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Retention model for the separation of anionic metal–EDTA complexes in ion chromatography

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ABSTRACT

A retention model is derived for complex anions eluted from an anion-exchange column with multiple ionic eluents containing hydrogencarbonate, carbonate, and hydroxyl species and the sample solution, containing transition metals, anions and complexing ligand. The theory is based on the generalized ion-exchange equilibrium, protonation and complex-formation equilibria. The unknown parameters of chromatographic ion-exchange equilibrium constants for sample and eluent species are determined from the experimental retention data by iterative minimization, using a non-linear regression algorithm. The model was utilized to predict the retention behaviour of $CdEDTA^{2-}$, $CoEDTA^{2-}$, $MnEDTA^{2-}$ and $NiEDTA^{2-}$ ions. The capacity factors of complex ions were determined for wide ranges of pH values and eluent concentrations. Good agreement was obtained between the observed and predicted retentions.

INTRODUCTION

Complexing eluents have been used to improve the selectivity of the chromatographic separation of metal ions [1]. When a basic solution contains an excess of a strong complexing anion of high charge such as ethylenediaminetetraacetate (EDTA) ion, most metal ions will occur as anionic complexes. The metal–EDTA complexes ($MEDTA^{2-}$, $MHEDTA^{-}$) are anions and can be separated by anion exchange. Hence this method provides simultaneous metal and anion separation [2–4].

Multidentate chelating ligands can form strong complexes with alkaline earth metal, transition metal and lanthanide ions and have an important role in ion chromatography. The chromatographic separation will depend on the charge of the complexes, the stability of the complexes, the ion-exchange behaviour on the ion exchanger [5] and the eluent type and concentration.

The problem of the prediction of retention and the optimization of eluent composition can be solved on the basis of valid models of retention [6,7]. If the eluent contains only a single competing anion, a relatively straightforward model can be derived [1,8–10]. A system that contains several ionic species, such as CO_3^{2-}, HCO_3^- and OH^- in the eluent and different complex forms of analytes in the sample is very complicated. This is probably due to its theoretical complexity and the lack of a commonly accepted model of simultaneous equilibria. At the eluent pHs used, three eluent species will be present and simultaneous ion-exchange equilibria will take place. In order to have a reliable retention model all the eluent species in the system must be considered.

The aim of this work was to develop a theoretical model for the retention of complex anions. Until some definitive study of retention behaviour has

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been made, much of the chromatography of metal complexes and other difficult ionic separations will remain unpredictable. In this paper we provide a detailed description and evaluation of a new model as a predictive tool for retention. This will be a rigorous method that takes into consideration all of the relevant equilibria.

THEORY

Understanding the chromatographic behaviour in this system requires a modelling of interplay between ion-exchange and complexation reactions. We shall consider the equilibrium distribution and chromatography of Cd^{2+}, Co^{2+}, Mn^{2+} and Ni^{2+} on anion exchangers with EDTA ions as the complexing ligand using a carbonate eluent for separation.

Ion-exchange equilibria and complexation of sample ions

The ion-exchange equilibrium for binding of a solute anion A^{y-} to a stationary phase that has been conditioned with an eluent containing a competing anion E^{x-} is given by

$$y\,R_x\text{–}E + x\,A^{y-} \overset{K_{A/E}}{\rightleftharpoons} x\,R_y\text{–}A + y\,E^{x-} \tag{1}$$

where R represents the stationary phase. The equilibrium constant for this reaction is given by [1]

$$K_{A/E} = \frac{(A^{y-})^x\,[E^{x-}]^y}{[A^{y-}]^x\,(E^{x-})^y} \tag{2}$$

where the parentheses and square brackets refer to molar concentrations in the stationary and the mobile phase, respectively. In ion chromatography, activity effects could be ignored because of the low concentrations of the sample and the eluent that are used. The volumetric distribution coefficient of A^{y-} can be obtained from eqn. 2

$$D_A = \frac{(A^{y-})}{[A^{y-}]} = K_{A/E}^{1/x}\left(\frac{(E^{x-})}{[E^{x-}]}\right)^{y/x} \tag{3}$$

We can assume that the eluent ion, E^{x-}, occupies x ion-exchange sites on the stationary phase. The molar concentration of solid phase can be defined through the ion-exchange capacity, Q, of the column, $(E^{x-}) = Q/x$, and eqn. 3 can be rewritten as

$$D_A = K_{A/E}^{1/x}\left(\frac{Q}{x}\right)^{y/x}[E^{x-}]^{-y/x} \tag{4}$$

The logarithmic form provides the relationship

$$\log D_A = \frac{1}{x}\log K_{A/E} + \frac{y}{x}\log\left(\frac{Q}{x}\right) - \frac{y}{x}\log\,[E^{x-}] \tag{5}$$

In the formation of anionic metal complexes with EDTA ligand, pH-dependent side-reactions occur. Multivalent metal ions tend to form protonated complexes, basic complexes and other mixed-ligand complexes. In the pH range of interest the forms of complex anions of the metals examined are $CdEDTA^{2-}$, $CdHEDTA^{-}$, $Cd(OH)_3^{-}$, $Cd(OH)_4^{2-}$, $CoEDTA^{2-}$, $CoHEDTA^{-}$, $Co(OH)_3^{-}$, $MnEDTA^{2-}$, $MnHEDTA^{-}$, $NiEDTA^{2-}$ and $NiHEDTA^{-}$.

