Mol. Liq. 199 (2014) 445. [24]
- M. Hojo, T. Ueda, M. Ike, M. Kobayashi, H. Nakai, J. Mol. Liq. 145 (2009) 152. 25
- [26] M. Hojo, Y. Imai, Bull. Chem. Soc. Jpn. 56 (1983) 1963.
- [27] M. Hojo, Pure Appl. Chem. 80 (2008) 1539.
- Z. Chen, M. Hojo, J. Phys. Chem. B 101 (1997) 10896. [28]
- M. Hojo, T. Ueda, M. Nishimura, H. Hamada, J. Phys. Chem. B 103 (1999) 8965. [29]
- 301 M. Hojo, A. Watanabe, T. Mizobuchi, Y. Imai, J. Phys. Chem. 94 (1990) 6073.
- R.R. Holmes, R.O. Day, Y. Yoshida, J.M. Holmes, J. Am. Chem. Soc. 114 (1992) 1771. R.M. Fuoss, C.A. Kraus, J. Am. Chem. Soc. 55 (1933) 2387. [31]
- 1321
- H. Weingartner, V.C. Weiss, W. Schroer, J. Chem. Phys. 113 (2000) 762.
 S. Petrucci, E.M. Eyring, J. Phys. Chem. 95 (1991) 1731. [33]
- [34]
- R.L. Jarek, S.K. Shin, J. Am. Chem. Soc. 119 (1997) 10501. [35]
- M. Hojo, Y. Kondo, K. Zei, K. Okamura, Z. Chen, M. Kobayashi, Bull. Chem. Soc. Jpn. 87 [36] (2014) 98
- M. Hojo, T. Ueda, A. Inoue, S. Tokita, J. Mol. Liq. 148 (2009) 109. [37]
- [38] M. Hojo, T. Ueda, M. Yamasaki, A. Inoue, S. Tokita, M. Yanagita, Bull. Chem. Soc. Jpn. 75 (2002) 1569.
- [39] G.V. Oshovsky, D.N. Reinhoudt, W. Verboom, J. Am. Chem. Soc. 128 (2006) 5270.
- [40] M. Hojo, H. Hasegawa, Z. Chen, Bull. Chem. Soc. Jpn. 69 (1996) 2215.
- M. Iida, Y. Hata, Bull. Chem. Soc. Jpn. 65 (1992) 707. [41]
- [42] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents, Physical Properties and Methods of Purification, fourth ed. John Wiley & Sons, New York, 1986.
- [43] V. Gutmann, The Donor-Acceptor Approach to Molecular Interactions, Plenum, New York, 1978.
- P. Eberspächer, E. Wismeth, R. Buchner, J. Barthel, J. Mol. Liq. 129 (2006) 3. [44]
- [45] Y. Marcus, J. Solut. Chem. 13 (1984) 599.
- [46] A.K. Covington, T. Dickinson, Physical Chemistry of Organic Solvent Systems, Plenum, London, 1973.