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Prediction of inorganic and organic ion behaviour with polyvalent eluents in ion chromatography

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Abstract

A model is presented that relates the capacity factor, k', to experimental stationary and mobile phase elution variables (resin capacity, dry resin mass, dead volume, concentration and pH) and to the protonation constants of the specimens involved. Application of the model to elution with different concentrations of phthalic acid using a low-capacity quaternary ammonium column permits the determination of the selectivity coefficients of each ion-exchange equilibrium and the establishment of the theoretical k' (pH) curves at a constant eluent concentration, which are seen to coincide with the experimental curves. The model is able to predict solute behaviour and optimize separation by establishing the corresponding acidity conditions. Likewise, this model is a possible tool for studying ion-exchange and non-polar interactions of ions with ion-exchange columns.

1. Introduction

Selectivity coefficients and distribution coefficients are based on ion-exchange equilibria [1]. In liquid chromatography the capacity factor, k', is used as a measure of the elution power of the mobile phase with respect to a solute ion in a given resin. Thus, by relating the capacity factor with the solute and mobile and stationary phase characteristics, expressions may be derived that allow us to predict the corresponding retention times in a particular column on modifying experimental elution variables such as eluent concentration or pH.

Many workers have applied this method to both gravity ion chromatography (gravity-IC) [2] and high-performance ion chromatography (HPIC) [3–5], using monoanionic eluents in all instances, i.e., those giving rise to a single anion-exchange species (ions from strong acids, monovalent ions of weak acids or polyvalent ions operating in a pH range where a single species predominates).

If the sample also contains monoanionic species, the expression $\log k' = \text{constant} - (j/i) \log C$, were C is the eluent concentration and i and j are the eluent and sample ionic charges, respectively, has been systematically applied [6]. This expression is also employed in cation exchanges [7]. Maki and Danielson [8] applied this proportionality to the retention of inorganic ions (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, I^-, SCN^- and SO_4^{2-}) with different naphthalenesulfonic acids as eluents. On comparing the slopes of the

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experimental straight lines, log k' versus log C, applying the theoretical i and j values, they found that with the exception of the monovalent ions using 2-naphthalenemonosulfonic acid ($j/i = 1$), the remaining slopes are all greater than expected. They argued that apparently for both 1,5-naphthalenedisulfonate and 1,3, 6 or 7-naphthalenetrisulfonate, the effective charge of the bulky eluent with two widely spaced sulfonate groups is less than the true charge during the ion-exchange process involving small anions. Likewise, slope discrepancies exist when phthalic acid (pH 6.25) is used as the eluent, in spite of its lesser bulk. In this case, the anion is presumed to exhibit entirely a charge of 2 [9]. A case in point was reported by Haddad and Cowie [10], who employed phthalic acid as the mobile phase at pH 5.3, where the mono- and divalent forms coexist in the same proportion (50%); consequently, they considered the eluent to behave as a single species of charge −1.52. Analogously, Haddad and Cowie regarded the samples as single species possessing a fractional charge of a magnitude dependent upon the protonation constants.

When the sample consists of polyanionic species and the eluent used remains monoanionic, the proportionality between k' and concentration is not direct, as the participation of all the ion species present must be considered in the ion exchange. Beukenkamp et al. [11] deduced an expression corresponding to gravity-IC, although the resulting equation has rarely been applied.

The purpose of this study was to obtain an expression to relate k' to eluent concentration and pH, with the aim of applying it to the general case of polyanionic eluents and samples. To this effect we considered all the ion-exchange reactions that may occur between the ion species present in both the eluent and sample, each being regulated by a factor capable of determining degree of contribution.

At constant pH, pairs of values (k', eluent concentration) are obtained experimentally; on substitution in the mathematical expression they enable us to calculate the corresponding selectivity coefficients, along with the respective contributions of each equilibrium.

Subsequently, and in this case keeping the eluent concentration constant, the corresponding relationship between k' and pH may be established. This in turn facilitates the establishment of acidity conditions for optimum separation.