The anion-exchange processes for metal–EDTA complexes underlying the separation are given by the following equilibria

$$2\,R\text{–}E + MEDTA^{2-} \overset{K_{MEDTA/E}}{\rightleftharpoons} R_2\text{–}MEDTA + 2\,E^{-} \tag{6}$$

$$R\text{–}E + MHEDTA^{-} \overset{K_{MHEDTA/E}}{\rightleftharpoons} R\text{–}MHEDTA + E^{-} \tag{7}$$

The ion-exchange equilibrium constants of sample ions can be written as

$$K_{MEDTA/E} = \frac{(MEDTA^{2-})\,[E]^2}{[MEDTA^{2-}]\,(E)^2} \tag{8}$$

$$K_{MHEDTA/E} = \frac{(MHEDTA^{-})\,[E]}{[MHEDTA^{-}]\,(E)} \tag{9}$$

Eqns. 8 and 9 can be rearranged to obtain the concentrations of $MEDTA^{2-}$ and $MHEDTA^{-}$ in the stationary phase

$$(MEDTA^{2-}) = K_{MEDTA/E}\cdot\frac{[MEDTA^{2-}]\,(E)^2}{[E]^2} \tag{10}$$

$$(MHEDTA^{-}) = K_{MHEDTA/E}\cdot\frac{[MHEDTA^{-}]\,(E)}{[E]} \tag{11}$$

In this case the volumetric distribution coefficient is expressed as follows

$$D_{\mathrm{M}} = \frac{(\mathrm{MEDTA}^{2-}) + (\mathrm{MHEDTA}^{-})}{[\mathrm{M}^{2+}] + [\mathrm{MHEDTA}^{-}] + [\mathrm{MEDTA}^{2-}] + \sum_{i=1}^{n} [\mathrm{M(OH)}_i^{2-i}]} \tag{12}$$

In the numerator there are the M species bound to the stationary phase and in the denominator all the M species present in the mobile phase. Substitution of eqns. 10 and 11 in eqn. 12 gives

$$D_{\mathrm{M}} = \frac{K_{\mathrm{MEDTA/E}} \cdot \dfrac{[\mathrm{MEDTA}^{2-}]\,(\mathrm{E})^2}{[\mathrm{E}]^2} + K_{\mathrm{MHEDTA/E}} \cdot \dfrac{[\mathrm{MHEDTA}^{-}]\,(\mathrm{E})}{[\mathrm{E}]}}{[\mathrm{M}^{2+}] + [\mathrm{MHEDTA}^{-}] + [\mathrm{MEDTA}^{2-}] + \sum_{i=1}^{n} [\mathrm{M(OH)}_i^{2-i}]} \tag{13}$$

We can define Φ as the molar fraction of the total concentration of metal–anion complex in the eluent. Then eqn. 13 can be rewritten as

$$D_{\mathrm{M}} = \frac{K_{\mathrm{MEDTA/E}}\,(\mathrm{E})^2}{[\mathrm{E}]^2} \cdot \Phi_{\mathrm{MEDTA}} + \frac{K_{\mathrm{MHEDTA/E}}\,(\mathrm{E})}{[\mathrm{E}]} \cdot \Phi_{\mathrm{MHEDTA}} \tag{14}$$

Ion-exchange equilibria of eluent ions

The carbonate eluent contains three competing anions, CO_3^{2-}, HCO_3^- and OH^-. The molar concentrations of these species can be calculated from the two protonation constants of carbonate at the pH of the mobile phase. In the presence of eluent species simultaneous ion-exchange equilibria take place. The ion-exchange capacity of the separator column is given by

$$Q = 2\,(\mathrm{CO}_3^{2-}) + (\mathrm{HCO}_3^-) + (\mathrm{OH}^-) \tag{15}$$

Taking into account ion-exchange equilibria for the eluent species

$$\mathrm{CO}_3^{2-} + 2\,\mathrm{R{-}HCO}_3 \overset{K_{\mathrm{CO_3/HCO_3}}}{\rightleftharpoons} \mathrm{R_2{-}CO}_3 + 2\,\mathrm{HCO}_3^- \tag{16}$$

$$\mathrm{OH}^- + \mathrm{R{-}HCO}_3 \overset{K_{\mathrm{OH/HCO_3}}}{\rightleftharpoons} \mathrm{R{-}OH} + \mathrm{HCO}_3^- \tag{17}$$

