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Ion-exchange mechanisms of some transition metals on a mixed-bed resin with a complexing eluent

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Abstract

Ion-exchange chromatography was used for the simultaneous elution of transition metals. The mobile phase consisted of an acetate buffer with pyridine-2,6-dicarboxylic acid (PDCA) as a chelating agent; the stationary phase was a mixed-bed resin that displays both anion- and cation-exchange properties. Under the selected conditions, the only species of the analyte that occur in solution are the anionic chelates $M(PDCA)_2$ while both the free cations and the chelates may be present in the resin. The mechanisms involved in this complex chromatographic pattern are described, considering either cation or anion exchange. It was found that the chromatographic behaviour of the transition metals can be explained by electrostatic interactions, the prevailing mechanism being pure anion exchange. Selectivity coefficients between the eluted species and either PDCA or acetate were derived from the experiments. The results were compared with those obtained after replacement of the mixed-bed resin by a low capacity anion-exchange resin. In this case, additional mechanisms such as adsorption had to be taken into account in the explanation of the retention behaviour of the transition metals.

1. Introduction

The chromatography of transition metals is a challenge concerning both their separation and detection. Their similar affinities for most common cation exchangers make it difficult to separate them by standard cation-exchange chromatography. In addition, chemically suppressed conductivity cannot be used for the detection of transition metals since the pH increase inherent in the method precipitates them as their hydroxides [1].

The latter problem can be overcome by post-column addition of a chelating agent that converts the metals into coloured complexes to be detected by visible spectrometry [1,2]. An alternative to the former problem consists in adding an anionic chelating agent such as tartrate, oxalate or citrate to the mobile phase and to carry out the separation of the resulting complexes on cation [3] or anion exchangers [4], or using reversed-phase chromatography [3,5,6]. The principles and applications of the different methods have been described [7]. The chromatographic performances of various sulfonated substrates, viz., silica gel, poly(styrene–divinylbenzene) [8] and methacrylate [9], have been compared. They showed a strong influence of non-specific interactions and poor efficiencies were reported for polymer-based stationary phases. However, even silica-based exchangers lack selectivity and show relatively low efficiencies.

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Some workers have suggested the use of a mixed-bed resin that features both anion- and cation-exchange sites to achieve a better separation [10,11]. The mobile phase contains a complexing agent for transition metals [pyridine-2,6-dicarboxylic acid (PDCA)] that accounts for chromatographic selectivity while another chelatant [pyridyl-2-azo-4-resorcinol (PAR)] is used as a postcolumn reagent. The metal–PDCA complexes successively eluted from the column are readily dissociated and recomplexation occurs to yield metal–PAR complexes, which are detected spectrophotometrically. This method was applied to the determination of transition metals in the primary coolants of light water nuclear reactors [12] and is compatible with on-line preconcentration to achieve limits of detection lower than 1 ppb [13]. It was assumed that anion exchange is the dominant retention mechanism [14], although no evidence was given.

The purpose of this work was to determine the chromatographic behaviour of some transition metals, Fe(III), Ni(II), Co(II), Cu(II) and Zn(II), when determined by this complex method. Mathematical models were developed to evaluate the relative contributions of the cation- and anion-exchange mechanisms to their retention.

2. Experimental

PDCA was purchased from Fluka and PAR from Merck. All other chemicals were of Suprapur grade from Merck. Standard solutions of metals were prepared by dilution of Specpure standard solutions from Johnson Matthey (1 g l^{-1}). They were acidified to pH 2 with HNO_3. The water used throughout these experiments was purified with a Milli-Q system (Millipore).

The chromatographic set-up consisted of an ActIon Analyser (Waters) including an inert Model 625 pump driven by a Model 600E controller unit. The built-in injector (Waters Model 125) was equipped with a 100-μl loop. A reagent delivery module (RDM) (Waters) was connected to the flow stream at the column outlet via a T-shaped connector; the postcolumn reagent was delivered by argon pressure. Detection was performed with a diode-array detector (Waters Model 990) set at 520 nm unless stated otherwise.

The experiments were carried out on a CG5 (guard) + CS5 (analytical) set of columns (Dionex). In this type of resin, quaternary ammonium and sulfonate functional groups co-exist in the pellicular layer located on the core of the bead [15,16]. The cation- and anion-exchange capacities are 0.071 and 0.033 mequiv./ml resin, respectively. A MFC-1 column (Dionex) was inserted upstream from the injector for eluent purification. The purely anion-exchange set of columns was an AG4A (guard) + AS4A (analytical), of quaternary ammonium type (Dionex).

The determination of the transition metals was carried out with the following optimized mobile phase (denoted E_0): $6 \cdot 10^{-3}$ *M* PDCA – $5 \cdot 10^{-2}$ *M* CH_3COOH–$5 \cdot 10^{-2}$ *M* CH_3COONa pumped at a flow-rate of 1 ml min^{-1}. Various eluent compositions were used to test for the models and will be stated when needed. The postcolumn reagent was delivered at a flow-rate of 0.4 ml min^{-1}. It consisted of $4 \cdot 10^{-4}$ *M* PAR–3 *M* NH_3–1 *M* CH_3COOH (pH 9.7). The transition metal cations were injected in a single run at a concentration of 100 μg l^{-1} each.

