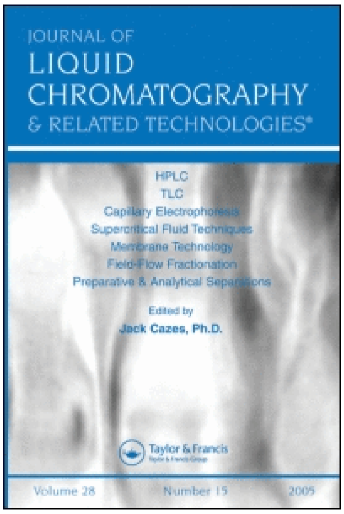

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GEL CHROMATOGRAPHIC BEHAVIOR OF LABILE METAL COMPLEXES

TRIMETA- AND TETRAMETAPHOSPHATE COMPLEXES WITH BIVALENT METAL CATIONS

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ABSTRACT

The gel chromatographic behavior of metal ions in a labile complex formation system was expressed as a function of the ligand concentration in an eluent and the stability constants of the complexes. Trimeta- and tetrametaphosphate complexes with bivalent metal ions were used as examples. The retention volumes of the metal complexes were found to be always greater than those of the corresponding free ligands.

INTRODUCTION

Much attention has been drawn to the gel chromatographic behavior of metal complexes. In some cases inert complexes have been used as samples(1-3). Labile systems have also been investigated, and it was recognized that the complex equilibria among solutes play an important role(4-8). The distribution coefficients of EDTA complexes and monomeric oxoanions of phosphorus have been found to be dependent on pH of an eluent(4,7). The mutual separation of these oxoanions were performed by adjusting eluent pH at a desired value(8).

In a previous paper(5) the authors reported a theoretical consideration on the gel chromatographic behavior of labile metal complexes. It was shown that the retention volume of magnesium in gel chromatography can be expressed as a function of tetrametaphosphate concentration in an eluent and the stability constant of the complex. To confirm the versatility of this theoretical approach the present paper describes the gel chromatographic behavior of magnesium, calcium, strontium, nickel and zinc in the presence of trimetaphosphate (P_{3m}) and tetrametaphosphate(P_{4m}). It can be expected from the previous work(9,10) that only one-to-one complexes are predominantly formed under the present experimental conditions. A solution containing a ligand was used as an eluent in order to prevent dissociation of a complex during elution. The stability constants of metal complexes were estimated and compared with those in the literature. The retention volumes of the metal complexes were found to be greater than those of the corresponding ligands.

MATERIALS AND METHODS

Sodium trimetaphosphate trihydrate and sodium tetrametaphosphate tetrahydrate were prepared according to the literature(11), and the purity was checked by paper chromatography.

A liquid chromatograph with an atomic absorption detector (Perkin-Elmer 403) previously described in detail (12-14) was used. A Sephadex G-15 column (8x650 mm) was equipped with a constant temperature jacket controlled at 25°C. A flow rate was maintained at 1.7 ml/min.

An eluent contained sodium salt of P_{3m} or P_{4m} of a desired concentration, ca. 10^{-3} M hydrochloric acid and 0.1 M sodium chloride as background electrolytes(pH 3.4). Hydrochloric acid was added to the eluent in order to prevent the adsorption of some kinds of bivalent metal ions to a Sephadex gel(15). In this eluent P_{3m} and P_{4m} acids are almost completely dissociated. Sample solutions which contain sodium salt of P_{3m} or P_{4m}, sodium chloride and hydrochloric acid of the same composition as that of the eluent were prepared so as to contain bivalent metal ion of specific concnetrations, i.e., $2\text{x}10^{-5}$ M for magnesium and zinc and $1\text{x}10^{-4}$ M for calcium, strontium and nickel. After the column was sufficiently equilibrated with the eluent, one ml of sample solution was applied to the column.

RESULTS AND DISCUSSION

Representative elution patterns are shown in Fig. 1. It is evident that the retention volume of a metal is greatly dependent on the ligand concentration of an eluent. In order to describe the change in the apparent retention volume of a metal, $\bar{V}_M$, with ligand concentration in an eluent, a one-to-one complex formation reaction is considered

$$M \quad + \quad L \quad \rightleftarrows \quad ML \tag{1}$$

where M, L and ML represent metal ion, ligand ion and complex, respectively. The stability constant of ML is expressed as follows

$$K = \frac{[ML]_m}{[M]_m[L]_m} \tag{2}$$

where subscript m represents a mobile phase.