The inter-eluent ion-exchange equilibrium constants are

$$K_{\mathrm{CO_3/HCO_3}} = \frac{(\mathrm{CO}_3^{2-})\,[\mathrm{HCO}_3^-]^2}{[\mathrm{CO}_3^{2-}]\,(\mathrm{HCO}_3^-)^2} \tag{18}$$

and

$$K_{\mathrm{OH/HCO_3}} = \frac{(\mathrm{OH}^-)\,[\mathrm{HCO}_3^-]}{[\mathrm{OH}^-]\,(\mathrm{HCO}_3^-)} \tag{19}$$

From eqns. 18 and 19, we can write

$$(\mathrm{CO}_3^{2-}) = K_{\mathrm{CO_3/HCO_3}}\,[\mathrm{CO}_3^{2-}] \cdot \frac{(\mathrm{HCO}_3^-)^2}{[\mathrm{HCO}_3^-]^2} \tag{20}$$

and

$$(\mathrm{OH}^-) = K_{\mathrm{OH/HCO_3}}\,[\mathrm{OH}^-] \cdot \frac{(\mathrm{HCO}_3^-)}{[\mathrm{HCO}_3^-]} \tag{21}$$

The concentrations of CO_3^{2-} and OH^- on the stationary phase are now expressed in terms of (HCO_3^-) through the corresponding equilibrium constants, eqns. 18 and 19. By combination of eqns. 15, 20 and 21, the following quadratic equation is obtained

$$Q = \frac{2\,K_{\mathrm{CO_3/HCO_3}}\,[\mathrm{CO}_3^{2-}]}{[\mathrm{HCO}_3^-]^2} \cdot (\mathrm{HCO}_3^-)^2 + \left(1 + \frac{K_{\mathrm{OH/HCO_3}}\,[\mathrm{OH}^-]}{[\mathrm{HCO}_3^-]}\right)(\mathrm{HCO}_3^-) \tag{22}$$

Solution of eqn. 22 gives

$$(\mathrm{HCO}_3^-) = \frac{\sqrt{b^2 + 4aQ} - b}{2a} \tag{23}$$

where

$$a = \frac{2\,K_{\mathrm{CO_3/HCO_3}}\,[\mathrm{CO}_3^{2-}]}{[\mathrm{HCO}_3^-]^2}$$

and

$$b = 1 + \frac{K_{\mathrm{OH/HCO_3}}\,[\mathrm{OH}^-]}{[\mathrm{HCO}_3^-]}$$

and the value of (HCO_3^-) can be substituted into eqn. 14

$$D_{\mathrm{M}} = \frac{K_{\mathrm{MEDTA/HCO_3}}\,(\sqrt{b^2+4aQ}-b)^2}{4a^2\,[\mathrm{HCO_3^-}]^2} \cdot \Phi_{\mathrm{MEDTA}} + \frac{K_{\mathrm{MHEDTA/HCO_3}}\,(\sqrt{b^2+4aQ}-b)}{2a\,[\mathrm{HCO_3^-}]} \cdot \Phi_{\mathrm{MHEDTA}} \tag{24}$$

Calculation of molar fractions of complex anions (Φ)

We now have to determine the ratio of the concentration of the effective complex formed by metal ions, which take part in ion-exchange equilibrium, and the total metal ion concentration. They are considered in terms of the above-mentioned Φ function. The value of Φ depends on the molar concentrations of ions that are present in the solution and react with the metal ions. The values of Φ can be calculated as follows

$$\Phi_{\mathrm{MEDTA}} = \frac{K_{\mathrm{MEDTA}}\,[\mathrm{EDTA}]}{1 + K_{\mathrm{MEDTA}}\,[\mathrm{EDTA}] + K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H)_1}}\,[\mathrm{H}]\,[\mathrm{EDTA}] + \sum_{i=1}^{n} \gamma_i\,[\mathrm{OH}]^i} \tag{25}$$

and

$$\Phi_{\mathrm{MHEDTA}} = \frac{K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H)_1}}\,[\mathrm{H}]\,[\mathrm{EDTA}]}{1 + K_{\mathrm{MEDTA}}\,[\mathrm{EDTA}] + K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H)_1}}\,[\mathrm{H}]\,[\mathrm{EDTA}] + \sum_{i=1}^{n} \gamma_i\,[\mathrm{OH}]^i} \tag{26}$$

where K_{MEDTA} and K_{MHEDTA} are the stability constants of metal–anion complexes, $K_{\mathrm{EDTA(H)_1}}$ is the first protonation constant of EDTA, [EDTA] is the concentration of the free form of EDTA and γ is the complex formation constant of metal–hydroxo complexes.