3. Results and discussion

In the following AcO^- denotes acetate and HA^- and A^{2-} the two ionic forms of PDCA. Charges will be omitted in formulae for ease of reading.

3.1. Mobile and stationary phase compositions

PDCA is a diacid, $pK_2 = 2.10$ and $pK_1 = 4.68$ at 20°C, for an ionic strength $I = 0.1$ *M* [17]. The pK_A of acetic acid under the same conditions [18], 4.65, was checked experimentally. From these data, the equilibrium composition of the eluent E_0 can be deduced (Table 1). In this medium, all the investigated transition metals are predominantly in the form of the anionic

Table 1
Composition of the mobile and stationary phases in the determination of transition metals by ion chromatography on the CS5 column

Species	Eluent E_0	Resin
[Na]	$5.00 \cdot 10^{-2}$ $M = 5.00\ 10^{-2}$ mequiv. ml^{-1}	0.0710 mequiv. ml^{-1} (100%)
[HA]	$3.96 \cdot 10^{-3}$ $M = 3.96\ 10^{-3}$ mequiv. ml^{-1}	
[A]	$2.04 \cdot 10^{-3}$ $M = 4.08\ 10^{-3}$ mequiv. ml^{-1}	0.0245 mequiv. ml^{-1} (74%)
[AcOH]	$5.86 \cdot 10^{-2}$ M	
[AcO]	$4.15 \cdot 10^{-2}$ $M = 4.15\ 10^{-2}$ mequiv. ml^{-1}	0.0085 mequiv. ml^{-1} (26%)

complexes MA_2^{2-} (divalent cations) and FeA_2^- [Fe(III)].

The only cationic species in the eluent E_0 are Na^+ and H^+. According to their respective concentrations in solution ($[Na]_s = 5 \cdot 10^{-2}$ M and $[H]_s = 3.2 \cdot 10^{-5}$ M) and orders of affinity versus most sulfonated resins ($Na^+ > H^+$), sodium is likely to be the only cation involved in a cation-exchange mechanism with metals. This will be true for every eluent where $[Na]_s$ is at least ten times $[H]_s$. As a consequence,

$$[Na]_r = Ce_c = 0.071 \text{ mequiv. } ml^{-1}$$

where the subscript r represents the resin and Ce_c is the cation-exchange capacity of the mixed-bed stationary phase.

There are three competing exchangeable anions in the eluent: AcO^-, HA^- and A^{2-}. In order to determine the selectivity coefficients between these species, a 10^{-5} M solution of PDCA was injected on to the column and eluted with acetate buffer at different pH values. In this mobile phase, the concentration of AcO^- was maintained constant at 0.1 M and the pH was adjusted by adding increasing concentrations of AcOH. Spectrophotometric detection at 270 nm was applied. The distribution coefficient of the eluted species was measured.

If both HA^- and A^{2-} are involved in an exchange mechanism, the conditional distribution coefficient D_A of PDCA must take into account its two ionic species:

$$D_A = \frac{[HA]_r + [A]_r}{[H_2A]_s + [HA]_s + [A]_s}$$

Fig. 1 shows the evolution of the logarithm of the distribution coefficient of PDCA as a function of the eluent pH. When A^{2-} is largely predominant in the aqueous phase, i.e., for pH values higher than 6, a plateau is observed; this is evidence for the predominance of the dianionic form of PDCA in the resin. In this pH range, D_A may be simplified to

$$D_A = \frac{[A]_r}{[A]_s}$$

From the mean value of D_A for pH > 6 and knowing that $[AcO]_s = 0.1$ M, and $[AcO]_r = Ce_a = 0.033$ mequiv. ml^{-1}, where Ce_a is the anion-exchange capacity of the resin, the selectivity coefficient between A^{2-} and AcO^-, K^A_{2AcO}, can be deduced:

$$K^A_{2AcO} = \frac{[A]_r[AcO]_s^2}{[A]_s[AcO]_r^2} = 135 \pm 25$$

When the pH value is decreased to below 4.7, A^{2-} is transformed into HA^- in the mobile phase. Owing to the higher affinity of the resin for A^{2-} than for HA^-, protonation in the stationary phase does not occur: a plateau that would similarly correspond to the predominance of HA^- in both phases is not observed in Fig. 1. Between pH 3.3 and 4.3, A^{2-} remains the unique PDCA species in the resin.

The composition of the stationary phase in contact with the eluent E_0 used for transition metal determination can then be deduced (Table 1).

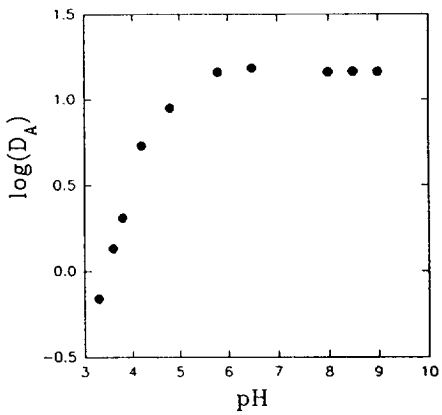

Fig. 1. Influence of the pH on the distribution coefficient of PDCA. Chromatographic conditions: column, CG5 + CS5; mobile phase, 0.1 *M* AcONa (pH adjusted with AcOH or NaOH); flow-rate, 1.0 ml min^{-1}; detection, UV at 270 mm; injection loop, 100 μl; PDCA, 10^{-5} *M*.