The apparent distibution coefficient of M, $\bar{K}_d$, can be expressed by eq.(3)

$$\bar{K}_d = \frac{[M]_s + [ML]_s}{[M]_m + [ML]_m} \tag{3}$$

where subscript s represents a stationary phase. $\bar{V}_M$ can be expressed using the volume of the mobile phase, V_m, and that of the stationary phase in a given column, V_s, and $\bar{K}_d$.

$$\bar{V}_M = V_m + \bar{K}_d V_s \tag{4}$$

Equation (4) can be rearranged to eq.(5) using eq.(2) and eq.(3), and V_M and V_{ML},

$$\bar{V}_M = \frac{V_M + K[L]_m V_{ML}}{1 + K[L]_m} \tag{5}$$

where V_M is the retention volume of the free metal, and V_{ML} is that

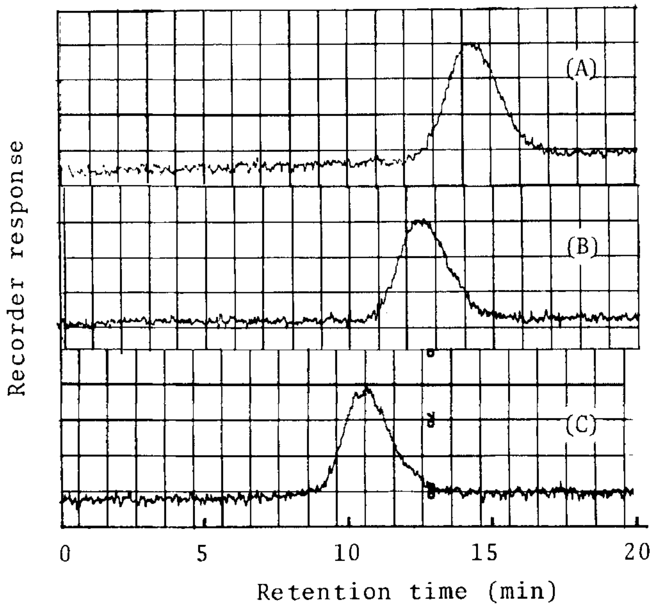

FIGURE 1.

Representative elution patterns for the Ca-P_{4m} system. The compositions of the eluents:

(A) 0.1 M NaCl + ca.10^{-3} M HCl

(B) 0.1 M NaCl + ca.10^{-3} M HCl + $4x10^{-4}$ M $Na_4P_4O_{12}$

(C) 0.1 M NaCl + ca.10^{-3} M HCl + $7x10^{-3}$ M $Na_4P_4O_{12}$

of the metal complex for the hypothetical system, in which the complex is present and the free metal is absent. It can be concluded that the apparent retention volume of the metal is expressed in terms of the free ligand concentration in the mobile phase and the stability constant of the complex in the mobile phase. This enables us to treat the gel chromatographic behavior of the labile complex by the theory similar to one applied in electrophoresis in which solutes migrate in a single phase(16,17).

V_M was determined by the elution of metal ion with 0.1 M sodium chloride and ca.10^{-3} M hydrochloric acid solution. Equation

(5) is valid only when V_M and V_{ML} are constant under these experimental conditions. In order to check the constancy of V_M, sample concentration dependence of V_M was examined (Fig. 2). It is clear that V_M values of magnesium, calcium, strontium, zinc and nickel

