

Measurement of stability constants for complexes of divalent cations with tartaric acid by ion chromatography

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ABSTRACT

Single-column ion chromatography was used with ethylenediammonium tartrate in the eluent for the rapid separation of divalent metal ions and for the measurement of the complexation constants of divalent metal ions with tartrate. A theoretical framework was developed for the interpretation of the effect of pH, tartaric acid and ethylenediamine concentrations on the retention factors. Equilibrium constants for the ion-exchange process were evaluated and the concomitant enthalpy and entropy changes calculated.

INTRODUCTION

Since liquid chromatography began to evolve as an analytical and instrumental technique in the 1960s, high-performance liquid chromatography (HPLC) has become a widely employed method for the analysis and purification of non-volatile substances. It has also found limited use in the measurement of physico-chemical data.

Ion chromatography, introduced by Small *et al.* [1] in 1975, represents an extension of HPLC to the analysis of inorganic ions by employing a conductivity detector and a dual column system. In 1980 Fritz *et al.* [2] developed a single-column method for ion chromatography which allows for both a decrease and increase with indirect and direct detection, respectively. As a result, ion chromatography has become a convenient method for determining the level of ionic species in many industrial processes and for monitoring of air and water pollutants in the environment. Now a variety of detectors are available and ion chromatography is used also in other fields such as biochemistry, pharmacy and forensic

science. The fundamentals and applications of ion chromatography have been reviewed in recent books [3–5].

Eluents with complexing agents [6] have often been employed in ion chromatography to enhance selectivity for metal ions. The use of a complexing agent in the eluent also improves the sharpness of separation and broadens the scope of cation chromatography with a conductivity detector. The presence of the complexing agent, however, frequently makes the detection of metal ions difficult. Elchuk and Cassidy [7] circumvented this problem in the chromatographic analysis of lanthanides with α -hydroxyisobutyric acid by using postcolumn derivatization and spectrophotometric detection.

Often, however, postcolumn derivatization engenders excess band broadening. For this reason, Sevenich and Fritz [8–10] used ethylenediamine together with α -hydroxyisobutyrate in the eluent to carry out the analysis without postcolumn derivatization.

Ion chromatography is now well suited to separate ions and conductivity detectors have been

greatly improved in recent years [11] to provide sensitive and "universal" detection of ions in solution. However, only a few theoretical studies have been conducted to establish the effect of complexation on changing the conditions during cation elution. Although Sevenich and Fritz [8] showed that the retention factors decrease with increasing pH, different trends have also frequently been observed.

The aim of this work was to develop a theoretical model for the retention of divalent cations which form complexes with tartrate ligand. The experimentally observed effects of temperature, pH, tartaric acid and ethylenediamine concentrations on the retention and separation of cations is then examined within the theoretical framework.

EXPERIMENTAL

Instrument

A Model HLC-601 fully automated high-speed ion chromatograph (Shimadzu, Tokyo, Japan) was used. The microcomputer-controlled single-plunger pump with a Bourdon tube pulsation damper of 5-ml volume was used to generate eluent flow in the range 0.1–9.9 ml/min at a maximum pressure of 70 kg/cm². The motor-driven sample injection valve was equipped with a 100- μ l sample loop.

The column was thermostated with a precision of $\pm 0.1^\circ\text{C}$ in the temperature range 30–60°C by an oven with hot-air circulation. Prior to entering the injection valve and the column, the eluent first passed through a heat-exchanger coil which was also located in the oven.

The 1.4- μ l conductivity cell of the detector was equipped with a.c. five-pole ring electrodes and its cell constant was 10 cm⁻¹. The highest detector sensitivity was $2 \cdot 10^{-2}$ $\mu\text{S}/\text{cm}$. The detector cell was maintained at a temperature 3°C higher than that of the column by a 50- μ l heating coil, made of $1/16$ -in. 316 stainless-steel tubing (100 cm \times 0.25 mm I.D.) in order to maintain a stable baseline.

Column

A 50 mm \times 4.6 mm I.D. TSK-Gel IC-Cation column (Tosoh, Tokyo, Japan) was packed with 10- μ m sulphonated polystyrene-type cation-exchange resin particles, having a capacity of 46 $\mu\text{equiv.}/\text{g}$.

Materials

Fresh deionized, distilled water prepared with a Mega-Pure System, Model MP-12A (Corning Glass, New York, USA) was used. Analytical-reagent grade CaCl₂, CdCl₂, Zn(NO₃)₂, Co(NO₃)₂, Ni(NO₃)₂, Mn(NO₃)₂, tartaric acid, ethylenediamine (EDA), sodium hydroxide and nitric acid were supplied by Shimakyu Chemical (Osaka, Japan).

Isocratic elution was carried out with solutions containing 0.2, 1.0, 2.0, 3.0, 4.0 and 5.0 mM tartaric acid and 0.2, 0.4, 0.8, 1.2 mM ethylenediamine. The eluent pH was adjusted by using sodium hydroxide or nitric acid. All eluents were filtered through a 0.5- μ m filter before use.

