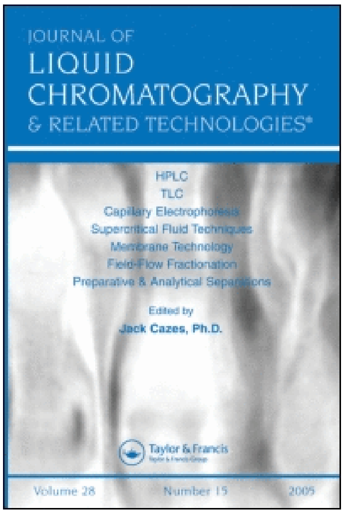

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DONNAN EXCLUSION CHROMATOGRAPHY
APPLICATION TO COMPLEX FORMATION STUDIES

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ABSTRACT

A new method for the evaluation of stability constants of complex species has been proposed, based on the principle of Donnan exclusion chromatography. The stability constants for trimetaphosphate complexes of magnesium and calcium ions have been evaluated to be log β_1 = 1.50 and 1.64 (I=1.00, 25°±2°C), respectively.

INTRODUCTION

A remarkable feature of Donnan exclusion chromatography may be that ions are separated by utilizing the repulsion between a sample ion and the functional groups of an ion-exchanger, and that the eluting position of the ion depends exclusively on its ionic charge when the ionic size is not very large(1,2). By use of this principle, the determination of the ionic charge of a chemical species present in a solution may become possible. In the case of simple ions or inert complex ions, this charge determination may be easy, since a simple linear relationship holds between the distribution coefficient and the ionic charge. On the other hand, when the ions are present as an equilibrium mixture of different dissociated states as in most weak metal complexes or moderate weak acids, the situation may become more complicated. In this paper, we introduce equations for determining ion-pair formation constants as well as average charges in equilibrium mixtures, and apply them to the trimetaphosphate complexes of magnesium and calcium or to protonated orthophosphate.

EXPERIMENTAL

Chemicals. Sodium trimetaphosphate $Na_3P_3O_9 \cdot 3H_2O$ was prepared in our laboratory. Crotonaldehyde *trans*-$CH_3CH{=}CHCHO$ and sodium salts of orthophosphate $NaH_2PO_4 \cdot 2H_2O$ or Na_2HPO_4, phosphonate $Na_2PHO_3 \cdot 5H_2O$ and phosphinate $NaPH_2O_2 \cdot H_2O$ and all other reagents used were of commercially available reagent grade.

Eluents. As eluents, solutions containing tetramethylammonium chloride (abbreviated as Me_4NCl) and magnesium or calcium chloride at various ratios were used at an ionic strength of unity. These eluents contain a small amount of hydrochloric acid or tetramethylammonium hydroxide for pH adjustment.

Elution procedure for distribution coefficient determination. A dextran-type cation-exchanger, SP-Sephadex C-25 (40 – 120 μm particle size) was packed in a Pyrex tubing column of 15 mm I.D. (169.3 – 152.3 ml). This column was pre-conditioned by passing the eluent through it until the effluent of the same composition was obtained. Then, 1 ml of the solution, made by dissolving a sample component in the eluent, was applied to the top of the column, followed by continuous elution at flow rate of 0.5 ml/min and at room temperature of 25° ± 2°C. The effluent was collected by a fraction collector into fractions of 1 ml or introduced into a flow cell of a UV detector.

Determination of sample components. For all samples, phosphorus oxoanion in the effluents was determined colorimetrically at 830 nm wavelength with molybdenum(V)-molybdenum(VI) reagent. For lower oxoanions of phosphorus, sodium hydrogen sulfite solution was added as an oxidizing agent. Crotonaldehyde, used as an elution standard, was detected automatically at 224 nm wavelength by a spectrophotometric detector with a flow cell.

Calculation of distribution coefficient. An elution standard which does not interact with an ion-exchanger at all was needed to calculate the distribution coefficient. Crotonaldehyde does not tend to be adsorbed by dextran gel matrix and is not large enough to be sterically excluded. Therefore, crotonaldehyde is an excellent standard, since it can be determined UV-spectrophotometrically with high sensitivity. The value of the distribution coefficient, K_D, was calculated by the following relationship, assuming that K_D for a neutral species such as crotonaldehyde is unity.

$$V_e = V_0 + K_D \cdot V_D \qquad (1)$$

where V_e is the peak elution volume, V_D the net volume of the exchanger phase and V_0 corresponds to the elution volume for an extremely highly charged anion of small size (K_D=0).