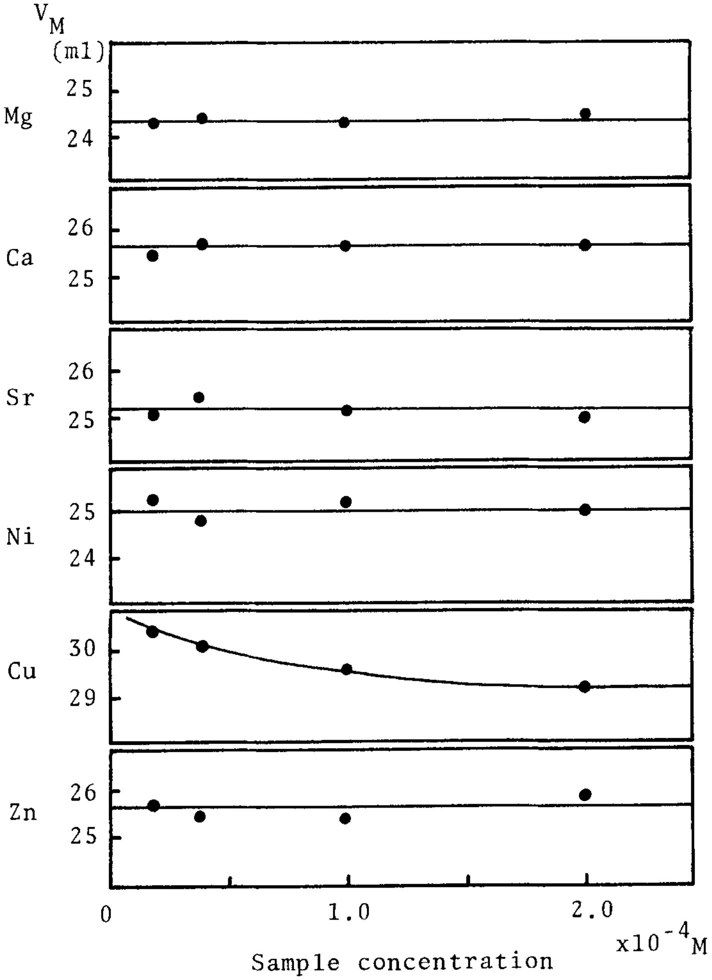

FIGURE 2.
Sample concentration dependence of V_M.

do not vary with sample concentrations. A V_M value of copper decreases with the increase in sample concentrations, which may be attributed to the adsorption of copper ions to the gel matrix.

Equation (5) can be rearranged to eq.(6).

$$\bar{V}_M = V_{ML} + \frac{1}{K} \cdot \frac{V_M - \bar{V}_M}{[L]_m} \qquad (6)$$

When the metal concentration in a sample is much smaller than the total ligand concentration, $[L]_m$ can be replaced by the total ligand concentration.

The plots of V_M vs. $(V_M - \bar{V}_M)/[L]_m$ for the calcium-trimetaphosphate and calcium-tetrametaphosphate systems are shown in Fig. 3.

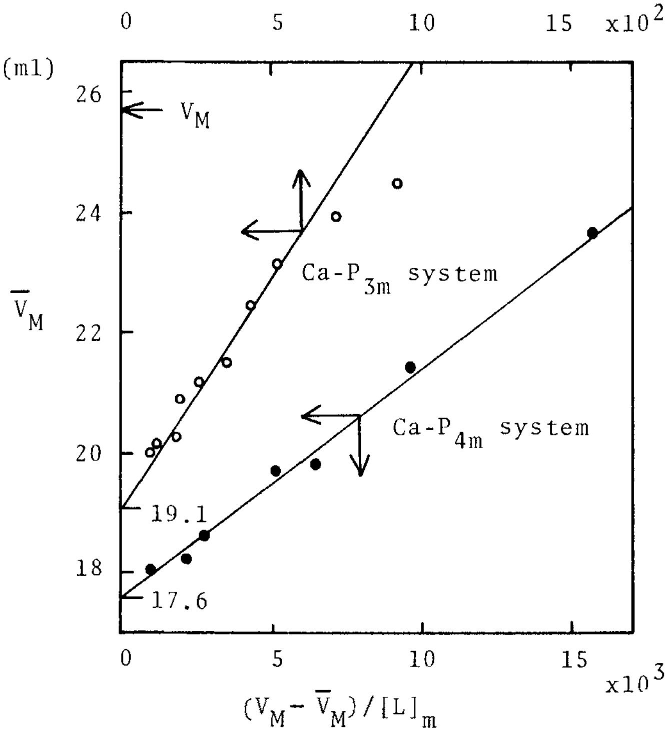

FIGURE 3.
Plots of $\bar{V}_M$ vs. $(V_M-\bar{V}_M)/[L]_m$ for the Ca-P_{3m} and Ca-P_{4m} systems.