3.2. Retention models for transition metals

Under the conditions chosen for their analytical separation, the transition metals occur exclusively as their MA_2^{2-} complexes [FeA_2^- for Fe(III)] in the mobile phase. Since both anion- and cation-exchange sites co-exist on the resin, the metals may be retained as M^{2+}, Fe^{3+} or FeA^+, or as their anionic complexed form, considering that, for a pellicular resin, the distribution of the neutral form MA may be neglected. For both hypotheses, a model was developed and tested. The validation experiments consisted in selected alterations of the mobile phase and quantification of the subsequent effects on the retention of the transition metals. Models will be exposed first, followed by a description of the experiments and a discussion of the fitting results.

Hypothesis of cation exchange

The model developed here compares with that proposed by Haddad and Foley [19] for divalent cations eluted from a cation-exchange column with an eluent containing a single competing cation and a complexing ligand. This model was recently adapted to a more complex elution pattern, taking into account multiple ionic eluents [20].

Here, Na^+ is the exchangeable competing ion in the resin. Given a divalent metal, M^{2+}, the equilibria involved are

$$M_s^{2+} + 2A_s^{2-} \rightleftharpoons MA_{2s}^{2-} \quad \beta_2^M = \frac{[MA_2]_s}{[M]_s[A]_s^2} \tag{1}$$

$$2Na_r^+ + M_s^{2+} \rightleftharpoons M_r^{2+} + 2Na_s^+ \quad K_{2Na}^M = \frac{[M]_r[Na]_s^2}{[M]_s[Na]_r^2} \tag{2}$$

Following the hypothesis of a cation-exchange mechanism, M^{2+} is the only metal species allowed to enter the resin while MA_2^{2-} is the predominant species in solution, by at least three orders of magnitude under the conditions of our experiments. The distribution coefficient of the metal is

$$D_M = \frac{[M]_r}{[MA_2]_s} \tag{3}$$

Substitution of Eqs. 1 and 2 in Eq. 3 yields

$$D_M = K_{2Na}^M \cdot \frac{[Na]_r^2}{[Na]_s^2} \cdot \frac{1}{\beta_2^M [A]_s^2} \tag{4}$$

Since $[Na]_r$ is equal to the cation-exchange capacity Ce_c, we obtain from Eq. 4

$$\log D_M = \log K_{2Na}^M + 2\log Ce_c - 2\log[Na]_s - \log \beta_2^M - 2\log[A]_s \tag{I}$$

The distribution coefficient of the metal is a function of the concentration of the competing cation and that of the complexing agent in the mobile phase.

In the case of Fe(III), two cationic species may be retained on the resin:

$$Fe_s^{3+} + 3Na_r^+ \rightleftharpoons Fe_r^{3+} + 3Na_s^+$$

$$K_{3Na}^{Fe} = \frac{[Fe]_r[Na]_s^3}{[Fe]_s[Na]_r^3} \tag{5}$$

$$FeA_s^+ + Na_r^+ \rightleftharpoons FeA_r^+ + Na_s^+$$

$$K_{Na}^{FeA} = \frac{[FeA]_r[Na]_s}{[FeA]_s[Na]_r} \tag{6}$$

Combining the expression of the corresponding distribution coefficient, $D_{Fe} = ([Fe]_r + [FeA]_r)/[FeA_2]_s$ with Eqs. 5 and 6 and the complexation

constants in the solution ($K_1^{Fe} = [FeA]_s/[Fe]_s[A]_s$ and $\beta_2^{Fe} = [FeA_2]_s/[Fe]_s[A]_s^2$), and still assuming that $[Na]_r$ is equal to the cation-exchange capacity Ce_c, the following equation is obtained:

$$D_{Fe} = K_{3Na}^{Fe} \cdot \frac{Ce_c^3}{[Na]_s^3} \cdot \frac{1}{\beta_2^{Fe}[A]_s^2} + K_{Na}^{FeA} Ce_c \cdot \frac{K_1^{Fe}}{\beta_2^{Fe}[A]_s[Na]_s} \quad \text{(II)}$$