Methods

In all experiments, 100- μ l samples were injected without precolumn derivatization. The flow-rate was 0.8 ml/min and experiments were carried out at 30, 40, 50 and 60°C. The detector settings were in ranges of 200, 500 and 1000 and the gain was 100 or 200. The recorder full-scale was set to 1 V. The column was periodically washed with 0.1% nitric acid in order to remove polyvalent ions from the resin. The samples were prepared by dissolving the chloride or nitrate of the metals in the eluent to obtain a concentration of 0.05 mM. The pH of the eluent was measured with a Model AT-200 potentiometric automatic titrator (Kyoto Electronics, Tokyo, Japan) at each temperature with temperature compensation and was adjusted to the predetermined value by using 1 M nitric acid or 1 M sodium hydroxide solution. Chromatographic experiments started with setting of the oven temperature and pumping the eluent through the system. After the oven temperature had reached the desired value, the detector range was adjusted so that the signal output was about 50% of the 1 V full-scale at the background conductivity.

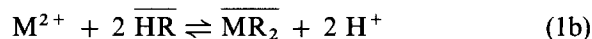
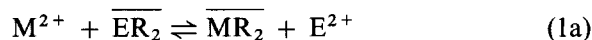
The mobile phase volume in the heat exchanger and in the connecting tubing was measured carefully together with the extra-column volume associated with the injector and detector and were taken into account in the calculation of the void volume of the column. The flow-rate was measured each time before injection by using 0.5 mM potassium chloride solution as inert elute and the reproducibility was found to be within 0.1%.

THEORY

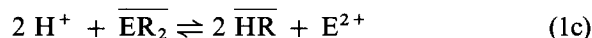
In ion chromatography, separations occur owing to differences in the retention of an elute by oppositely charged binding sites of the stationary phase. In the process described here, the sample cations interact with the sulphonic acid groups of the ion-exchange resin, and compete with the eluting cations for the exchange sites. When a pulse of sample cations is injected onto the column equilibrated with eluting cations, the sample cations are retained by the exchange sites at the chromatographic surface with concomitant expulsion of eluting cations. This pulse of eluting cations moves down the column unretained, whereas sample cations are gradually eluted in a process characterized by their competition with the eluting cations for the ion-exchange sites of the stationary phase.

Equilibrium considerations

The three cation-exchange processes underlying the separation are given by the following three equilibria:



and



where M^{2+} , H^+ and E^{2+} are the divalent metal cations, hydrogen ion and fully protonated ethylenediamine in the mobile phase, respectively. \overline{MR}_2 , \overline{HR} and \overline{ER}_2 indicate that the species are bound to the stationary phase. The subscript 2 on \overline{R} indicates that two exchange sites bind a cationic species. The pertinent equilibrium constants are given by

$$K_m^e = \frac{[\overline{MR}_2][E^{2+}]}{[M^{2+}][\overline{ER}_2]} \quad (2a)$$

$$K_m^h = \frac{[\overline{MR}_2][H^+]^2}{[M^{2+}][\overline{HR}]^2} \quad (2b)$$

and

$$K_h^e = \frac{[\overline{HR}]^2[E^{2+}]}{[H^+]^2[\overline{ER}_2]} \quad (2c)$$

Let f represent the fraction of the exchange sites in the stationary phase which are occupied by hydrogen ions. At low sample concentrations, *i.e.*, under conditions of linear chromatography, the fraction of the exchange sites which are occupied by ethylenediamine cations can be approximated by $1 - f$. Then

the equilibrium constants K_h^e and K_m^e can be calculated by the following relationships:

$$K_h^e = 2f^2 C[E^{2+}]/(1 - f)[H^+]^2 \quad (3)$$

and

$$K_m^e = 2[\overline{MR}_2][E^{2+}]/[M^{2+}]C(1 - f) \quad (4)$$

where C is the resin capacity.

The fraction of the protonated exchange sites f can be evaluated when K_h^e is known:

$$f = \frac{-[H^+]^2 K_h^e + \sqrt{[H^+]^4 K_h^{e2} + 8C[E^{2+}][H^+]^2 K_h^e}}{4C[E^{2+}]} \quad (5)$$

For any equilibrium reaction the enthalpy change, ΔH^0 , is a constant at a given temperature and can be calculated from the well known Van 't Hoff equation:

$$\Delta H^0 = -d(R \ln K)/d(1/T) \quad (6)$$

where K is the equilibrium constant, R is the gas constant and T is the absolute temperature. The entropy change at any temperature, ΔS^0 , can be calculated from

$$\Delta S^0 = \Delta H^0/T + R \ln K \quad (7)$$

Retention factor

The magnitude of retention is most conveniently expressed by the dimensionless retention factor, k' , which can be evaluated directly from the chromatogram. In linear chromatography:

$$k' = (t_r - t_0)/t_0 = \phi K_{\text{Chrom}} \quad (8)$$

where t_r is the retention time of the elute, t_0 is the mobile phase hold-up time, ϕ is the phase ratio and K_{Chrom} is the chromatographic equilibrium constant. K_{Chrom} represents the distribution of the elute between the two phases, and can be calculated by

$$K_{\text{Chrom}} = (1 - f)CK_m^e \alpha_m / 2[E^{2+}] \quad (9)$$

where α_m is given by

$$\alpha_m = [M^{2+}]/[M]_t \quad (10)$$

i.e., it is the fraction of the total metal in mobile phase which exists as the free metal ion.