The concentration of the free form of EDTA can be obtained by the following equation for the average number of ligand units per metal

$$\bar{n} = \frac{C_{\mathrm{EDTA}} - [\mathrm{EDTA}]\,\alpha_{\mathrm{EDTA(H)}}}{C_{\mathrm{M}}} =$$

$$\frac{K_{\mathrm{MEDTA}}\,[\mathrm{EDTA}] + K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H)_1}}\,[\mathrm{H}]\,[\mathrm{EDTA}]}{1 + K_{\mathrm{MEDTA}}\,[\mathrm{EDTA}] + K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H)_1}}\,[\mathrm{H}]\,[\mathrm{EDTA}] + \sum_{i=1}^{n} \gamma_i\,[\mathrm{OH}]^i} = \Phi_{\mathrm{MEDTA}} + \Phi_{\mathrm{MHEDTA}} \tag{27}$$

where C_{EDTA} is the total concentration of EDTA in the sample and

$$\alpha_{\mathrm{EDTA(H)}} = 1 + [\mathrm{H^+}]\,K_{\mathrm{EDTA(H)_1}} + [\mathrm{H^+}]^2\,K_{\mathrm{EDTA(H)_1}}\,K_{\mathrm{EDTA(H)_2}} +$$
$$+ [\mathrm{H^+}]^3\,K_{\mathrm{EDTA(H)_1}}\,K_{\mathrm{EDTA(H)_2}}\,K_{\mathrm{EDTA(H)_3}} + [\mathrm{H^+}]^4\,K_{\mathrm{EDTA(H)_1}}\,K_{\mathrm{EDTA(H)_2}}\,K_{\mathrm{EDTA(H)_3}}\,K_{\mathrm{EDTA(H)_4}}$$

The numerator in eqn. 27 gives the concentration of EDTA in MEDTA complexes and the denominator gives the total metal concentration. Eqn. 27 is a quadratic equation in [EDTA].

By solution of eqn. 27 one can obtain the concentration of the free ionic species of EDTA in the following form (where $n_{\mathrm{OH^-}} = 1$)

$$[\mathrm{EDTA}] = \frac{-e + \sqrt{e^2 - 4df}}{2d} \tag{28}$$

where

$$d = K_{\mathrm{MEDTA}}\,\alpha_{\mathrm{EDTA(H)}} + K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H_1)}}\,[\mathrm{H}]\,\alpha_{\mathrm{EDTA(H)}}$$

$$e = C_{\mathrm{M}}\,K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H_1)}}\,[\mathrm{H}] + C_{\mathrm{M}}\,K_{\mathrm{MEDTA}} + \gamma_1\,[\mathrm{OH}]\,\alpha_{\mathrm{EDTA(H_1)}} +$$
$$+ \alpha_{\mathrm{EDTA(H)}} - C_{\mathrm{EDTA}}\,K_{\mathrm{MEDTA}} - C_{\mathrm{EDTA}}\,K_{\mathrm{MHEDTA}}\,K_{\mathrm{EDTA(H_1)}}\,[\mathrm{H}]$$

$$f = -C_{\mathrm{EDTA}} - \gamma_1\,[\mathrm{OH}]\,C_{\mathrm{EDTA}}$$

We now can substitute the values of Φ into eqn. 24 to obtain one of the final forms of the model

$$D_M = ml + pq \tag{29}$$

where

$$m = \frac{K_{MEDTA/HCO_3}(\sqrt{b^2+4aQ}-b)^2}{4a^2[HCO_3^-]^2}$$

$$l = \frac{K_{MEDTA}\cdot\dfrac{-e+\sqrt{e^2-4df}}{2d}}{1+K_{MEDTA}\cdot\dfrac{-e+\sqrt{e^2-4df}}{2d}+K_{MHEDTA}\,K_{EDTA(H)_1}[H]\cdot\dfrac{-e+\sqrt{e^2-4df}}{2d}+\gamma_1[OH]}$$

$$p = \frac{K_{MHEDTA/HCO_3}(\sqrt{b^2+4aQ}-b)}{2a[HCO_3^-]}$$

$$q = \frac{K_{MEDTA}\,K_{EDTA[H]_1}[H]\cdot\dfrac{-e+\sqrt{e^2-4df}}{2d}}{1+K_{MEDTA}\cdot\dfrac{-e+\sqrt{e^2-4df}}{2d}+K_{MHEDTA}\,K_{EDTA(H)_1}[H]\cdot\dfrac{-e+\sqrt{e^2-4df}}{2d}+\gamma_1[OH]}$$