Hypothesis of anion exchange

As determined previously, both AcO^- and A^{2-} potentially participate in an anion-exchange mechanism. In this case, the elution of a divalent metal is governed by the following two equilibria:

$$MA_{2s}^{2-} + A_r^{2-} \rightleftharpoons MA_{2r}^{2-} + A_s^{2-}$$

$$K_A^{MA_2} = \frac{[MA_2]_r[A]_s}{[MA_2]_s[A]_r} \quad (7)$$

$$MA_{2s}^{2-} + 2AcO_r^- \rightleftharpoons MA_{2r}^{2-} + 2AcO_s^-$$

$$K_{2AcO}^{MA_2} = \frac{[MA_2]_r[AcO]_s^2}{[MA_2]_s[AcO]_r^2} \quad (8)$$

The distribution coefficient of a metal, in its complexed form, is given by

$$D_M = \frac{[MA_2]_r}{[MA_2]_s} \quad (9)$$

Since

$$Ce_a = [A]_r + [MA_2]_r + [AcO]_r \quad (10)$$

where $[MA_2]_r$ is negligible, substitution of Eqs. 7, 8 and 9 in Eq. 10 gives

$$Ce_a = \frac{[A]_s}{K_A^{MA_2}} \cdot D_M + \frac{[AcO]_s}{(K_{2AcO}^{MA_2})^{1/2}} \cdot \sqrt{D_m} \quad \text{(III)}$$

The distribution coefficient depends on the concentrations of both competing anions.

In the case of Fe(III), the only difference is in the charge of the complex:

$$2FeA_{2s}^- + A_r^{2-} \rightleftharpoons 2FeA_{2r}^- + A_s^{2-}$$

$$K_A^{2FeA_2} = \frac{[FeA_2]_r^2[A]_s}{[FeA_2]_s^2[A]_r} \quad (11)$$

$$FeA_{2s}^- + AcO_r^- \rightleftharpoons FeA_{2r}^- + AcO_s^-$$

$$K_{AcO}^{FeA_2} = \frac{[FeA_2]_r[AcO]_s}{[FeA_2]_s[AcO]_r} \quad (12)$$

Hence an equivalent expression to Eq. 10 may be written:

$$Ce_a = \frac{[A]_s}{K_A^{2FeA_2}} \cdot (D_{Fe})^2 + \frac{[AcO]_s}{K_{AcO}^{FeA_2}} \cdot D_{Fe} \quad \text{(IV)}$$

Supposing either cation or anion exchange, the concentration of the PDCA and that of the acetate buffer in the mobile phase are independent parameters that determine the value of the distribution coefficient of each metal ion. The form of the dependence will be the discriminating factor that allows one to decide which mechanism is actually governing the retention.

3.3. Variation of the distribution coefficient of the metal ions with the eluent composition

The experimental verification of these models was performed by measurements of the retention time of the investigated metals with different eluting phases. The corresponding distribution coefficients were deduced in the usual way. In the first series of experiments, the concentration of the acetate buffer was varied, all other parameters remaining constant, while in the second series the concentration of the PDCA was the investigated parameter. Initially, interpretations will concern divalent metals only; the behaviour of Fe(III) will be analysed separately.

Influence of concentration of acetate buffer

Each eluent contained a constant concentration of PDCA, $6 \cdot 10^{-3}$ *M*. The concentration of acetate was varied from $4 \cdot 10^{-3}$ to 0.25 *M* and the pH was adjusted to 4.5 by addition of acetic acid. Under these conditions the speciation of PDCA was constant all over the experiments.

Considering a purely cation-exchange mechanism, only $[Na]_s$ varies in Eq. I. Log D_M versus log$[Na]_s$ is expected to be linear with a slope of −2. Fig. 2 shows that such is not the case, and, particularly, the existence of a plateau cannot be explained by the cation-exchange model.

A similar profile is observed (Fig. 3) when log

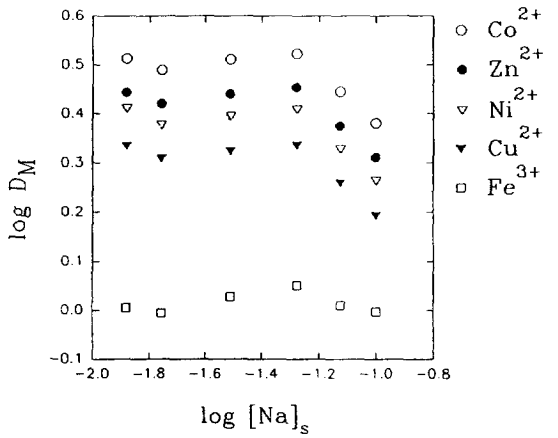

Fig. 2. Variation of the distribution coefficient of the transition metals with $[Na]_s$. Chromatographic conditions: column, CG5 + CS5; mobile phase, $6 \cdot 10^{-3}$ *M* PDCA with AcOH and AcONa at various concentrations (pH 4.5); flow-rate, 1.0 ml min^{-1}; postcolumn reagent, $4 \cdot 10^{-4}$ *M* PAR–3 *M* NH_3–1 *M* CH_3COOH (pH 9.7); flow-rate, 0.4 ml min^{-1}; detection, visible at 520 nm; injection loop, 100 μl.

D_M is plotted versus $\log[AcO]_s$, but this may be explained quantitatively in the frame of an anion-exchange model by the modification of the resin phase. The concentrations of AcO^- and A^{2-} in the resin phase are also displayed (dotted lines).