RESULTS AND DISCUSSION

It was found in the previous work (1,2) that the distribution coefficient of a certain simple anion, excluded by a cation-exchanger, depends only on its charge, irrespective of the chemical structure as far as the size is such that a steric exclusion may not occur. In this case the distribution coefficient is given by

$$K_D = R^x \tag{2}$$

where x is the ionic charge and R is a constant which is dependent only on the concentration of the background electrolyte in an eluent and the kind of an ion-exchanger used. This equation should fit for any simple ions or inert complex ions.

In the case of an equilibrium mixture with different charge states, such as labile metal complexes or polybasic acids, however, the situation becomes more complicated. When a sample complex solution is applied to the column which has been pre-conditioned with eluent containing an appropriate concentration of metal ions, the anionic complex is excluded electrostatically by fixed groups of a cation-exchanger and carried down the column more quickly than neutral species with holding the equilibrium of complex formation. Excess free metal ions or other cations in the sample solution are adsorbed at the top of the column so that they cannot affect the equilibrium. Consequently the complex is eluted at the position according to its average charge. Let us consider a M∿L system with a cation-exchanger. The distribution coefficient of sample anion L at excess cation M can be written as

$$D = K_{D,L}\alpha_L + K_{D,ML}\alpha_{ML} + K_{D,M_2L}\alpha_{M_2L} + \cdots \tag{3}$$

assuming that any cationic M∿L complexes do not form under the conditions studied here. The K_{D,M_jL} is the characteristic distribution coefficient of component

M_jL, and α_{M_jL} its mole fraction. When all the α's are calculable by known stability constants, D can be predicted. Conversely, with a series of D observed at different M concentrations, eqn (3) can be solved for each stability constant.

In the case of a binary system ($M_{j-1}L \rightleftharpoons M_jL$), a simple relation is obtained between D and average charge of the equilibrium mixture,

$$D = K_{D,M_jL} - \frac{\bar{i} - i_{M_jL}}{i_{M_{j-1}L} - i_{M_jL}} \left(K_{D,M_jL} - K_{D,M_{j-1}L} \right) \qquad (4)$$

which is derived from eqn (3) and using a definition of average charge

$$\bar{i} = \frac{i_{M_{j-1}L}[M_{j-1}L] + i_{M_jL}[M_jL]}{[M_{j-1}L] + [M_jL]} \qquad (5)$$

where i's are anion charges of subscribed $M \sim L$ complex. Eqn (4) means that the $D \sim \bar{i}$ plot should fall into the straight line binding point $(i_{M_{j-1}L}, K_{D,M_{j-1}L})$ and (i_{M_jL}, K_{D,M_jL}) when D is plotted against average charge of the mixture. This relation is confirmed by the chromatographic D measurements on orthophosphate (M=H, $L=PO_4$) with varying pH (Fig. 1).

For the equilibrium $L \rightleftharpoons ML$ (j=1), stability constant β_1 can easily be evaluated from eqns (1) and (3).

$$\beta_1 = \frac{1}{[M]} \cdot \frac{D - K_{D,L}}{K_{D,ML} - D} = \frac{1}{[M]} \cdot \frac{V_e - V_L}{V_{ML} - V_e} \qquad (6)$$

For a ternary system which consists of L, ML and M_2L, the following equations are derived for analysis.

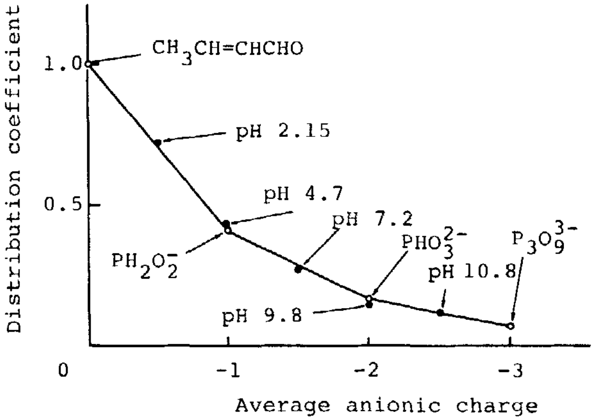

FIGURE 1

The relationship between distribution coefficient and average anionic charge. ●: orthophosphate at described pH. o: standard species.