The phase ratio, ϕ , of the column is calculated as

$$\phi = \frac{W}{V_m \rho_\tau} = \frac{(1 - \varepsilon_e)(1 - \varepsilon_i)}{\varepsilon_e + (1 - \varepsilon_e)\varepsilon_i} \quad (11)$$

and

$$V_m = V_0[\varepsilon_e + (1 - \varepsilon_e)\varepsilon_i] \quad (12)$$

where V_0 is the empty column volume, V_m is the space occupied by the mobile phase, W is the weight of ion-exchange resin present in the column and ε_i , ε_e and ρ_r are the intraparticle porosity, interparticle porosity and the true density of ion-exchange resin, respectively.

Combining eqns. 8, 9 and 11 we obtain for the retention factor the following expression:

$$k' = \frac{W(1-f)CK_m^e\alpha_m}{V_m\rho_r \cdot 2[E^{2+}]} \quad (13)$$

In the pH range of interest, ethylenediamine is fully protonated. The value of α_m can be calculated from the two acid ionization constants of tartaric acid, K_1 and K_2 , to obtain the fractions of the total tartrate, A^{2-} , and acid tartrate, HA^- , at the pH of the mobile phase, *i.e.*, β_a and β_{ha} , by using the following relationships:

$$\beta_a = \frac{[A^{2-}]}{[A]_t} = \frac{1}{\left(1 + \frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2}\right)} \quad (14)$$

and

$$\beta_{ha} = \frac{[HA^-]}{[A]_t} = \frac{1}{\left(1 + \frac{[H^+]}{K_1} + \frac{K_2}{[H^+]}\right)} \quad (15)$$

so that α_m is evaluated as

$$\alpha_m = \frac{[M^{2+}]}{[M]_t} = \frac{1}{1 + K_{ma}^a[A^{2-}] + K_{mha}^{ha}[HA^-]} \quad (16)$$

Measurements by ion chromatography can be used to evaluate the stability constant of the complex, K_{ma}^a , formed from the metal ion and the tartrate ligand A^{2-} and given by

$$K_{ma}^a = [MA]/[M^{2+}][A^{2-}] \quad (17)$$

Combining eqns. 13 and 16, we obtain

$$\frac{1}{k'} = \frac{2[E^{2+}](1 + K_{ma}^a[A^{2-}] + K_{mha}^{ha}[HA^-])}{\phi(1-f)CK_m^e} \quad (18)$$

Eqn. 18 also contains the stability constant of the complex, K_{mha}^{ha} , formed between the metal ion and the acid tartrate ligand HA^- , and is given by:

$$K_{mha}^{ha} = [MHA^+]/[M^{2+}][HA^-] \quad (19)$$

However, the magnitude of the product $K_{mha}^{ha}[HA^-]$ in eqn. 18 is usually much smaller than that of the other terms in the denominator, and it can therefore be neglected. Further, $[A^{2-}] = \beta_a[A]_t$, so that we can express the reciprocal of retention factor as

$$\frac{1}{k'} = \frac{2[E^{2+}](1 + K_{ma}^a\beta_a[A]_t)}{\phi(1-f)CK_m^e} \quad (20)$$

According to eqn. 20, a plot of $1/k'$ against $[A]_t$ yields a straight line and the formation constant K_{ma}^a can be obtained as the ratio of its slope and intercept.

The resolution of two elutes also depends on the separation factor, α_{21} , which is defined for any two components as

$$\alpha_{21} = k'_2/k'_1 \quad (21)$$

where k'_1 and k'_2 are the retention factors for components 1 and 2, respectively.

RESULTS AND DISCUSSION

According to eqn. 14, the signal from the conductivity detector is proportional to the elute concentration and to the difference between the limiting equivalent conductances of the eluting and elute cations. The addition of a complexing agent to the eluent will not disturb this rule but may decrease the degree of ionization of the elute and lower the detector signal.

Fig. 1A shows the retention factor at various tartrate concentrations. According to eqn. 20, a plot of $1/k'$ against $[A]_t$ yields a straight line and this is shown in Fig. 2. Perfect straight lines were obtained. From such plots the formation constant K_{ma}^a can be obtained as the ratio of the slope and intercept. The adjusted retention times t'_r from the data of Sevenich and Fritz [8] with 2.0 mM tartrate in the eluent at room temperature are also plotted in Fig. 2 for comparison. The adjusted retention time is defined as the difference between the retention time of the elute peak and the mobile phase hold-up time. From Fig. 2, it can be seen that the slope obtained by Sevenich and Fritz is different from that obtained here. The divergence of the slopes is attributed to the use of different EDA concentrations, which affects the magnitude of f , and to the difference in temperature, which affects the magnitude of K_{ma}^a and K_m^e according to eqn. 20.