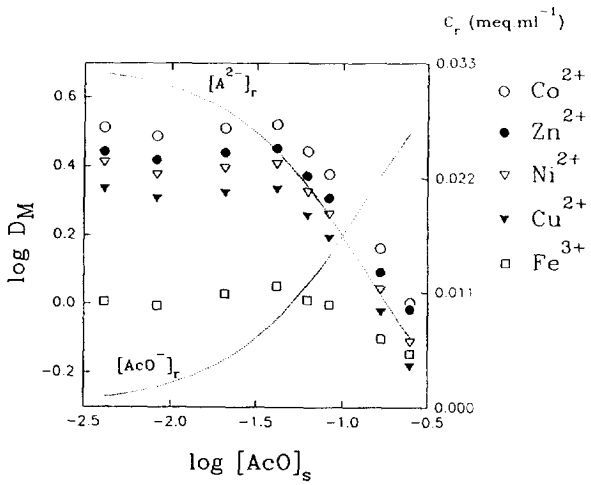

Fig. 3. Variation of the distribution coefficient of the transition metals with $\log[AcO]_s$. Dotted lines: concentrations in the resin of the anionic species of the eluent. Chromatographic conditions as in Fig. 2.

First, the existence of a plateau is evidence for the steady elution behaviour of the analytes as long as $[A]_r$ is the prevailing species ($[A]_r > \frac{3}{4}Ce_a$). In this domain, the retention is governed by the exchange between MA_2^{2-} and A^{2-}, and Eq. III may be simplified to

$$Ce_a = \frac{[A]_s}{K_A^{MA_2}} \cdot D_M$$

where $[A]_s$ has a known constant value of $4.51 \cdot 10^{-3}$ mequiv. ml^{-1}. D_M is constant, and the selectivity coefficients between A^{2-} and each divalent metal cation can be deduced (Table 2).

Second, when $[AcO]_s$ increases, the composition of the stationary phase is modified and $[AcO]_r$ is no longer negligible; a ternary exchange takes place, $[A]_r$ decreases and so does D_M. Eq. III can be rewritten as

$$D_M = -\frac{K_A^{MA_2}}{[A]_s (K_{2AcO}^{MA_2})^{1/2}} \cdot [AcO]_s \sqrt{D_M} + \frac{K_A^{MA_2}}{[A]_s} \cdot Ce_a$$

If D_M is plotted versus $[AcO]_s\sqrt{D_M}$, straight lines are expected with an intercept $K_A^{MA_2}Ce_a/[A]_s$ and a slope $-[K_A^{MA_2}/(K_{2AcO}^{MA_2})^{1/2}[A]_s]$. Fig. 4 shows that linearity is achieved for the highest concentrations of acetate ions in solution, above $3 \cdot 10^{-2}$ *M*, when the acetate ions occupy over 20% of the anion-exchange sites of the resin.

Table 2
Selectivity coefficients between A^{2-} and the PDCA complexes of the divalent metals

Experiment	Cu	Ni	Zn	Co
I	0.34	0.40	0.44	0.52
II	0.36	0.42	0.46	0.55
III	0.34	0.40	0.44	0.52
Mean	0.35 ± 0.03	0.41 ± 0.04	0.45 ± 0.05	0.53 ± 0.05

Values deduced from different experiments: I = variation of $[AcO]_s$, exchange with A^{2-} only; II = variation of $[AcO]_s$, exchange with A^{2-} and AcO^-; III = variation of $[PDCA]_s$.

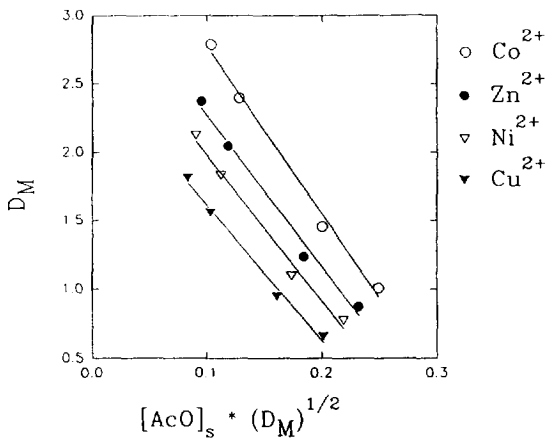

Fig. 4. Variation of the distribution coefficient of the transition metals with $[AcO]_s(D_M)^{1/2}$. Validation of the anion-exchange model for the divalent cations. Chromatographic conditions as in Fig. 2.

The linear part of the curves was fitted to obtain estimates of both $K_A^{MA_2}$ and $K_{2AcO}^{MA_2}$ (Tables 2 and 3); Table 4 gives the values of the selectivity coefficient K_{2AcO}^{A}, as calculated by the ratio of the two former coefficients. $K_A^{MA_2}$ values are in good agreement with those determined from the plateau but the K_{2AcO}^{A} values are larger by ca. 25% than the values determined in the first part of this work.

Influence of concentration of PDCA

In this series of experiments, $[AcOH] = 5 \cdot 10^{-2}$ *M*, $[AcONa] = 5 \cdot 10^{-2}$ *M* and the concentration of PDCA in the eluent was varied from $1.6 \cdot 10^{-3}$ to $1.6 \cdot 10^{-2}$ *M*; the final pH was adjusted to 4.5 with NaOH. Under such conditions, $[AcO]_s$ was constant and equal to $4.15 \cdot 10^{-2}$ M, but $[Na]_s$ varied and its variations were taken into account in the calculations to come.