Ion-exchange equilibria of metal–hydroxo complexes

For Co and Cd, hydroxo species must also be considered. Taking into account the anion-exchange equilibrium

$$R\text{–}HCO_3 + M(OH)_3^- \overset{K_{M(OH)_3/HCO_3}}{\rightleftharpoons} R\text{–}M(OH)_3 + HCO_3^- \tag{30}$$

following the same derivation as above, eqn. 24 becomes

$$D_M = \frac{K_{MEDTA/HCO_3}(\sqrt{b^2+4aQ}-b)^2}{4a^2[HCO_3^-]^2}\cdot\Phi_{MEDTA} + \frac{K_{MHEDTA/HCO_3}\sqrt{b^2+4aQ}-b}{2a[HCO_3^-]}\cdot\Phi_{MHEDTA} + \\ + \frac{K_{M(OH)_3/HCO_3}\sqrt{b^2+4aQ}-b}{2a[HCO_3^-]}\cdot\Phi_{M(OH)_3^-} \tag{31}$$

where

$$\Phi_{M(OH)_3^-} = \frac{\gamma_3[OH]^3}{1+K_{MEDTA}[EDTA]+K_{MHEDTA}\,K_{EDTA(H)_1}[H][EDTA]+\sum_{i=1}^{3}\gamma_i[OH]^i} \tag{32}$$

For Co there are four hydroxo ligands and a similar derivation can be obtained.

In general, the volume distribution coefficient for solute M is designated as D_M and is related to the capacity factor k'_M by the expression

$$D_M = \frac{V_0\,k'_M}{V_{stat}} \tag{33}$$

where V_0, the void volume of the column, and V_{stat}, the volume of stationary phase, are known or easily evaluated.

EXPERIMENTAL

Reagents and solutions

The anion eluents ($NaHCO_3$, Na_2CO_3 and NaOH mixtures) were prepared by dissolving analytical-reagent grade salts (Merck, Darmstadt, Germany) in high-purity water obtained using a Milli-Q system (Millipore, Bedford, MA, USA) filtered through a 0.45-μm filter. Standard solutions of metal ions, namely Co(II), Ni(II), Cd(II), Mn(II), were prepared by dilution of concentrated stock solutions (Merck). Standard solutions of fluoride, chloride, nitrate and sulphate anions were prepared by dissolution of analytical-reagent grade salts (Fluka, Buchs, Switzerland) and the chelating agent EDTA (Carlo Erba, Milan, Italy).

Unless stated otherwise, all samples (injection volume 100 μl) were $5.0 \cdot 10^{-5}$ *M* in metal ion and $1.5 \cdot 10^{-4}$ *M* in EDTA; the sample pH was adjusted to the appropriate value using NaOH.

Instrumentation

A Dionex Series 4000i ion chromatograph was used with a conductivity detector equipped with an AMMS1 anion suppressor (Dionex, Synnyvale, CA, USA). The chromatograms were recorded with an SP 4270 data module integrator (Carlo Erba).

The separation column (Dionex AS9, 250 × 4 mm) was based on a 15-μm polystyrene–divinylbenzene substrate agglomerated with anion-exchange latex that had been completely aminated. The latex has a polyacrylate backbone and carries the actual ion-exchange sites. Ion-exchange capacity was determined empirically (26 μequiv. per column). All chromatograms were obtained at room temperature. The flow-rate was 2.0 ml/min. Retention times were the means of triplicate injections of single samples.

RESULTS AND DISCUSSION

The retention behaviour of the four analytes considered (NiEDTA, MnEDTA, CoEDTA and CdEDTA) was evaluated for different pH values and various eluent concentrations of the investigated system as shown in Table I. Figs. 1 and 2 show typical chromatograms obtained with different eluent compositions. Modelling of retention requires, as described above, evaluation of the analyte–eluent

TABLE I

CONCENTRATIONS OF ELUENT SPECIES (CO_3^{2-} + HCO_3^-)

C_{eluent} (m*M*)	pH	$C_{CO_3^{2-}}$ (10^{-2} m*M*)	$C_{HCO_3^-}$ (10^{-2} m*M*)	C_{OH^-} (10^{-2} m*M*)
2.0	9.10	18.2	181.6	1.26
2.0	9.57	45.6	154.4	3.71
2.0	9.92	79.6	120.4	8.32
2.0	10.35	128.0	72.0	22.39
2.0	11.07	180.6	19.3	117.5
2.5	9.93	100.1	149.1	8.51
3.0	9.63	75.9	224.0	4.26
3.0	10.30	183.9	116.0	20.00
3.0	10.80	250.1	49.9	63.10
3.5	9.40	58.2	291.6	2.51
5.0	9.80	166.9	333.0	6.31
5.0	10.76	410.2	89.7	57.54
7.0	9.40	116.4	583.2	2.51
7.0	9.87	259.4	440.5	7.41
7.0	10.25	409.8	290.2	17.78
7.0	10.60	531.8	168.2	39.81
7.0	11.10	636.4	63.6	125.9

