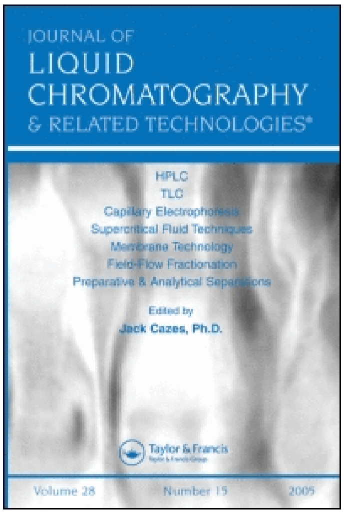

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# Complex Formation of Monomeric Phosphorus Oxoacids with Sodium Ion in Donnan Exclusion Chromatography

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# COMPLEX FORMATION OF MONOMERIC PHOSPHORUS OXOACIDS WITH SODIUM ION IN DONNAN EXCLUSION CHROMATOGRAPHY

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## ABSTRACT

A method for evaluation of stability constants of very unstable and labile complexes has been proposed by the use of Donnan exclusion chromatography. The stability constants of sodium complexes of monomeric phosphorus oxoacids have been evaluated to be $\log \beta_1 = -0.04$ for phosphinate, $\log \beta_1 = 0.86$ and $\log \beta_2 = 0.24$ for hydrogen orthophosphate and $\log \beta_1 = 0.61$ and $\log \beta_2 = 0.16$ for phosphonate, respectively, at $I = 1.00$ $(CH_3)_4NCl$, $t = 25.0° \pm 0.1°C$.

## INTRODUCTION

Sodium salt of monomeric phosphorus oxoacid is a labile and very unstable complex due to a weak ionic bond. Although it has been supposed that monomeric phosphorus oxoacid hardly forms complexes ( or ion-pair ) with alkaline metal ion, the influence of metal ion cannot be ignored in chromatographic study using metal

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ion as an eluent or in biochemical reactions *in vivo*.. Therefore, the magnitude of the metal ion influence to monomeric phosphorus oxoacids must be estimated. The magnitude may be represented as the stability constant that is able to be measured in Donnan exclusion chromatography, whereas it is difficult to directly measure the concentration of free metal ion or free anion with an ion-selective electrode because the measurement must be done in a solution containing considerably concentrated metal ion. There are a few investigations reported. Smith and Alberty (1) have investigated orthophosphate complexes with monovalent cations by potentiometry. Phosphonate complex with sodium ion has been determined with a conductivity method by Frei, Podlahová and Podlaha (2). On the other hand, the secondary overall stability constant, $\beta_2$ can be also determined in Donnan exclusion chromatography. In the present paper, the stability constants of sodium complexes of phosphinate, $PH_2O_2^-$, phosphonate, $PHO_3^{2-}$ and hydrogen orthophosphate, $HPO_4^{2-}$ are evaluated.

## EXPERIMENTAL

A dextran gel-type cation-exchanger, SP-Sephadex C-25 column of 1.0 cm I.D., was equipped with a constant temperature jacket controlled at 25.0° ± 0.1°C. Eluents were sodium chloride solutions of various concentrations ( 0 – 1.00 M ). Tetramethylammonium chloride was added to maintain ionic strength at unity. The eluents and the sample solutions contain a small amount of tetramethylammonium hydroxide to adjust pH to 10. A buffer solution is intentionally not used to prevent a side reaction. Flow rate was 0.7 ml/min.

Sample sodium salts of orthophosphate $Na_2HPO_4$, phosphonate $Na_2PHO_3 \cdot 5H_2O$ and phosphinate $NaPH_2O_2 \cdot H_2O$ were of commercially available reagent grade. Sodium trimetaphosphate $Na_3P_3O_9 \cdot 3H_2O$ and linear polyphosphate ( Graham's salt, average degree of polymerization = 53 ) were prepared in our laboratory.