The linear relationships thus obtained indicate the validity of the theory mentioned above including the constancy of V_M and V_{ML}. The y-intercepts gave the retention volumes of the complexes(V_{ML}), and from their slopes, the stability constants(K) were obtained. The experimental uncertainty greatly influences the value of $(V_M - \bar{V}_M)/[L]_m$, when the difference between V_M and $\bar{V}_M$ is small.

Equation (5) can also be altered to eq.(7), in which $\bar{V}_M$ can be expressed as a function of $\log[L]_m$. A similar equation has been employed in the analysis of electrophoretic mobility data of ineteracting systems(16,17).

$$\bar{V}_M = \frac{V_M + V_{ML}}{2} + \frac{V_M - V_{ML}}{2} \tanh\frac{2.303}{2}(-\log K - \log[L]_m) \qquad (7)$$

K and V_{ML} were obtained by the least squares method. In Fig.4,

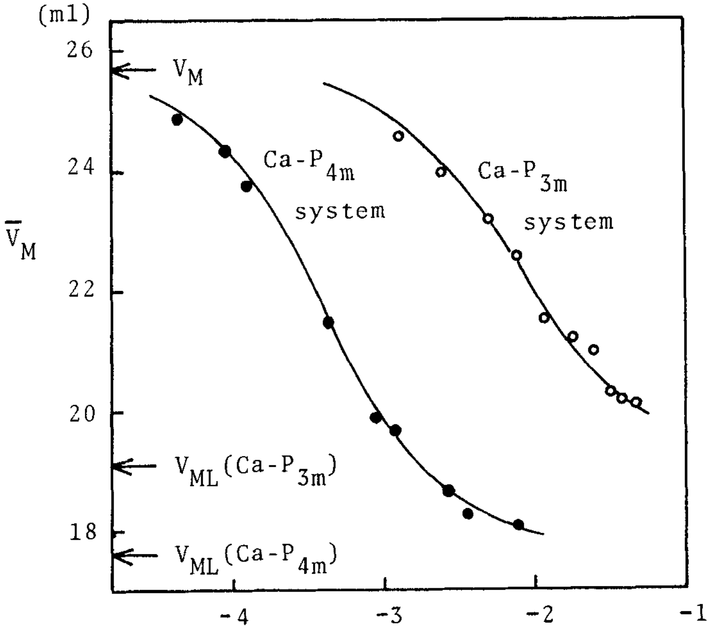

FIGURE 4.

Plots of $\bar{V}_M$ vs. $\log[L]_m$ for the Ca-P_{3m} and Ca-P_{4m} systems.
The solid line refer to the calculated curves based on equation(7).

the plots of $\bar{V}_M$ vs. $\log[L]_m$ for the calcium-trimetaphosphate and calcium-tetrametaphosphate systems are shown. In Table 1 the stability constants thus obtained are listed together with the reported values obtained by other methods. Even though the methods are based on quite different principles the values are well consistent with each other, which supports the theory mentioned above.

In Table 2, K_{av} values of the metal complexes and the ligands are shown. It is noteworthy that the K_{av} values of the complexes are always greater than those of the corresponding ligands. A similar phenomenon was observed for EDTA complexes(20). The conformational change in these ligands by chelate formation and/or the dehydration of the ligands accompanying with the complexation may be the main reasons.

It has been pointed out that ion-pair formation should be taken into account when elution behavior of ionic species is examined in gel chromatography(3). The K_{av} values of trimetaphosphate and tetrametaphosphate obtained in this work with 0.1 M sodium chloride solution may be affected by the ion-pairing with sodium ions. In order to correlate the gel chromatographic behaviors of phosphorus oxoanions with their complexation reactions, more precise study is now in progress in our laboratory.

TABLE 2

K_{av} Values of Trimeta- and Tetrametaphosphate and Their Complexes

	free ligand	complexes				
		Mg	Ca	Sr	Ni	Zn
P_{3m}	0.14	0.27	0.28	0.30	0.28	0.31
P_{4m}	0.11	0.19	0.21	0.18	0.22	0.20

$K_{av}=(V_r - V_0)/(V_t - V_0)$; V_r is the retention volume, V_t is the total bed volume and V_0 is the void volume determined with Blue Dextran 2000.