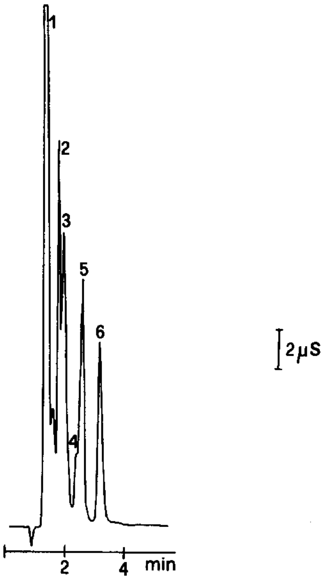

Fig. 1. Chromatogram of (1) Cl^-, (2) Mn–EDTA, (3) Cd–EDTA, (4) Al–EDTA, (5) Ni–EDTA and (6) Co–EDTA. Chromatographic conditions: $C_{eluent} = 2.0$ m*M*; pH = 11.07; sample (100 μl), 1.0 m*M* EDTA; detection, conductivity.

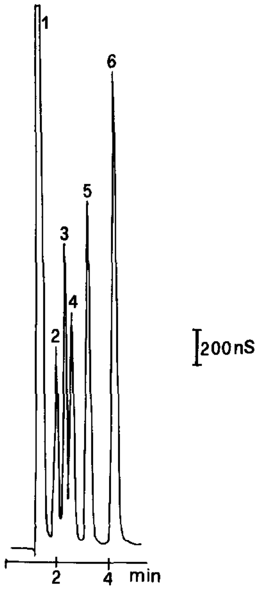

Fig. 2. Chromatogram of (1) Cl^-, (2) Cd–EDTA, (3) NO_3^-, (4) Al–EDTA, (5) Co–EDTA and (6) SO_4^{2-}. Chromatographic conditions: $C_{eluent} = 3.0$ m*M*; pH = 10.80; sample (100 μl), 1.0 m*M* EDTA; detection, conductivity.

and inter-eluent ion-exchange equilibrium constants. These unknown parameters, K_{MEDTA/HCO_3}, K_{MHEDTA/HCO_3}, K_{CO_3/HCO_3}, K_{OH/HCO_3} and $K_{M(OH)_n/HCO_3}$, can be determined from the experimental retention data by iterative minimization using a non-linear regression algorithm. In particular, a Nelder and Mead simplex algorithm, which compares observed and predicted retentions for different concentrations and pH, was successfully used.

The chemical equilibrium constants used for these calculations were taken from the literature [5,11]. Calculated values of the ion-exchange equilibrium constants, from experimental data, for complex forms of metal ions and for eluent species are given in Tables II–V. It can be seen that the values of the ion-exchange equilibrium constants obtained are reliable and independent of the experimental conditions. It is noteworthy that these constants are sufficient to determine the position of the simultaneous ion-exchange processes.

A comparison of predicted and observed retention volume is given in Tables VI–IX and Fig. 3

TABLE II

CHROMATOGRAPHIC ION-EXCHANGE EQUILIBRIUM CONSTANTS FOR COMPLEX FORMS OF Co IONS AND FOR ELUENT SPECIES CALCULATED FROM EXPERIMENTAL DATA

Ion-exchange constant	Eluent concentration ($CO_3^{2-} + HCO_3^-$) (m*M*)						Mean ± S.D.
	2.0	2.5	3.0	3.5	5.0	7.0	
$K_{CoHEDTA/HCO_3}$	1.000	0.967	0.936	0.962	1.000	0.988	0.98 ± 0.04
K_{CoEDTA/HCO_3}	8.250	8.567	8.114	8.500	8.502	8.500	8.41 ± 0.30
K_{OH/HCO_3}	10.612	10.713	10.821	10.716	10.611	10.705	10.70 ± 0.13
K_{CO_3/HCO_3}	13.498	13.723	13.997	13.761	13.986	13.000	13.66 ± 0.61
$K_{Co(OH)_3/HCO_3}$	9.888	9.703	9.999	9.764	9.894	9.745	9.83 ± 0.20

TABLE III

CHROMATOGRAPHIC ION-EXCHANGE EQUILIBRIUM CONSTANTS FOR COMPLEX FORMS OF Mn IONS AND FOR ELUENT SPECIES CALCULATED FROM EXPERIMENTAL DATA

Ion-exchange constant	Eluent concentration ($CO_3^{2-} + HCO_3^-$) (m*M*)						Mean ± S.D.
	2.0	2.5	3.0	3.5	5.0	7.0	
$K_{MnHEDTA/HCO_3}$	0.387	0.383	0.400	0.370	3.990	0.311	0.38 ± 0.05
K_{MnEDTA/HCO_3}	4.471	4.344	3.305	4.374	4.068	4.567	4.40 ± 0.28
K_{OH/HCO_3}	11.477	11.017	11.405	11.312	10.500	11.487	11.20 ± 0.63
K_{CO_3/HCO_3}	13.994	13.824	14.000	13.608	13.983	13.948	13.89 ± 0.25