After the column was pre-conditioned with the eluent of a given sodium ion concentration, 100 μl of sample solution ( $1 \times 10^{-3}$ M as P atom ) was applied to the column. The effluent was collected with a fraction collector into fractions of 0.5 ml. The determination of sample components and the calculation of the distribution coefficient are the same as described previously (3 – 5).

## RESULTS AND DISCUSSION

The stability constants of trimetaphosphate complex with magnesium and calcium have been estimated in the previous paper (4). These values are small and the order 30 – 50. Sodium complexes of monomeric phosphorus oxoacids have weaker stability constants than trimetaphosphate. Although phosphinate is taken as a species that is hard to form an ion-pair, we found the elution position of monomeric phosphorus oxoacids shifts to a large volumes with the increase of sodium ion concentration in an eluent. It is evident that monomeric phosphorus oxoacid, even phosphinate, forms a complex ( or ion-pair ) with sodium ion.

The cation-exchanger column of 1.0 cm I.D. was used in this work instead of 1.5 cm I.D. because it includes enough of a non-adsorption region for the resulting sodium complexes with a low negative charge between zero and two. The theoretical basis was confirmed by plotting the logarithm of the distribution coefficient against anionic charge. This plot is found to be linear and the slope is almost the same as that of a 1.5 cm I.D. column ( 0.39 to 0.38 ). It can be said that the distribution coefficient is independent of column size.

A contraction in the bed volume is caused by the increase of sodium ion in an eluent. It is necessary, for the calculation of the distribution coefficient, to acertain the cause of the contraction. Thus, we found that the effluent volume between crotonaldehyde and long-chained linear polyphosphate ( Graham's salt ) is constant at any sodium ion concentration in an eluent. That is to say, the contraction is due to the decrease of the volume of the external interstitial solution ( *cf*. ref. 5 ). The distribution coefficient may be calculated by considering the decrease of the bed volume at a given concentration of sodium ion, because the volume of the Donnan exchanger phase is constant.

A one-to-one sodium complex of phosphinate is eluted at the position between monovalent and neutral species. The distribution coefficient increases with an increase in the sodium ion concentration ( TABLE 1 ). The stability constant, $\beta_1$, for $Na^+ + PH_2O_2^- \rightleftharpoons NaPH_2O_2$ is obtained by extrapolating $[Na^+]$ to zero concentration.

$$\beta_1 = \lim_{[Na^+]\to 0} \phi = \lim_{[Na^+]\to 0} \left( \frac{1}{[Na^+]} \cdot \frac{D - K_{D,PH_2O_2^-}}{K_{D,NaPH_2O_2} - D} \right) \quad (1)$$

where D is the distribution coefficient of sample anion, $K_D$ is the characteristic distribution coefficient of the components and $[Na^+]$ is the concentration of sodium

TABLE 1

Experimental Data for Phosphinate

| $[Na^+]$ (M) | 0.4 | 0.5 | 0.6 | 0.7 | 0.8 | 0.9 |
|---|---|---|---|---|---|---|
| D | 0.554 | 0.571 | 0.578 | 0.601 | 0.604 | 0.629 |
| $\bar{n}$ | 0.241 | 0.270 | 0.281 | 0.321 | 0.326 | 0.369 |
| $\phi$ | 0.794 | 0.741 | 0.654 | 0.676 | 0.607 | 0.650 |

ion in an eluent. The ratio of the amount of bound sodium ions in moles to the total amount of the ligand ion, $\bar{n}$, should not be close to an integral value, because an enormous error results as can be seen from eqn. (1). The $\phi$ is calculated at the concentration of sodium ion so that the ratio is between 0.1 and 0.9. The $\phi$ is plotted against the concentration of sodium ion in an eluent ( Fig. 1 ). The stability constant of sodium phosphinate is found to be only 0.91 ( log $\beta_1$ = -0.04 ). This means that about 8.4 % of phosphinate ion forms sodium complex even in 0.1 M sodium chloride solution. This is a striking method that the stability constant can be evaluated so far as it is near unity at I = 1.00.