2. Theory

2.1. Polyprotic eluent

Monoanionic sample anion

Consider a polyprotic eluent, H_nP, with accumulated protonation constants β_i, and a type HA sample with a constant, β_{1A}, operating in a pH range where the different protonated forms of both the eluent and sample may coexist. As initially the resin, R, is associated with the different eluent forms ($R_iH_{n-i}P$, with $1 \leq i \leq n$), the following ion-exchange reactions occur within it:

$$\begin{array}{ll}
A^- + RH_{n-1}P \rightleftharpoons RA + H_{n-1}P^- & x_1 \\
A^- + \frac{1}{2}R_2H_{n-2}P \rightleftharpoons RA + \frac{1}{2}H_{n-2}P^{2-} & x_2 \\
A^- + \frac{1}{i}R_iH_{n-i}P \rightleftharpoons RA + \frac{1}{i}H_{n-i}P^{i-} & x_i \\
A^- + \frac{1}{n}R_nP \rightleftharpoons RA + \frac{1}{n}P^{n-} & x_n
\end{array} \tag{1}$$

In this process each equilibrium participates with a contribution x_i. The global balance is given by the following:

$$\left(\sum x_i\right)A^- + \sum\left(\frac{x_i}{i}R_iH_{n-i}P\right) \rightleftharpoons \left(\sum x_i\right)RA + \sum\left(\frac{x_i}{i}H_{n-i}P^{i-}\right) \tag{2}$$

Taking into account that the condition $\Sigma_{i=1}^{n} x_i = 1$ is always satisfied, the global selectivity coefficient, E, like the equilibrium constant for ion exchange for the global reaction 2, is given by

$$E_0 = \frac{[RA]\cdot[H_{n-1}P^-]^{x_1}\cdot[H_{n-2}P^{2-}]^{\frac{x_2}{2}}\cdot\ldots\cdot[H_{n-i}P^{i-}]^{\frac{x_i}{i}}\cdot\ldots\cdot[P^{n-}]^{\frac{x_n}{n}}}{[A^-]\cdot[RH_{n-1}P]^{x_1}\cdot[R_2H_{n-2}P]^{\frac{x_2}{2}}\cdot\ldots\cdot[R_iH_{n-i}P]^{\frac{x_i}{i}}\cdot\ldots\cdot[R_nP]^{\frac{x_n}{n}}} = \frac{[RA]\cdot\prod[H_{n-i}P^{i-}]^{\frac{x_i}{i}}}{[A^-]\cdot\prod[R_iH_{n-i}P]^{\frac{x_i}{i}}} \tag{3}$$

This selectivity coefficient remain constant with pH.

On the other hand, we define the mass distribution coefficient, D_g, for the exchange of an ion A^- as

$$D_g = \frac{[RA]}{[A^-] + [HA]} = \frac{[RA]}{[A^-] + (1 + \beta_{1A} h)} \tag{4}$$

where $h = [H^+]$. If the ratio $[RA]/[A]$ obtained from Eq. 3 is substituted in Eq. 4, we find that

$$D_g = \frac{E_0}{(1 + \beta_{1A} h)} \cdot \frac{\prod [R_i H_{n-i} P]^{\frac{x_i}{i}}}{\prod [H_{n-i} P^{i-}]^{\frac{x_i}{i}}} \tag{5}$$

In turn, the capacity factor, k', is related to the mass distribution coefficient by the following expression [1]:

$$k' = \frac{t_r - t_0}{t_0} = D_g \cdot \frac{W}{V_0} \tag{6}$$

where W is the dry resin mass and V_0 the dead volume. By substituting the value of D_g obtained in Eq. 5 in Eq. 6, we observe

$$k' = \frac{W E_0}{V_0 (1 + \beta_{1A} h)} \cdot \frac{\prod [R_i H_{n-i} P]^{\frac{x_i}{i}}}{\prod [H_{n-i} P^{i-}]^{\frac{x_i}{i}}} \tag{7}$$