If the exchange mechanism were of the cation-exchange type for the divalent metals, straight lines with a slope of −2 would be expected on plotting $\log D_M + 2 \log[Na]_s$ versus $\log[A]_s$ (Eq. I). In Fig. 5, straight lines are observed but with a slope of −0.6. This result confirms that cation

Table 3
Selectivity coefficients between AcO^- and the PDCA complexes of the divalent metals

Experiment	Cu	Ni	Zn	Co
II	65	75	84	97
III	59	71	84	96
Mean	62 ± 6	73 ± 7	84 ± 8	96 ± 9

Values deduced from different experiments: II = variation of $[AcO]_s$; III = variation of $[PDCA]_s$. See text for details.

Table 4
Selectivity coefficients between AcO^- and A^{2-}

Experiment	Cu	Ni	Zn	Co
II	181	179	183	176
III	174	178	191	185
Mean	181 ± 15			

Values deduced from the retention behaviour of the divalent metals in different experiments: II = variation of $[AcO]_s$; III = variation of $[PDCA]_s$. See text for details.

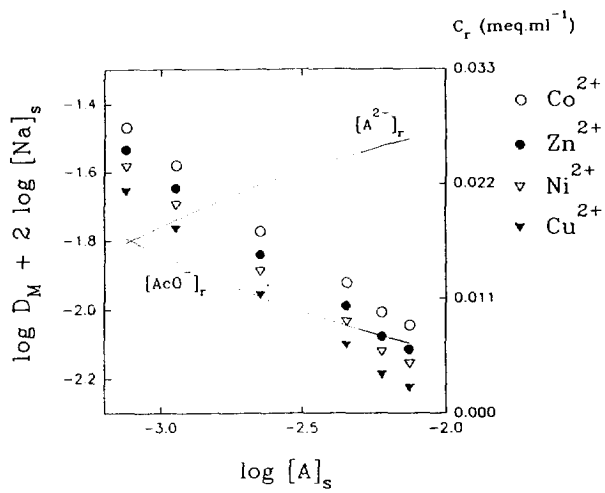

Fig. 5. Variation of $\log D_M + 2 \log[Na]_s$ versus $\log[A]_s$ for the divalent cations. Chromatographic conditions: column, CG5 + CS5; mobile phase, $5 \cdot 10^{-2}$ *M*–AcOH, $5 \cdot 10^{-2}$ *M* AcONa with PDCA at various concentrations (pH 4.5, adjusted with NaOH); flow-rate, 1.0 ml min^{-1}; postcolumn reagent, $4 \cdot 10^{-4}$ *M* PAR–3 *M* NH_3–1 *M* CH_3COOH (pH 9.7); flow-rate, 0.4 ml min^{-1}; detection, visible at 520 nm; injection loop, 100 μl.

exchange cannot account for the retention behaviour of divalent metals.

On plotting log D_M as a function of log$[A]_s$ (Fig. 6), a steady decrease can be observed with a slope reaching −1 in the region where A^{2-} prevails in the resin ($[A]_r > \frac{3}{4}Ce_a$). In this region, the exchange with acetate can be omitted and Eq. III can be simplified to

$$Ce_a = \frac{[A]_s}{K_A^{MA_2}} \cdot D_M$$

$$\log D_M = \log K_A^{MA_2} + \log Ce_a - \log[A]_s$$

The observed linear relationship between log D_M and log$[A]_s$ confirms the theoretical model.

The rest of the plot can be represented according to the following expression of Eq. III:

$$[A]_s D_M = -\frac{K_A^{MA_2}[AcO]_s}{(K_{2AcO}^{MA_2})^{1/2}} \cdot \sqrt{D_M} + Ce_a K_A^{MA_2}$$

Fig. 7 shows that $[A]_s D_M$ does not vary with $\sqrt{D_M}$ over the first three points (no exchange with AcO). The remaining points for each cation lie on a straight line that corresponds to anion exchange of MA_2^{2-} with both AcO^- and A^{2-}. Estimates of $K_A^{MA_2}$ and $K_{2AcO}^{MA_2}$ can be deduced from regression analysis (Tables 2, 3 and 4) and

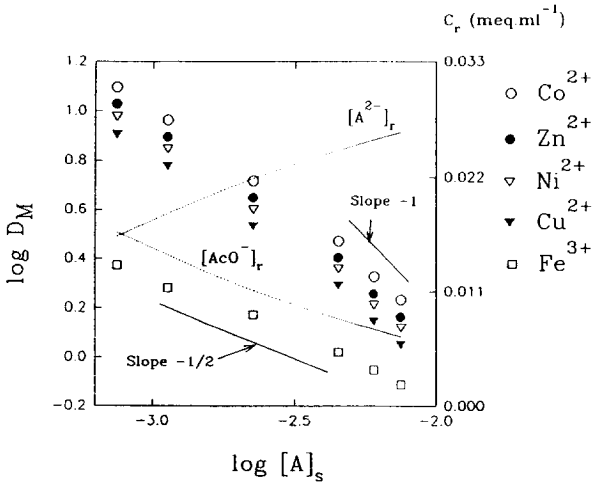

Fig. 6. Variation of the distribution coefficient of the transition metals with log$[A]_s$. Dotted lines: concentrations in the resin of the anionic species of the eluent. Chromatographic conditions as in Fig. 5.