Sodium complexes of hydrogen orthophosphate and phosphonate were similarly examined. For these complexes, the secondary overall stability constant, $\beta_2$ can be also obtained because disodium complex is not still a cationic species adsorbed onto fixed groups of a cation-exchanger. To evaluate the stability constant, the following equation was derived

$$\phi \equiv \frac{1}{[Na^+]} \cdot \frac{D - K_{D,P}}{K_{D,NaP} - D} = \beta_1 + \frac{K_{D,Na_2P} - D}{K_{D,NaP} - D}[Na^+] \cdot \beta_2 \qquad (2)$$

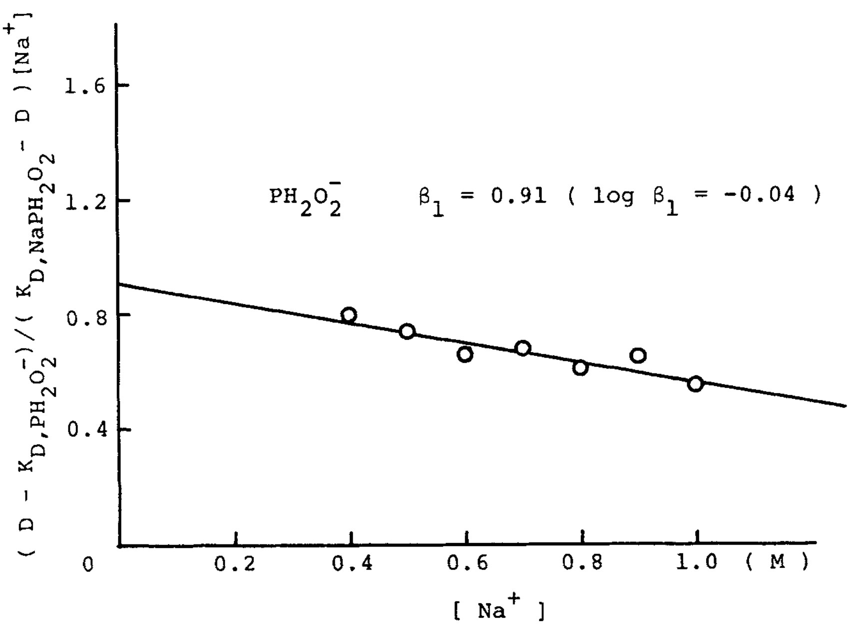

FIGURE 1

Evaluation of stability constant of sodium phosphinate complex ( I = 1.00, 25.0° ± 0.1°C ).

By plotting against $(K_{D,Na_2P} - D)[Na^+]/(K_{D,NaP} - D)$, $\beta_1$ and $\beta_2$ can be obtained from the intercept and the slope, respectively. The experimental data for hydrogen orthophosphate and phosphonate are tabulated in TABLE 2 and shown in Fig. 2. The stability constants ( $\beta_1$ and $\beta_2$ ) are evaluated to be 7.23 and 1.74 ( log $\beta_1$ = 0.86 and log $\beta_2$ = 0.24 ) for hydrogen orthophosphate, and 4.12 and 1.43 ( log $\beta_1$ = 0.61 and log $\beta_2$ = 0.16 ) for phosphonate, respectively, at I = 1.00 $(CH_3)_4NCl$, t = 25.0° ± 0.1°C. The values are very small and lie in the range where it is difficult to measure the ionic concentration with an ion-selective elctrode. The