In order to resolve this expression, we must establish the concentrations of each of the n eluent–resin forms. An equation may be developed to show that in the resin phase the total concentration of species occupying active points is reflected by the corresponding exchange capacity, Q. If, moreover, we take into account that the amount of resin-bound sample is negligible (<1%) compared with the amount of associated eluent, then

$$Q = \sum (i [R_i H_{n-i} P]) \tag{8}$$

The remaining $(n-1)$ equations may be defined if as a first approximation we accept that the bond between the eluent species $H_{n-i} P^{i-}$ and the resin is i times more intense than when bonding occurs between two monovalent charges. As the concentration of each resin-bound eluent species is proportional to its concentration in solution, these $(n-1)$ equations are given by

$$\frac{[R_i H_{n-i} P]}{[R H_{n-1} P]} = \frac{i k [H_{n-i} P^{i-}]}{k [H_{n-1} P^-]} \tag{9}$$

On resolving the system represented by Eqs. 8 and 9, we find that

$$[R_i H_{n-i} P] = \frac{Q i \beta_{n-i} h^{n-i}}{n^2 + \sum [(n-i)^2 \beta_i h^i]} \tag{10}$$

The substitution of Eq. 10 in the numerator of the Eq. 7 and of the different eluent species concentrations as a function of their molar fractions in the denominator of Eq. 7 yields the following equation:

$$\begin{aligned} k' &= \frac{W E_0}{V_0 (1 + \beta_{1A} h)} \cdot \frac{\prod \left(\frac{Q i \beta_{n-i} h^{n-i}}{n^2 + \sum [(n-i)^2 \beta_i h^i]} \right)^{\frac{x_i}{i}}}{\prod \left[\frac{C \beta_{n-i} h^{n-i}}{1 + \sum (\beta_i h^i)} \right]^{\frac{x_i}{i}}} \\ &= \frac{W E_0}{V_0 (1 + \beta_{1A} h)} \\ &\quad \cdot \prod \left[\frac{Q i \left(1 + \sum \beta_i h^i \right)}{C \left(n^2 + \sum [(n-i)^2 \beta_i h^i] \right)} \right]^{\frac{x_i}{i}} \end{aligned} \tag{11}$$

where C is the total eluent concentration. This expression contains n unknowns, i.e., the $(n-1)$ contributions x_i of each equilibrium to the total ion exchange and the value of the global selectivity coefficient, E_0.

Resolution of this expression requires the determination of the capacity factors of the eluate at different eluent concentrations, operating at a known and constant pH. Under these conditions, the above expression is reduced to

$$k' = P \prod \left[\frac{1}{C} \right]^{\frac{x_i}{i}} = \frac{P}{C^{[\Sigma(\frac{x_i}{i})]}} \tag{12}$$

where P is a constant encompassing the selectivity coefficient, the sample and eluent protonation constants, operating pH, dead volume, resin capacity and resin dry mass. Knowing the contributions x_i and the selectivity coefficient, E_0, Eq. 11 allows us to determine the curves k'(pH) corresponding to a monovalent sample with a polyvalent eluent.

As a particular case, a multiply charged species, behaving within the operating pH range as a monoanionic species, would exhibit the following generic exchange equilibrium:

$$\mathrm{A}^{j-} + \frac{j}{i}\,\mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P} \rightleftharpoons \mathrm{R}_j\mathrm{A} + \frac{j}{i}\,\mathrm{H}_{n-i}\mathrm{P}^{i-} \tag{13}$$

The reasoning is the same as above, but in this case the distribution coefficient is given by

$$D_\mathrm{g} = \frac{[\mathrm{R}_j\mathrm{A}]}{[\mathrm{A}^{j-}]} \tag{14}$$

This yields the following expression:

$$k' = \frac{W}{V_0} \cdot E_0 \cdot \prod \left[\frac{Qi\left(1 + \sum \beta_i h^i\right)}{C\left(n^2 + \sum [(n-i)^2 \beta_i h^i]\right)} \right]^{\frac{jx_i}{i}} \tag{15}$$

When operating at a constant pH, the derived capacity factor is

$$k' = \frac{P}{C^{\left[j \Sigma \left(\frac{x_i}{i}\right)\right]}} \tag{16}$$

This is the expression usually employed for the elution of inorganic ions using likewise totally dissociated inorganic eluents [12], and whose logarithmic representation establishes whether the process is predominantly an ion exchange [13]. On the other hand, the different value of the contributions explains the slope variations observed in some reports [9].