TABLE IV

CHROMATOGRAPHIC ION-EXCHANGE EQUILIBRIUM CONSTANTS FOR COMPLEX FORMS OF Ni IONS AND FOR ELUENT SPECIES CALCULATED FROM EXPERIMENTAL DATA

Ion-exchange constant	Eluent concentration ($CO_3^{2-} + HCO_3^-$) (m*M*)						Mean ± S.D.
	2.0	2.5	3.0	3.5	5.0	7.0	
$K_{\mathrm{NiHEDTA/HCO_3}}$	0.609	0.678	0.699	0.675	0.694	0.658	0.67 ± 0.05
$K_{\mathrm{NiEDTA/HCO_3}}$	7.866	7.800	7.990	7.961	7.550	7.990	7.86 ± 0.28
$K_{\mathrm{OH/HCO_3}}$	10.995	10.633	10.600	10.547	10.000	11.496	10.71 ± 0.80
$K_{\mathrm{CO_3/HCO_3}}$	13.993	13.578	13.998	13.425	13.972	13.000	13.66 ± 0.60

TABLE V

CHROMATOGRAPHIC ION-EXCHANGE EQUILIBRIUM CONSTANTS FOR COMPLEX FORMS OF Cd IONS AND FOR ELUENT SPECIES CALCULATED FROM EXPERIMENTAL DATA

Ion-exchange constant	Eluent concentration ($CO_3^{2-} + HCO_3^-$) (m*M*)						Mean ± S.D.
	2.0	2.5	3.0	3.5	5.0	7.0	
$K_{\mathrm{CdHEDTA/HCO_3}}$	0.562	0.568	0.575	0.580	0.579	0.570	0.572 ± 0.01
$K_{\mathrm{CdEDTA/HCO_3}}$	4.746	4.669	4.509	4.830	4.500	4.907	4.70 ± 0.27
$K_{\mathrm{OH/HCO_3}}$	11.610	11.685	11.852	11.793	11.910	11.998	11.81 ± 0.24
$K_{\mathrm{CO_3/HCO_3}}$	14.000	13.652	13.992	13.836	13.998	13.999	13.91 ± 0.23
$K_{\mathrm{Cd(OH)_3/HCO_3}}$	3.574	3.652	3.940	3.714	3.841	3.111	3.64 ± 0.48
$K_{\mathrm{Cd(OH)_4/HCO_3}}$	5.639	5.665	5.935	5.750	5.848	5.080	5.65 ± 0.50

TABLE VI

COMPARISON OF PREDICTED AND OBSERVED RETENTION VOLUMES OF CoEDTA

Eluent		Retention volume (ml)		Difference (%)[a]
$C_{(CO_3^{2-} + HCO_3^-)}$ (m*M*)	pH	Measured	Calculated	
2.0	9.10	41.80	41.92	0.28
2.0	9.57	19.72	19.36	1.83
2.0	9.92	11.38	12.19	7.12
2.0	10.35	8.46	8.18	3.31
2.0	11.07	6.38	5.06	20.69
2.5	9.93	10.42	10.3	1.15
3.0	9.63	12.00	12.65	5.42
3.0	10.30	6.34	6.51	2.68
3.0	10.80	6.50	4.94	24.00
3.5	9.40	15.20	15.15	0.33
5.0	9.80	6.30	6.80	7.9
5.0	10.76	4.34	3.87	10.83
7.0	9.40	8.64	8.05	6.83
7.0	9.87	5.16	5.04	2.33
7.0	10.25	4.04	3.99	1.24
7.0	10.60	3.50	3.50	0
7.0	11.10	3.16	3.05	3.48

[a] Mean of standard deviations = 5.85%.

TABLE VII

COMPARISON OF PREDICTED AND OBSERVED RETENTION VOLUMES OF MnEDTA

Eluent		Retention volume (ml)		Difference (%)[a]
$C_{(CO_3^{2-}+HCO_3^-)}$ (mM)	pH	Measured	Calculated	
2.0	9.10	23.8	23.3	2.10
2.0	9.57	11.22	11.22	0
2.0	9.92	6.70	7.39	10.3
2.0	10.35	5.10	5.25	2.94
2.0	11.07	3.56	3.56	0
2.5	9.93	6.20	6.23	0.48
3.0	9.63	7.20	7.45	3.5
3.0	10.30	4.08	4.28	4.9
3.0	10.80	3.92	3.47	11.48
3.5	9.40	8.82	8.74	0.91
5.0	9.80	4.14	4.44	7.25
5.0	10.76	3.10	2.92	5.81
7.0	9.40	5.40	5.08	5.93
7.0	9.87	3.50	3.53	0.86
7.0	10.25	2.86	2.99	4.55
7.0	10.60	2.56	2.74	7.03
7.0	11.10	2.30	2.50	8.70

[a] Mean of standard deviations = 4.51%.