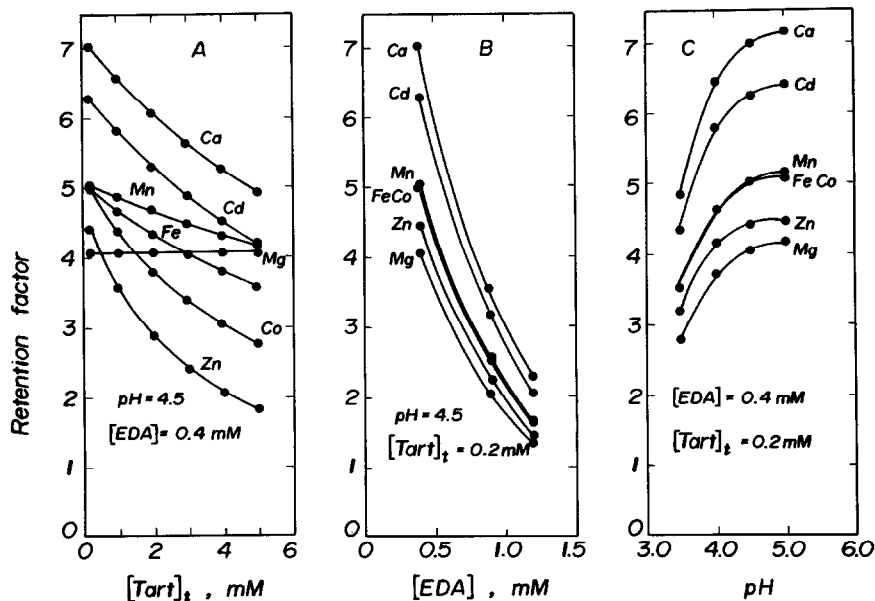


Fig. 1. Effect of the mobile phase composition on the retention factor of divalent metal ions in single-column ion chromatography with tartrate and ethylenediamine in the eluent at 30°C. (A) Fixed ethylenediamine concentration and changing tartrate concentration at pH 4.5; (B) fixed tartrate concentration and changing ethylenediamine concentration at pH 4.5; (C) fixed tartrate and ethylenediamine concentrations and changing pH.

The dependence of the logarithmic formation constants K_{ma}^a calculated from Fig. 2 on the reciprocal of absolute temperature are shown by the Van 't Hoff's plots in Fig. 3. The phase ratio, ϕ , was calculated to be 0.43, the ion-exchange capacity of

the resin was $0.04 \text{ mequiv. cm}^{-3}$ of true resin volume and β_a at pH 4.5 was calculated as 0.568 from eqn. 14. The two acid ionization constants of tartaric acid at near zero ionic strength used in our experiments were $K_1 = 9.1 \cdot 10^{-4}$ and $K_2 = 4.3 \cdot$

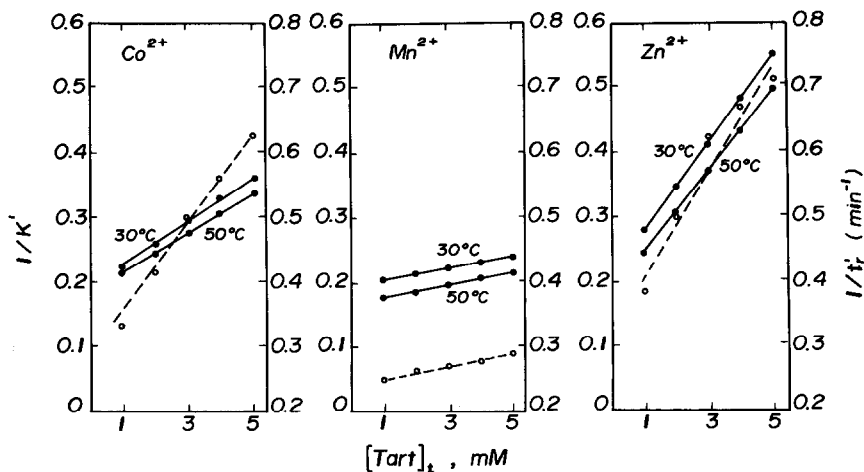


Fig. 2. Graph illustrating plots of the reciprocal retention factor of divalent metal ions against the concentration of tartrate in the mobile phase at pH 4.5. The concentration of ethylenediamine was 0.4 mM and measurements were made at 30 and 50°C (●). The data of Sevenich and Fritz [8] with 2.0 mM EDA in the eluent at room temperature are also plotted for comparison (○). The reciprocal of adjusted retention time is shown on the right-hand ordinate.