Dianionic sample anion

In this case two exchangeable ionic species exist (A^{2-} and HA^-), whose generic exchange equilibria are expressed by

$$\begin{aligned} &\mathrm{A}^{2-} + \frac{2}{i}\,\mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P} \rightleftharpoons \mathrm{R}_2\mathrm{A} + \frac{2}{i}\,\mathrm{H}_{n-i}\mathrm{P}^{i-} \quad x_{i0} \\ &\mathrm{HA}^- + \frac{1}{i}\,\mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P} \rightleftharpoons \mathrm{RHA} + \frac{1}{i}\,\mathrm{H}_{n-i}\mathrm{P}^{i-} \quad x_{i1} \end{aligned} \tag{17}$$

Each of the n equilibria considered for species A^{2-} contributes with a value x_{i0} to the total process, versus x_{i1} in the case of species HA^-. The global exchange equations are

$$\begin{aligned} &\left(\sum x_{i0}\right)\mathrm{A}^{2-} + \sum\left(\frac{2x_{i0}}{i} \cdot \mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P}\right) \\ &\quad \rightleftharpoons \left(\sum x_{i0}\right)\mathrm{RA} + \sum\left(\frac{2x_{i0}}{i} \cdot H_{n-i}P^{i-}\right) \\ &\left(\sum x_{i1}\right)\mathrm{HA}^- + \sum\left(\frac{x_{i1}}{i} \cdot \mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P}\right) \\ &\quad \rightleftharpoons \left(\sum x_{i1}\right)\mathrm{RHA} + \sum\left(\frac{x_{i1}}{i} \cdot H_{n-i}P^{i-}\right) \end{aligned} \tag{18}$$

with respective selectivity coefficients expressed by

$$\begin{aligned} E_0 &= \frac{[\mathrm{R}_2\mathrm{A}] \cdot \prod [\mathrm{H}_{n-i}\mathrm{P}^{i-}]^{\frac{2x_{i0}}{i}}}{[\mathrm{A}^{2-}] \cdot \prod [\mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P}]^{\frac{2x_{i0}}{i}}} \\ E_1 &= \frac{[\mathrm{RHA}] \cdot \prod [\mathrm{H}_{n-i}\mathrm{P}^{i-}]^{\frac{x_{i1}}{i}}}{[\mathrm{HA}^-] \cdot \prod [\mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P}]^{\frac{x_{i1}}{i}}} \end{aligned} \tag{19}$$

where $\Sigma\, x_{i0} = 1$ and $\Sigma\, x_{i1} = 1$.

In this case the mass distribution coefficient is defined by

$$\begin{aligned} D_\mathrm{g} &= \frac{[\mathrm{R}_2\mathrm{A}] + [\mathrm{RHA}]}{[\mathrm{A}^{2-}] + [\mathrm{HA}^-] + [\mathrm{H}_2\mathrm{A}]} \\ &= \frac{1}{(1 + \beta_{1\mathrm{A}}h + \beta_{2\mathrm{A}}h^2)} \\ &\quad \cdot \left(\frac{[\mathrm{R}_2\mathrm{A}]}{[\mathrm{A}^{2-}]} + \frac{[\mathrm{RHA}]\beta_{1\mathrm{A}}h}{[\mathrm{HA}^-]}\right) \end{aligned} \tag{20}$$

Substituting Eqs. 19 and 20 in Eq. 6 yields

$$\begin{aligned} k' &= \frac{W}{V_0(1 + \beta_{1\mathrm{A}}h + \beta_{2\mathrm{A}}h^2)} \\ &\quad \cdot \left(\frac{E_0 \prod [\mathrm{R}_i\mathrm{H}_{n-i}\mathrm{P}]^{\frac{2x_{i0}}{i}}}{\prod [\mathrm{H}_{n-i}\mathrm{P}^{i-}]^{\frac{2x_{i0}}{i}}} \right. \\ &\quad \left. + \frac{E_1\beta_{1\mathrm{A}}h \prod [R_iH_{n-i}P]^{\frac{x_{i1}}{i}}}{\prod [\mathrm{H}_{n-i}\mathrm{P}^{i-}]^{\frac{x_{i1}}{i}}}\right) \end{aligned} \tag{21}$$