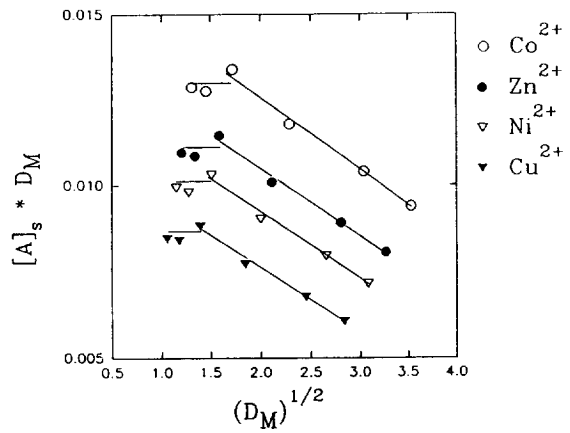

Fig. 7. Variation of $[A]_s D_M$ with $(D_M)^{1/2}$. Validation of the anion-exchange model for the divalent cations. Chromatic conditions as in Fig. 5.

the calculated values are in good agreement with those obtained from the previous series of experiments. Proposed mean values for the selectivity coefficients are also given in the corresponding tables.

From both series of experiments, it appears that the divalent cation complexes undergo an anion-exchange process in the column, the competing anions being AcO^- and A^{2-}.

Retention of Fe(III)

The behaviour of Fe(III) was studied separately, according to the models developed previously. Fig. 2 shows that, in the first series of experiments, D_{Fe} is almost constant when $[Na]_s$ varies over nearly one decade. This is not compatible with the cation-exchange model, which shows a strong dependence of the distribution coefficient on the concentration of the competing cation (Eq. II). Therefore, cation exchange can be excluded as the unique retention mechanism.

As far as the anion-exchange model is concerned, the variation of the distribution coefficient D_{Fe} with the concentration of the acetate in the eluent may be interpreted in the same way as for divalent metals: at low concentrations of acetate, D_{Fe} is constant because of single exchange with A^{2-}; at higher AcO^- concentrations, D_{Fe} decreases owing to the possible additional exchange with acetate ions (Fig. 3). In

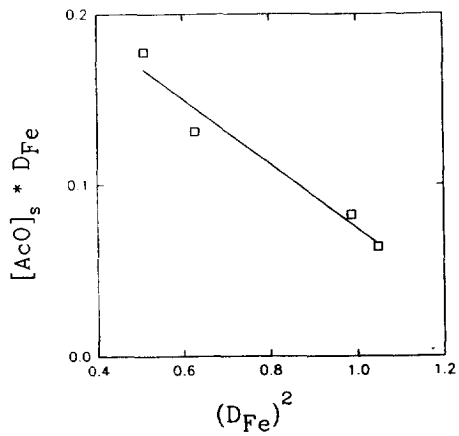

Fig. 8. Variation of $[AcO]_s D_{Fe}$ with $(D_{Fe})^2$. Validation of the anion-exchange model for iron(III). Chromatographic conditions as in Fig. 2.

this region, as suggested by Eq. IV, $[AcO]_s D_{Fe}$ is a linear function of $(D_{Fe})^2$ (Fig. 8). From the slope and intercept, the two selectivity constants were deduced: $K_A^{2FeA_2} = 0.19$ and $K_{AcO}^{FeA_2} = 7.9$.

In the second series of experiments, a linear dependence of log D_{Fe} on log$[A]_s$ with a slope of $-1/2$ (Fig. 6) is observed over the investigated concentration range of PDCA in the eluent. Considering Eq. IV, it can be concluded that the term describing the exchange with AcO^- must be omitted to allow proper fitting of the data. In this instance, only A^{2-} is involved in an anion-exchange mechanism with the Fe(III)–PDCA complexes and Eq. (IV) is reduced to

$$Ce_a = \frac{[A]_s}{K_A^{2FeA_2}} \cdot (D_{Fe})^2$$

This allows one to calculate the value of the selectivity coefficient between FeA_2^- and A^{2-}:

$$K_A^{2FeA_2} = \frac{[A]_s}{Ce_a} \cdot (D_{Fe})^2 = 0.21$$

which is close to the value determined from the first series of experiments.

It can be observed that the selectivity coefficient between acetate and PDCA calculated from these constants ($K_{2AcO}^A = 318$) is higher than the value deduced from the retention data for divalent cations. Although this may be attributed to imprecision of the determination, it is more likely the existence of additional interactions that contribute to the retention of Fe(III) together with the probably prevailing anion-exchange mechanism.