$$\phi \equiv \frac{1}{[M]} \cdot \frac{D - K_{D,L}}{K_{D,ML} - D} = \beta_1 + \frac{K_{D,M_2L} - D}{K_{D,ML} - D}[M] \cdot \beta_2 \qquad (7)$$

By plotting ϕ against $(K_{D,M2L} - D)[M]/(K_{D,ML} - D)$, β_1 and β_2 can be determined from the intercept and the slope, respectively, providing that M_2L is not a cationic species. If only M_2L is a cation, β_1 can be evaluated by extrapolating [M] to zero concentration.

$$\lim_{[M]\to 0} \phi = \beta_1 \qquad (8)$$

The elution behavior of trimetaphosphate with aqueous eluents of magnesium and calcium chlorides are shown in Figs. 2 and 3. In both cases, the elution positions continuously shift to larger volumes with

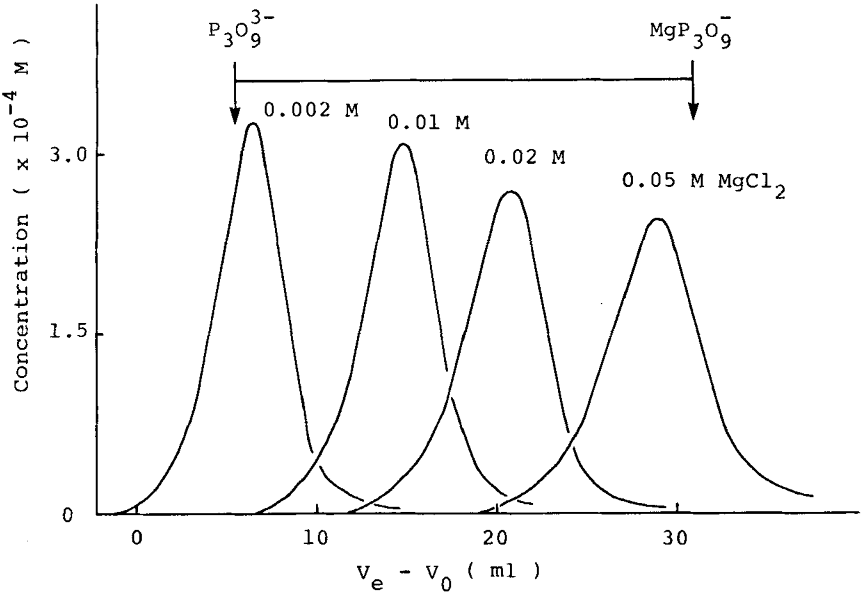

FIGURE 2

Elution behavior of trimetaphosphate with the tetramethylammonium chloride eluent containing magnesium ions (I=1.00). Column: SP-Sephadex C-25, 15mm I.D.. Sample: 1.7×10^{-3} M $Na_3P_3O_9 \cdot 3H_2O$; 1 ml.

increasing eluent metal concentrations, as expected from the decrease in the equilibrium average charge. The plot of eqn (8) gives a continuous increase of ϕ, indicating the presence of cationic M_2L complexes in solution (Fig. 4). By extrapolation, we can get the first stability constants log β_1 = 1.50 and 1.64 (I = 1.00 with Me_4NCl, t = 25° ± 2°C at room temperature) for magnesium and calcium complexes of trimetaphosphates, respectively.

Although the stability constant of trimetaphosphate complex with alkaline earth metal ions has been studied