TABLE VIII

COMPARISON OF PREDICTED AND OBSERVED RETENTION VOLUMES OF NiEDTA

Eluent		Retention volume (ml)		Difference (%)[a]
$C_{(CO_3^{2-}+HCO_3^-)}$ (mM)	pH	Measured	Calculated	
2.0	9.10	40.00	40.69	1.73
2.0	9.57	18.76	18.81	0.27
2.0	9.92	10.66	11.87	11.35
2.0	10.35	7.74	7.98	3.10
2.0	11.07	5.04	4.95	1.79
2.5	9.93	9.74	9.75	0.10
3.0	9.63	11.80	11.95	1.27
3.0	10.30	5.82	6.21	6.70
3.0	10.80	5.62	4.74	15.66
3.5	9.40	14.64	14.28	2.46
5.0	9.80	6.02	6.48	7.64
5.0	10.76	4.16	3.75	9.86
7.0	9.40	8.34	7.65	8.27
7.0	9.87	5.00	4.84	3.20
7.0	10.25	3.88	3.86	0.52
7.0	10.60	3.32	3.40	2.41
7.0	11.10	2.86	2.98	4.20

[a] Mean of standard deviations = 4.74%.

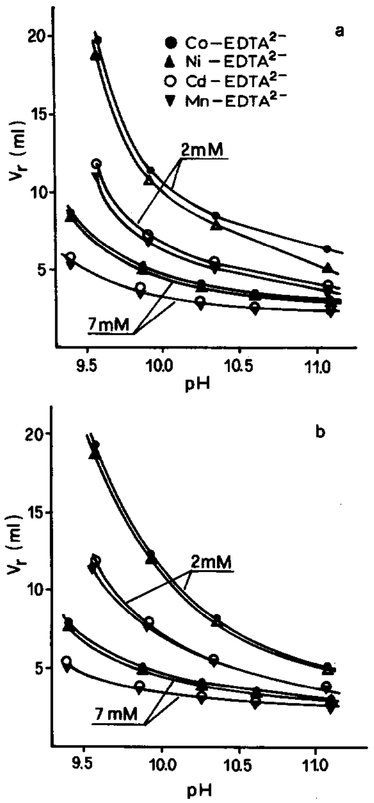

Fig. 3. Effect of pH on retention volumes (V_r) for two eluent concentrations (2 and 7 m*M*). (a) Experimental and (b) predicted values.

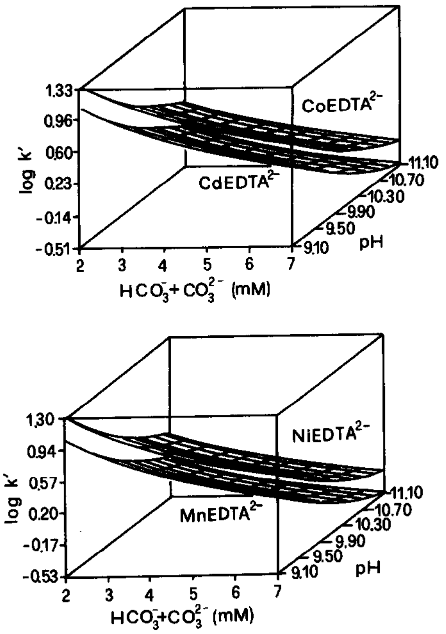

Fig. 4. Calculated retention surface for metal–EDTA complexes.

shows the good agreement between the two sets of data. The mean relative differences (%) between the evaluated and computed retention volumes confirm the good suitability of the proposed model. Calculated retention surfaces for metal–EDTA com-

TABLE IX

COMPARISON OF PREDICTED AND OBSERVED RETENTION VOLUMES OF CdEDTA

Eluent		Retention volume (ml)		Difference (%)[a]
$C_{(CO_3^{2-}+HCO_3^-)}$ (m*M*)	pH	Measured	Calculated	
2.0	9.10	25.00	24.70	1.20
2.0	9.57	11.82	11.83	0.08
2.0	9.92	7.06	7.74	9.63
2.0	10.35	5.38	5.45	1.30
2.0	11.07	3.92	3.63	7.40
2.5	9.93	6.56	6.51	0.76
3.0	9.63	7.36	7.80	5.98
3.0	10.30	4.24	4.43	4.48
3.0	10.80	4.16	3.55	14.66
3.5	9.40	9.42	9.18	2.55
5.0	9.80	4.32	4.60	6.48
5.0	10.76	3.22	2.98	7.45
7.0	9.40	5.58	5.29	5.20
7.0	9.87	3.62	3.64	0.55
7.0	10.25	3.96	3.06	3.38
7.0	10.60	2.64	2.79	5.68
7.0	11.10	2.40	2.53	5.42

[a] Mean of standard deviations = 4.83%.

plexes, obtained through eqns. 24, 29, 31 and 33, are also shown in Fig. 4 and according to the above data validate the proposed model.

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