TABLE 1-1

Stability Constants of Trimetaphosphate Complexes

	This work	Other works					
	logK a)	logK	Method b)	Medium	Ionic Strength	Temp. (°C)	Ref.
Mg	2.51	1.80	A	NMe_4Cl	0.1	25	(18)
Ca	2.11	1.64	A	NMe_4NO_3	1.0	25	(18)
		2.50	B	NaCl	0.15	37	(19)
		2.06	B	NaCl	0.1	20	(9)
Sr	2.23	1.91	A	NMe_4NCl	0.1	25	(18)
		1.95	B	NaCl	0.15	20	(19)
		2.03	B	NaCl	0.23	20	(9)
Ni	2.29	1.82	A	NMe_4NO_3	0.1	25	(18)
Zn	2.29	2.00	A	NMe_4NO_3	0.1	25	(18)
		1.94	B	$NaClO_4$	0.23	20	(9)

TABLE 1-2

Stability Constants of Tetrametaphosphate Complexes

	This work	Other works					
	logK c)	logK	Method b)	Medium	Ionic Strength	Temp. (°C)	Ref.
Mg	3.39	3.47	A	NMe_4NCl	0.1	25	(18)
Ca	3.39	3.04	A	NMe_4NO_3	1.0	25	(18)
		3.36	B	NaCl	0.15	37	(19)
		3.28	B	NaCl	0.1	20	(9)
Sr	3.18	2.80	B	NaCl	0.15	20	(19)
		2.70	B	NaCl	0.23	20	(9)
Ni	3.15	3.38	A	NMe_4NO_3	0.1	25	(18)
Zn	3.37	3.63	A	NMe_4NO_3	0.1	25	(18)
		2.86	B	$NaClO_4$	0.23	20	(9)

a) I = 0.10 ∿ 0.38 , b) A:potentiometry(ion-selective electrode) B:ion-exchange method, c) I = 0.10 ∿ 0.18

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REFERENCES

1. M. Yamamoto and Y. Yamamoto, Anal. Chim. Acta, 87, 375(1976).
2. K. Saitoh and N. Suzuki, Bull. Chem. Soc. Jpn., 51, 116(1978).
3. M. Sinibaldi and O. Corradini, J. Chromatogr., 148, 553(1978).
4. T. Deguchi, J. Chromatogr., 120, 159(1976).
5. T. Miyajima, N. Yoza and S. Ohashi, Anal. Lett., 10, 709(1977).
6. T. Miyajima and S. Ohashi, Bull. Chem. Soc. Jpn., 51, 2543 (1978).
7. K. Ujimoto, T. Yoshimura, I. Ando and H. Kurihara, J. Chromatogr., 174, 123(1979).
8. K. Ujimoto, I. Ando, T. Yoshimura, K. Suzuki and H. Kurihara, J. Chromatogr., 190, 161(1980).
9. G. Kura, S. Ohashi and S. Kura, J. Inorg. Nucl. Chem., 36, 1605(1974).
10. G. Kura and S. Ohashi, J. Inorg. Nucl. Chem., 38, 1151(1976).
11. G. Brauer, "Handbuch der Präparativen Anorganischen Chemie", Ferdinand Enke Verlag, Stuttgart, 1960, p.495.
12. N. Yoza and S. Ohashi, Anal. Lett., 6, 595(1973).
13. K. Kouchiyama, N. Yoza and S. Ohashi, J. Chromatogr., 147, 271(1978).
14. N. Yoza, K. Kouchiyama and S. Ohashi, At. Absorption Newslett., 18, 39(1979).
15. N. Yoza and S. Ohashi, J. Chromatogr., 41, 429(1969).
16. Y. Kiso and E. Falk, J. Chromatogr., 59, 401(1971).

17. Y. Kiso, M. Kobayashi, Y. Kitaoka, K. Kawamoto and J. Takada, J. Chromatogr., 36, 215(1968).

18. S. Y. Kalliney, in "Topics in Phosphorus Chemistry", vol 7, E. J. Griffith and M. Grayson, Eds., Interscience, New York (1967) p.294.

19. R. E. Gosselin and E. R. Coghlan, Arch. Biochem. Biophys., 45, 301(1953).

20. N. Yoza, T. Ogata, Y. Ueno and S. Ohashi, Bull. Chem. Soc. Jpn., 41, 2550(1968).