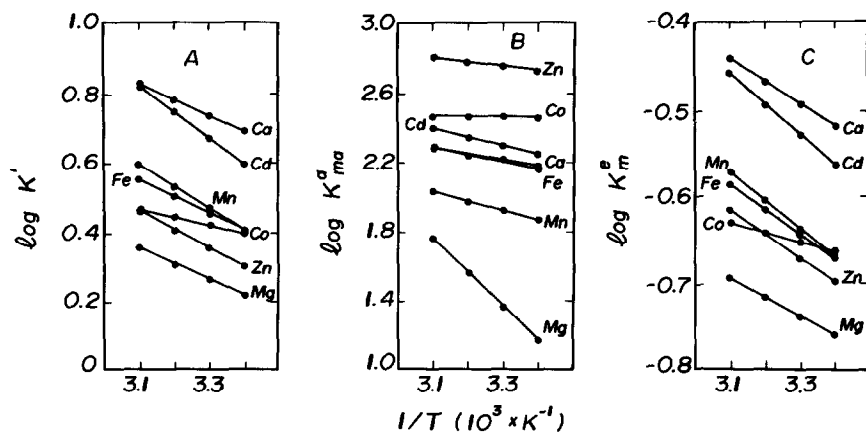


Fig. 3. Van 't Hoff plots of equilibrium data obtained with divalent metal ions. (A) Retention factor measured with 0.4 mM ethylenediamine and 0.2 mM tartaric acid in the mobile phase at pH 4.5; (B) stability constant for complexation with tartrate in aqueous solution of 1–13 millimolar ionic strength; (C) ion-exchange equilibrium constant with ethylenediammonium ion towards ion.

10^{-5} molal [12]. The f values calculated for various ethylenediamine concentrations and pH values are listed in Table I.

The retention factors of divalent metals measured by using 0.2 mM tartrate and 0.4 mM ethylenediamine at various pH values are shown in Fig. 1C. It can be seen that the retention factors increase with pH, a result which apparently contradicts the conclusions put forward by Sevenich and Fritz from their experimental observations [8]. The origin of this discrepancy has been examined as follows.

For any given ion chromatographic column the ion-exchange capacity and the phase ratio are

TABLE I

EFFECT OF ETHYLENEDIAMINE CONCENTRATION AND pH ON THE FRACTION OF PROTONATED SITES, f , IN THE STATIONARY PHASE

The f values were calculated from eqn. 5 by using 0.04 mequiv. cm^{-3} and 66 for the ion-exchange capacity of the resin and for the ion-exchange equilibrium constant, K_h^e , respectively.

[E ²⁺] (mM)	Fraction of protonated sites, f , at pH			
	3.5	4.0	4.5	5.0
0.2	0.45	0.17	0.058	0.019
0.4	0.34	0.12	0.041	0.013
0.8	0.26	0.090	0.030	0.009
2.0	0.17	0.058	0.019	0.006

constants and can be determined *a priori*. From eqns. 5 and 20, it can be seen that if the concentrations of ethylenediamine, [E²⁺], and tartaric acid, [A]_t, were constant and the oven temperature was the same, k' is a function of pH with K_h^e , K_m^e and $K_{ma}^a\beta_a$ as parameters. As $K_{ma}^a\beta_a$ has been calculated previously by using the data from Fig. 2, the pertinent K_h^e and K_m^e values can be obtained by minimizing the sum of squares of the deviations between the calculated and measured retention factors at more than two pH values. From the data in Fig. 1C, it was found that $K_h^e = 66$ gives the best fit of the retention factor data obtained at low pH where precipitation of hydroxides is circumvented and the chelation with ethylenediamine can be neglected. As K_h^e is not very sensitive to temperature under the conditions of the experiment, it can be assumed to be constant in the temperature range 30–60°C.

The enthalpy and entropy changes for the complexation of metal ions with tartrate calculated from Fig. 3B by using eqns. 6 and 7 are listed in Table II. The complexation processes is endothermic for all ions except cobalt and the entropy change is positive in all instances. The positive entropy change may be attributed to the water molecules that are displaced from the coordination sphere of metal ions.

A comparison of stability constants for the complexes of divalent metal ions with tartrate measured in this work with those from the literature which

TABLE II
ENTHALPY AND ENTROPY CHANGES AT 25°C

ΔH_{ma}^0 is associated with complex formation of divalent ion with tartrate, ΔH_{ex}^0 is for the ion-exchange process of metal ions with ethylenediammonium ion on the exchange sites and ΔH_{k}^0 is the retention enthalpy. The corresponding entropy changes are ΔS_{ma}^0 and ΔS_{ex}^0 .

Metal ion	Enthalpy change (kJ/g · mol)			Entropy change (J/g · mol · K)	
	ΔH_{ma}^0	ΔH_{ex}^0	ΔH_{k}^0	ΔS_{ma}^0	ΔS_{ex}^0
Zn ²⁺	2.5 ± 0.4	5.3 ± 0.4	5.4 ± 0.4	60.9 ± 0.2	5 ± 1
Mg ²⁺	38 ± 2	4.4 ± 0.3	4.4 ± 0.3	152 ± 2	0 ± 1
Ca ²⁺	3.0 ± 0.4	4.8 ± 0.4	4.8 ± 0.4	52 ± 1	6 ± 1
Cd ²⁺	8.0 ± 0.7	7.0 ± 0.4	7.0 ± 0.4	71 ± 1	12 ± 1
Co ²⁺	-0.9 ± 0.3	2.0 ± 0.3	2.1 ± 0.3	44 ± 1	-6 ± 1
Mn ²⁺	8.6 ± 0.6	6.1 ± 0.4	6.2 ± 0.4	65 ± 1	7 ± 1
Fe ²⁺	7.0 ± 0.6	5.2 ± 0.3	5.2 ± 0.3	65 ± 1	4 ± 1

were measured under various conditions by using other methods are listed in Table III. As can be seen, the stability constant measured by ion chromatography are in good agreement with those measured by other methods.