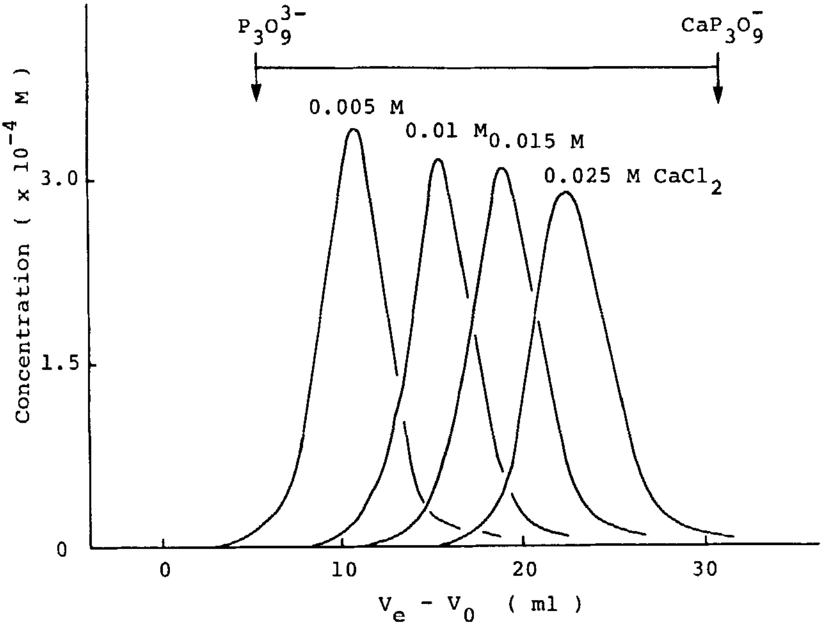

FIGURE 3

Elution behavior of trimetaphosphate with the tetramethylammonium chloride eluent containing calcium ions (I=1.00). Column: SP-Sephadex C-25, 15mm I.D.. Sample: 1.7 x 10^{-3} M $Na_3P_3O_9 \cdot 3H_2O$; 1 ml.

by different methods and at various conditions (3—7), trimetaphosphate complex in the medium where ionic strength is unity is so unstable that few measurements have been reported. The difference in the volume arises from the conditions in temperature, ionic strength, type of medium and so on. The conditions reported by Watters et al. (5), with a calcium-selective liquid ion-exchange membrane electrode are as same as ours in ionic strength and medium; hence the value of the stability constant

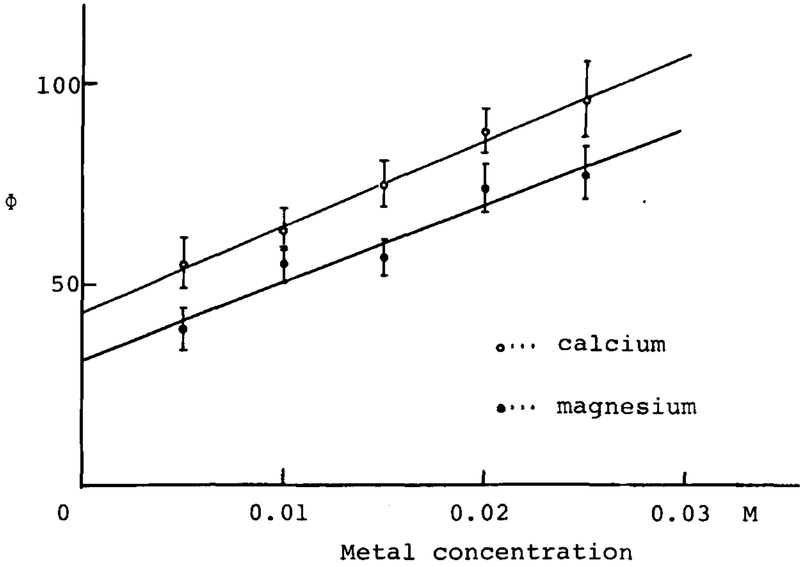

FIGURE 4

Evaluation of stability constants of magnesium and calcium trimetaphosphate complexes (I=1.00, 25°±2°C) by graphic extrapolation. Error bar indicates an experimental error of ±0.5 ml in elution volume.

agrees completely with ours. Other values have a similar tendency that the stability constant decreases with an increase in ionic strength. The feature of Donnan exclusion chromatography is that the approximate charges of complexes are directly observable from the elution position with good reproducibility (± 0.5 ml in effluent volume); this can thus avoid an erronious conclusion occasionally drawn for unstable complexes.

REFERENCES

1. Waki, H. and Tokunaga, Y., J. Chromatogr., 201, 259 (1980).

2. Tokunaga, Y., Waki, H. and Ohashi, S., unpublished data.

3. Davies, C. W. and Monc, C. B., J. Chem. Soc., 413 (1949).

4. Jones, H. W., Monc, C. B. and Davies, C. W., J. Chem. Soc., 2639 (1949).

5. Watters, J. I., Kalliney, S. and Machen, B. C., J. Inorg. Nucl. Chem., 31, 3823 (1969).

6. Kura, G., Ohashi, S. and Kura, S., J. Inorg. Nucl. Chem., 36, 1605 (1974).

7. Miyajima, T., Ibaragi, M., Yoza, N. and Ohashi, S., J. Liq. Chromatogr., 4, 259 (1981).