



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 $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion ($n\text{-Bu}_4N^+Ph_2PO_2^-$), both the precipitation of the non-charged species (ML or ML_2) 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 [$n\text{-Bu}_4N^+(PhO)_2PO_2^-$], no apparent interaction can be insisted between the alkali metal ions or Mg^{2+} and $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ diphenylphosphate ion, based on just no precipitation occurrence. Only Na^+ and Ba^{2+} can cause obvious precipitation with $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ bis(4-nitrophenyl)phosphate. A good evidence, however, has been provided by the conductometric titration of $5.0 \times 10^{-4} \text{ mol dm}^{-3}$ $n\text{-Bu}_4N^+(PhO)_2PO_2^-$ with $LiClO_4$ or $Mg(ClO_4)_2$ in MeCN that the “strong” interaction still operate between L^- and Li^+ or Mg^{2+} 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 H_2O and many organic solvents containing

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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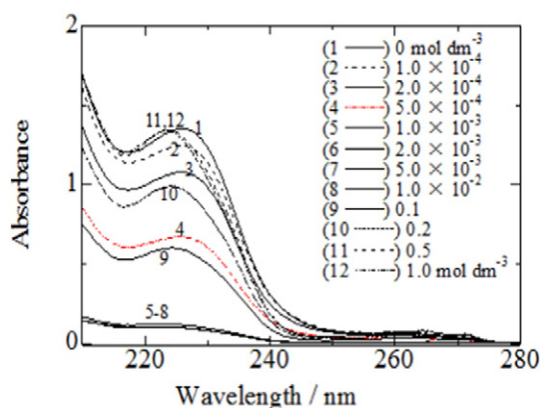


Fig. 1. UV spectra of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion (L^-) of $n\text{-Bu}_4\text{N}^+L^-$ (0.1 cm path-length) in MeCN with increasing concentration of LiClO_4 .

in the media of relatively high permittivity ($20 < \epsilon_r < 65$) [29]. We have attributed the higher ion-aggregation to the coordination (of M^+ or M^{2+}) as well as hydrogen bonding forces (of $R_3\text{NH}^+$) in addition to Coulombic forces [30]. Holmes [31] has examined the hydrogen-bonding between imidazole and diphenylphosphate by ^1H NMR, IR, and X-ray technique.

The concept of triple ions in low permittivity media ($\epsilon_r < 12$ 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 [$(\text{PhO})_2\text{PO}_2^-$], in acetone, but somehow strangely not in acetonitrile.

Acetonitrile (MeCN) is a relatively high permittivity solvent ($\epsilon_r = 35.94$ [42]) of low donor and acceptor numbers ($\text{DN} = 14.1$, $\text{AN} = 19.3$ [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 M^{2+} with nitrophthalates or sulfonates (*p*-toluenesulfonate, 1,5-naphthalenedisulfonate, and 1,3,6-naphthalenetrisulfonate) [22,24].

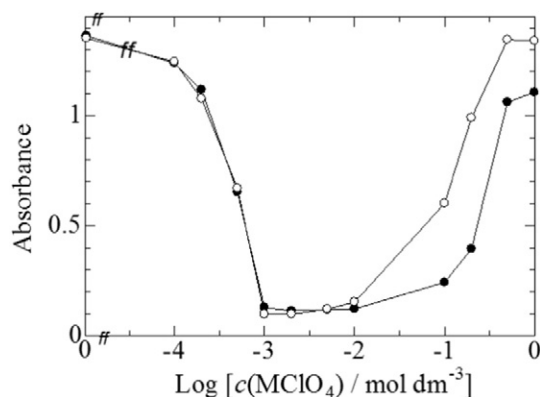
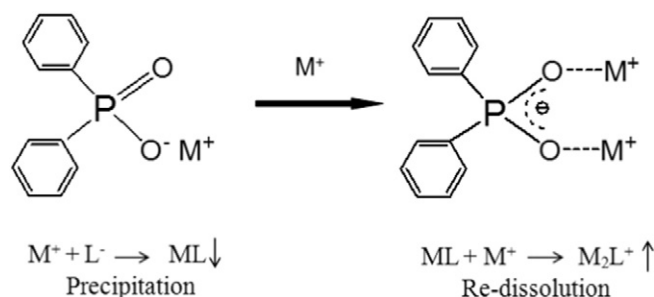


Fig. 2. Changes in absorbance ($\lambda_{\text{max}} = \text{ca. } 226 \text{ nm}$) of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate ion with increasing concentration of alkali metal ions in MeCN: (○) LiClO_4 ; (●) NaClO_4 .



Scheme 1. Successive formation of ML and M_2L^+ ($M = \text{Li}$ 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(4-nitrophenyl)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 solvation 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(4-nitrophenyl)phosphate acids were purchased from Aldrich. Tetrabutylammonium diphenylphosphinate ($n\text{-Bu}_4\text{N}^+\text{Ph}_2\text{PO}_2^-$) was prepared as follows: A 1.0 g of diphenylphosphinic acid was dissolved in methanol, and was titrated by $n\text{-Bu}_4\text{NOH}$ (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 [$n\text{-Bu}_4\text{N}^+(\text{PhO})_2\text{PO}_2^-$] was prepared from diphenylphosphinate acid in a similar way.

Metal perchlorates without hydrate water, LiClO_4 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, and $\text{Ba}(\text{ClO}_4)_2$ (all Aldrich), were used as received. Calcium perchlorate tetrahydrates from Aldrich was dried *in vacuo* at 150°C to obtain anhydrous $\text{Ca}(\text{ClO}_4)_2$. Triethylamine (Et_3N), Et_4NClO_4 , 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

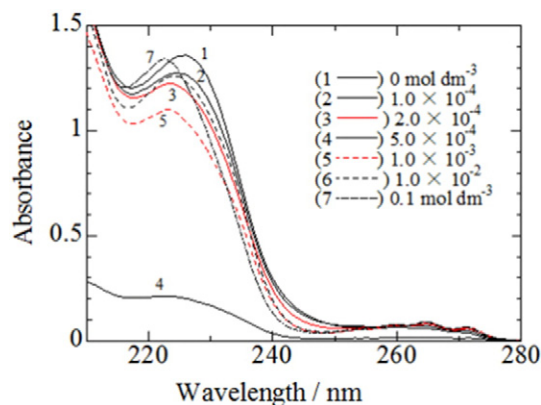


Fig. 3. UV spectra of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ diphenylphosphinate (0.1 cm path-length) with increasing concentration of $\text{Mg}(\text{ClO}_4)_2$ in MeCN.

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