On the basis of these results, we can explain why at a fixed ethylenediamine concentration but a low tartaric acid concentration, *i.e.*, 0.2 millimolar, the retention time increases with pH as shown in Fig. 1C. When the tartrate concentration is low, the retention of metal ions is influenced predominantly by the pushing effect of the ethylenediammonium ion, which occupies a large fraction of exchange sites. In contrast, at higher tartrate concentrations, *e.g.*, 2 millimolar, the retention of metal ions is predominantly affected by the pulling effect of tartrate ion. Consequently, their retention decreases with increasing pH owing to the greater complexing capacity of tartrate at higher pH [8].

At sufficiently high ethylenediamine concentrations, the value of the protonated fraction *f* is negligible. Therefore, according to eqn. 18, the retention factor should be inversely proportional to ethylenediamine concentration at constant tartrate concentration, temperature and pH. In order to examine the validity of eqn. 18, the data illustrated in Fig. 1B for the dependence of *k'* on the concentration of ethylenediamine were replotted in Fig. 4, which shows double logarithmic plots of the retention factor against ethylenediamine concentration for various divalent metal ions. The negative slopes

were all close to unity and thus lend support to the validity of eqn. 18. This shows, in fact, that a divalent metal can bind with two sulphonic acid groups on the ion-exchange column used. Further, the straight lines in Fig. 4 are parallel so that the separation factor for any two metals, $\log \alpha_{21} = \log k'_2 - \log k'_1$, is constant at varying ethylenediamine concentration. This means that ethylenediamine

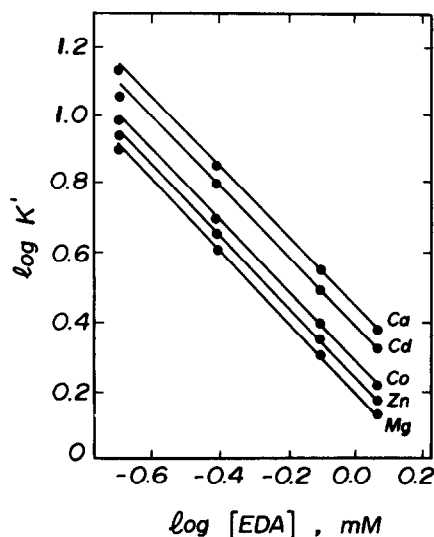


Fig. 4. Graph illustrating plots of the logarithmic retention factors for various divalent metal ions against the logarithmic ethylenediamine concentration in the eluent containing 0.2 mM tartaric acid at pH 4.5 and 30°C.

TABLE III

COMPARISON OF STABILITY CONSTANTS FOR COMPLEXES OF DIVALENT METAL IONS WITH TARTRATE MEASURED BY ION CHROMATOGRAPHY (IC) IN THIS WORK WITH THOSE REPORTED IN THE LITERATURE AND MEASURED EITHER BY DISTRIBUTION BETWEEN TWO PHASES (P) OR BY THE GLASS ELECTRODE (GE) OR BY ION-EXCHANGE (IE)

In the present work the range of ionic strength was 1–13 millimolal.

Ions	Temperature (°C)	Log K_{ma}^a	Reference ^a	Method ^a	Ionic strength ^a
Zn ²⁺	30	2.75 ± 0.03	—	IC	—
	40	2.76 ± 0.03	—	IC	—
	20	2.69 ± 0.08	13	P	a
	25	3.31 ± 0.08	14	P	b
Mg ²⁺	30	1.18 ± 0.01	—	IC	—
	40	1.39 ± 0.02	—	IC	—
	37	1.91	15	GE	c
Ca ²⁺	30	2.20 ± 0.01	—	IC	—
	40	2.22 ± 0.01	—	IC	—
	37	2.17	16	GE	d
Cd ²⁺	30	2.27 ± 0.01	—	IC	—
	40	2.31 ± 0.01	—	IC	—
	20	3.71 ± 0.03	13	P	a
	30	1.1 ± 0.2	17	P	f
Co ²⁺	30	2.48 ± 0.02	—	IC	—
	40	2.47 ± 0.02	—	IC	—
	20	2.8 ± 0.1	13	P	b
	25	3.08 ± 0.02	18	GE	a
	25	3.02 ± 0.02	19	IE	g
Mn ²⁺	25	2.50 ± 0.01	20	P	b
	30	1.89 ± 0.04	—	IC	—
	40	1.94 ± 0.04	—	IC	—
	20	2.92 ± 0.05	13	P	a
Fe ²⁺	32	1.44	21	GE	h
	30	2.17 ± 0.01	—	IC	—
	40	2.21 ± 0.01	—	IC	—
	20	2.24	22	IE	h

^a (a) Constant ionic strength of 0.1 millimolal by addition of KClO₄; (b) constants corrected to zero ionic strength; (c) 0.2 M NaClO₄; (d) 0.090 M NaClO₄; (e) 0.1 M NaClO₄; (f) constant ionic strength of 1 molal by addition of NaClO₄; (g) ionic strength between 0 and 0.155 molal; (h) constant ionic strength of 0.1 molal by addition of NaClO₄.

does not affect the selectivity of the chromatographic system to metal ions.