3.4. Comparison with a purely anion-exchange stationary phase

Anion exchange seems to be the prevailing retention mechanism for all the metals investigated. To confirm this result, a mixture of 100 $\mu g\ l^{-1}$ of each investigated cation was injected on to the mixed-bed column and on to a purely anion-exchange column (Dionex AS4A, an aminated styrene–divilbybenzene resin), using the same eluent E_0 in both cases (Fig. 9). For the four divalent species, the elution order is the same and the ratio of the distribution coefficient on the AS4A versus that on the CS5 for each metal is constant: $D_M(AS4A)/D_M(CS5) = 1.06 \pm 0.05$. As the anion-exchange sites on both phases are of the same chemical nature, this result is a good indication of a similar behaviour of the

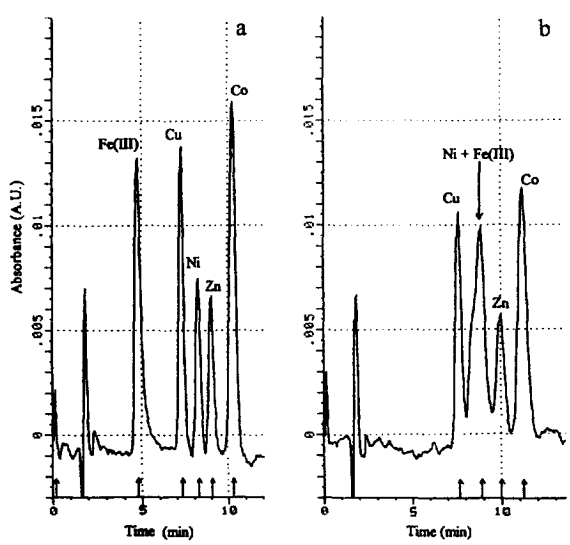

Fig. 9. Comparison of the retention of some transition metals (100 $\mu g\ l^{-1}$) on (a) the CS5 and (b) the AS4A column. Chromatographic conditions: mobile phase, $5 \cdot 10^{-2}$ *M* AcOH–$5 \cdot 10^{-2}$ *M* AcONa–$6 \cdot 10^{-3}$ *M* PDCA (pH 4.5); flow-rate, 1.0 ml min^{-1}; postcolumn reagent, $4 \cdot 10^{-4}$ *M* PAR–3 *M* NH_3–1 *M* CH_3COOH (pH 9.7); flow-rate, 0.4 ml min^{-1}; detection, visible at 520 nm; injection loop, 100 μl.

divalent cations in both chromatographic systems.

Fe(III) is much more retained on the purely anion-exchange resin than on the mixed-bed resin [D_{Fe}(AS4A)/D_{Fe}(CS5) = 2.14], and co-elution with Ni is observed. Complete separation of all the metals is not achieved with this type of resin.

The CS5 column, with a total anion-exchange capacity of 70 μequiv., should retain the anionic chelates more strongly than the AS4A column (20 μequiv.). The calculated distribution coefficient ratios show that such is not the case. Two other interactions can superimpose on ion exchange: (1) electrostatic repulsion between the anionic chelates and the sulfonate groups of the CS5 column (cation-exchange capacity 150 μequiv.) and (2) hydrophobic interactions which are stronger on the low capacity AS4A, and would specially affect the iron chelate, which is less polar than the divalent metal chelates because of its lower charge. Table 5 summarizes the separate contributions of these two interactions to the retention of the Fe(III) and of the divalent metals chelates. It can be inferred from this qualitative analysis that the resulting effect is a severe repulsion for divalent cation chelates on the CS5 column (electrostatic repulsion) that forces their early elution while they tend to undergo a slight additional retention on the AS4A column. Such additional contributions can explain the similar distribution coefficients on both columns, despite the different anion-exchange capacities. For this series of divalent metals, the CS5 column displays what could be termed a "reduced apparent affinity" towards the anion-exchange sites.

Similarly, the odd behavior of the iron chelate may be the result of an increased affinity for the AS4A stationary phase (hydrophobic interactions), while both effects tend to neutralize each other on the CS5 column. Given the similar distribution coefficients of iron and the divalent metals on the AS4A column, hydrophobic interactions certainly play an important part in the retention.

Such a complex behaviour induced by hydrophobic affinity has been observed by other workers [7].

Table 5
Contribution of possible additional interactions to the retention of the transition metals

	Electrostatic repulsion		Hydrophobic interaction		Global effect	
	CS5	AS4A	CS5	AS4A	CS5	AS4A
MA_2^{2-}	−−	~0	~0	+	−−	+
FeA_2^-	−	~0	+	++	~0	++

− = Decreased retention; + = increased retention; ~0 = little influence on the retention.

4. Conclusion

It can reasonably be concluded that on the CS5 mixed-bed column, the retention of transition metal cations is governed by electrostatic forces. Under the conditions of the recommended procedure (eluent E_0), the divalent metals and iron(III) follow an anion-exchange process involving their anionic PDCA chelates and the free divalent ligand. However, electrostatic repulsion between the cation-exchange sites and the chelates tends to decrease their "apparent affinity" for the resin, particularly for the divalent metal chelates. On a purely anion-exchange low-capacity phase, the contribution of hydrophobic adsorption is significant: the iron chelate is strongly retained and interferes with the divalent metal chelates, leading to an incomplete separation.

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