TABLE 2

Experimental Data for Hydrogen Orthophosphate and Phosphonate

| Hydrogen Orthophosphate | | | | | | |
|---|---|---|---|---|---|---|
| $[Na^+]$ (M) | 0.030 | 0.035 | 0.040 | 0.100 | 0.150 | 0.200 |
| D | 0.213 | 0.220 | 0.225 | 0.279 | 0.309 | 0.331 |
| $\bar{n}$ | 0.18 | 0.21 | 0.23 | 0.45 | 0.57 | 0.67 |
| A | 0.118 | 0.142 | 0.165 | 0.540 | 1.00 | 1.66 |
| B | 7.34 | 7.63 | 7.45 | 8.22 | 9.03 | 10.1 |
| **Phosphonate** | | | | | | |
| $[Na^+]$ (M) | 0.030 | 0.035 | 0.040 | 0.100 | 0.150 | 0.200 |
| D | 0.196 | 0.202 | 0.205 | 0.249 | 0.275 | 0.301 |
| $\bar{n}$ | 0.11 | 0.14 | 0.15 | 0.33 | 0.44 | 0.54 |
| A | 0.112 | 0.132 | 0.153 | 0.460 | 0.791 | 1.26 |
| B | 4.14 | 4.33 | 4.40 | 4.91 | 5.14 | 5.93 |

$$A = ( K_{D,Na_2P} - D ) [Na^+] / ( K_{D,NaP} - D ),$$

$$B = ( D - K_{D,P} ) / ( K_{D,NaP} - D ) [Na^+]$$

first overall stability constant, $\beta_1$, has been found to be log $\beta_1$ = 0.60 ( I = 0.2 $(C_3H_7)_4NCl$, t = 25°C ) for hydrogen orthophosphate by potentiometry (1), and log $\beta_1$ = 1.05 ( I = 0, t = 20°C ) for phosphonate by conductivity (2). It seems that these values have the same order as ours if we take into account the difference of conditions employed.

These results indicate, apparently, that the stability constant of a very unstable and ionic bonded complex can be evaluated as well as that of a stable and covalent bonded complex, because of the simple procedure

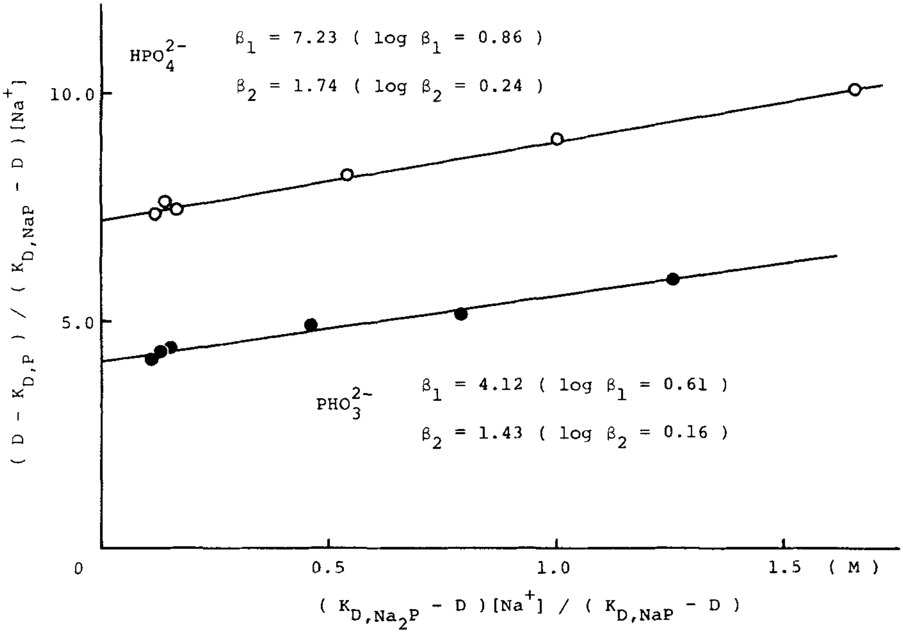

FIGURE 2

Evaluation of stability constants of sodium hydrogen orthophosphate and sodium phosphonate complexes ( I = 1.00, 25.0° ± 0.1°C ).

that sets metal ion concentration around the reciprocal of the stability constant. It is one of the most advantageous methods for measuring the stability constant. An unstable and labile complex such as a sodium salt of monomeric phosphorus oxoacid is very interesting not only in solution chemistry but also in biochemical studies dealing with non-high-energy phosphate.

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