From Fig. 1C it is also evident that the separation factor for any two metals does not vary much with changing pH. On the other hand, the poor resolution of Mn(II), Fe(II) and Co(II) at 0.2 mM tartrate concentration can be improved by increasing the tartrate level as shown in Fig. 1A. In contrast, the selectivity of chromatographic separation for Mg(II), Mn(II) and Cd(II) ions is improved by lowering the tartrate level.

As shown by the Van 't Hoff plots in Fig. 3A, the

capacity factor increases with increase in temperature. The retention enthalpies calculated from the slope of the Van 't Hoff's plots are listed in Table II.

The ion-exchange equilibrium constant K_m^c of metal ions with ethylenediamine is shown to increase with temperature in Fig. 3C. This reaction is accompanied by a small enthalpy change and a positive entropy change, as is shown in Table II, for all metals except cobalt. From Table II it is seen that the retention enthalpies are essentially the same as the enthalpy changes of the ion-exchange equilibria between the corresponding metal and ethylenedi-

amine ions, but are significantly different from those of the tartrate complexation reaction. This observation further supports the notion that at sufficiently low tartrate concentrations, the retention of metals is governed by the pushing effect of ethylenediammonium ion rather than by the pulling effect of the tartrate.

The preferred concentration range for ethylenediamine and/or tartaric acid in the eluent is from 0.1 to 10 millimolar. At lower concentrations the buffering capacity of the eluent is too low to give a stable and well controlled chromatographic system. On the other hand, if the concentration is too high, the concomitantly high background noise adversely affects the sensitivity of analysis.

It was found that with large samples the retention also depends on the elute concentration, and this manifestation of non-linear chromatography will be investigated in another study. In this study the elute concentrations were all kept low enough to ensure that the elution is linear. With 100- μ l samples the concentration of the elutes did not exceed 0.05 M . Under such conditions the signal-to-noise ratio is about 20:1 and the accuracy of the stability constant measurement by ion chromatography is expected to be commensurate.

Fig. 5 shows the chromatogram of magnesium and calcium ions obtained with 0.2 mM tartaric acid and 0.4 mM EDA in the eluent at pH 4.5 and 30°C. The background conductivity is 156 μ S/cm. The plate number is about 1700 for each peak. The elute concentration decreases in the chromatographic process and the magnitude of dilution, given by the ratio of the elute concentrations in the sample and in the eluent peak, can be calculated as the ratio of the peak width at half-height to the injection volume for triangular peaks. Thus, from Fig. 5, the peak concentrations are calculated to be 0.02 and 0.013 millimolar for magnesium and calcium, respectively.

The sensitivity of the elute in ion chromatographic analysis may be defined as the measured conductivity change per unit change in the elute concentration in the sample. From Fig. 5, the chromatographic sensitivities are 24 and 7.4 $S\text{ cm}^2/\text{equiv.}$ for magnesium and calcium, respectively. It is believed that the difference in the chromatographic sensitivities is due to the effect of dilution, the ionization fraction of the elutes and the differ-

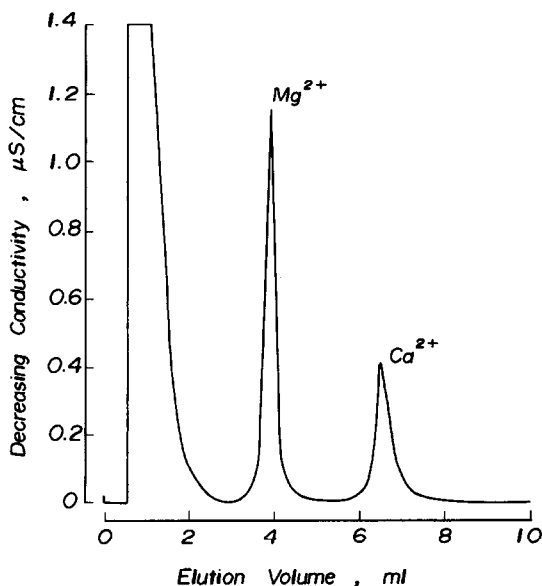


Fig. 5. Indirect detection of magnesium and calcium ions. Column, 4.6 \times 50 mm I.D. 10- μ m cation exchanger with capacity of 46 μ equiv./g; eluent, 0.2 mM tartaric acid-0.4 mM EDA (pH 4.5); temperature, 30°C; flow-rate, 0.8 ml/min; pressure, 16 kg/cm^2 ; sample, 100 μ l of solution 0.05 millimolar for both ions.

ence in the limiting equivalent conductivities of the eluent and the elute cations. Although there are two major eluent cations, the hydrogen ion is buffered by the tartaric acid and only the ethylenediammonium ion is replaced by the elute cation at the peak in order to maintain electroneutrality. From the limiting equivalent conductivity of magnesium and calcium ions at 25°C, *i.e.*, 53.0 and 59.5 $S\text{ cm}^2/\text{equiv.}$ [23], respectively, and Fig. 5 the limiting equivalent conductivity of the diprotonated EDA at 25°C is calculated to be 79 $S\text{ cm}^2/\text{equiv.}$ The fractions of ionization of magnesium and calcium ions are calculated from the respective stability constants in Table III and eqn. 16 to be 1.0 and 0.98, respectively.

The limiting equivalent conductivity of ethylenediammonium ion is larger than those of the elute ions so that negative elute peaks are obtained. The limiting equivalent conductivities of lead and some rare earth metal ions are *ca.* 70 $S\text{ cm}^2/\text{equiv.}$ [23], which is too close to that of EDA to give sufficient chromatographic sensitivity for quantitative analysis by the chromatographic system employed in this study.

In order to study the effect of eigenpeaks on the retention of the eluite, the sample was diluted from 10 to 0.05 millimolal with either distilled water or by the eluent. In either instance, the retention of the eluites did not show observable changes, whereas there was a large change in the peak which appears in the void.

CONCLUSIONS

Single-column ion chromatography using a TSK high-performance ion-exchange column with ethylenediammonium tartrate in the eluent was used for the rapid separation of common divalent cations. With the conductivity detector not only were trace amounts of the sample components determined but also the complexation reaction and ion-exchange process could be studied at the same time.

A theoretical model was developed to describe quantitatively the effect of pH, tartaric acid and ethylenediamine concentration on the retention factor of divalent cations in single-column ion chromatography. The equilibrium constant for the ion-exchange process was calculated from chromatographic retention data and the enthalpy and entropy change for the chromatographic process was also obtained.

Further, a method has been presented for the evaluation of the complexation constant between tartrate ligand and divalent metal ions by ion chromatography from their capacity factors measured at various tartaric acid concentrations.

The elution conditions, including temperature, pH, tartaric acid and ethylenediamine concentration, were found to influence the retention of divalent cations in different ways. The retention factor increases with both the temperature and the tartaric acid concentration, but decreases with increasing EDA concentration. The retention factor increases with pH at low tartaric acid concentration, but decreases with pH when the tartaric acid concentration is relatively high.

It is likely that the use of another driving ion, such as lithium, would have been more appropriate than ethylenediamine if we had used a postcolumn reactor with a fluorescence detector instead of the conductivity detector to detect the metal complex. Such a system and the optimization of sensitivity and separation efficiency is under investigation.

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SYMBOLS

A	tartaric acid
A^{2-}	free tartrate ion
C	ion-exchange resin capacity (mequiv. cm^{-3})
E^{2+}	fully protonated ethylenediamine
ER_2	adsorbed ethylenediammonium ion
f	fraction of the exchange sites in the stationary phase occupied by hydrogen ions
H^+	hydrogen ion
HA^-	free acid tartrate ion
HR	adsorbed hydrogen ion
k'	retention factor
K_1, K_2	acid ionization constants of tartaric acid (molal)
K_{Chrom}	chromatographic equilibrium constant
K_h^e	equilibrium constant for the exchange of hydrogen ion with the adsorbed ethylenediammonium ion
K_m^e	equilibrium constant for the exchange of metal ion with the adsorbed ethylenediammonium ion
K_m^h	equilibrium constant for the exchange of metal ion with the adsorbed hydrogen ion
K_{ma}^a	stability constant of the complex formed between the metal ion and the tartrate ligand (molal $^{-1}$)
$K_{\text{mha}}^{\text{ha}}$	stability constant of the complex formed between the metal ion and the acid tartrate ligand (molal $^{-1}$)
M^{2+}	divalent cation
MR_2	adsorbed divalent cation
R	gas constant (kJ/g · mol · K)
R	exchange site of the stationary phase
t_0	mobile phase hold-up time (min)
t_r	retention time of the eluite (min)
V_m	space occupied by the mobile phase in the column (cm^3)
V_0	empty column volume (cm^3)
W	weight of ion-exchange resin present in the column (g)

Greek symbols

α_{21}	separation factor defined in eqn. 21
α_m	fraction of the total metal present as free metal ion in the mobile phase
β_a	$[A^{2-}]/[A]_i$
β_{ha}	$[HA^-]/[A]_i$
ϕ	phase ratio of the column
ΔH^0	standard enthalpy change for an equilibrium reaction (kJ/g · mol)
ΔH_k^0	retention enthalpy (kJ/g · mol)
ΔS^0	standard entropy change for an equilibrium process (J/g · mol · K)
ε_i	intraparticle porosity
ε_e	interparticle porosity
ρ_r	true density of ion-exchange resin (g/cm ³)

Subscripts

ex	associated with the ion-exchange process of metal ions with ethylenediammonium ion on the exchange sites
i	inert ions not adsorbed to the exchange sites
m	metal ion
ma	associated with complex formation of divalent ion with tartrate
t	total concentration

Other

[]	concentration of the species specified within (molal)
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