Accepting the same considerations that led to Eq. 10, the latter is substituted in Eq. 21 to give

$$k' = \frac{W}{V_0(1 + \beta_{1A}h + \beta_{2A}h^2)} \cdot \left\{ E_0 \prod \left[\frac{Qi\left(1 + \sum \beta_i h^i\right)}{C\left\{n^2 + \sum \left[(n-i)^2 \beta_i h^i\right]\right\}} \right]^{\frac{2x_{i0}}{i}} + E_1 \beta_{1A} h \prod \left[\frac{Qi\left(1 + \sum \beta_i h^i\right)}{C\left\{n^2 + \sum \left[(n-i)^2 \beta_i h^i\right]\right\}} \right]^{\frac{x_{i1}}{i}} \right\} \tag{22}$$

This general expression contains $2n$ unknowns, i.e., the values of x_{i0} and x_{i1} and the selectivity coefficients E_0 and E_1. Again, in order to determine these values, we operate at a known and constant pH, using several eluent concentrations. In this case the expression may be represented as follows:

$$k' = \frac{P_1}{C^{\Sigma\left(\frac{2x_{i0}}{i}\right)}} + \frac{P_2}{C^{\Sigma\left(\frac{x_{i1}}{i}\right)}} \tag{23}$$

where P_1 and P_2 are constants. Resolution of the expression is possible by applying an algorithm allowing minimum square fitting (provided that $1 \leq i \leq n$ is always satisfied).

Polyanionic sample anion

In the case of an H_mA sample (weak acid with m ionic species), a total of m generic exchange equilibria may be determined; the resulting equation would have m terms symmetric with those of Eq. 22, with $n \cdot m$ unknowns:

Table 1
Protonation constants at 40°C

Acid	Log β_1	Log β_2
Phthalic	5.442	8.420
Acetic	4.769	
Lactic	3.873	
Succinic	5.654	9.842
Malic	5.117	8.561
Tartaric	4.372	7.390
Oxalic	4.338	5.628
Sulfuric	2.01	

Table 2
Contributions and global selectivity coefficients of mono-anionic sample anions

Anion	x_1	x_2	E_0
Acetate	0.637	0.363	0.198
Lactate	0.549	0.451	0.148
Fluoride	0.381	0.619	0.132
Chloride	0.423	0.577	0.220
Nitrite	0.304	0.696	0.381
Bromide	0.265	0.735	0.498
Nitrate	0.252	0.748	0.663
Sulfate	0.165	0.835	0.136

$$k' = \frac{W}{V_0\left(1 + \sum_{j=1}^{m} \beta_j h^j\right)} \cdot \sum_{j=0}^{m-1} \left\{ E_j \beta_j h^j \cdot \prod_{i=1}^{n} \left[\frac{Qi\left(1 + \sum_{i=1}^{n} \beta_i h^i\right)}{C\left\{n^2 + \sum_{i=1}^{n} \left[(n-i)^2 \beta_i h^i\right]\right\}} \right]^{\frac{m-j}{i} x} \right. \tag{24}$$

In theory, this would allow us to determine elution times as a function of pH, and corresponding to any ion-exchange process. However, although the mathematical resolution of this expression is feasible through the application of certain fitting methods, error propagation in the calculation of parameters is greatly amplified; as

Table 3
Contributions and global selectivity coefficients of dianionic sample anions

Anion	x_{10}	x_{20}	x_{11}	x_{21}	E_0	E_1
Succinate	0.349	0.651	0.358	0.642	0.0607	0.183
Malate	0.322	0.678	0.456	0.544	0.0385	0.188
Tartrate	0.426	0.574	0.275	0.725	0.0430	0.231
Oxalate	0.490	0.510	0.570	0.430	0.0649	0.300
Sulfate	0.168	0.832	0.844	0.156	0.1228	7.355

a result, a great volume of precise experimental data would be required.

3. Experimental

We verified the validity of the above equations using phthalic acid as mobile phase as it is very commonly used in ion chromatography.

As solutes we prepared solution mixtures of the different forms studied: completely dissociated inorganic ions (F^-, Cl^-, NO_2^-, Br^- and NO_3^-) that contribute a single ionic species to the ion-exchange equilibria, partially dissociated inorganic ions (SO_4^{2-}) and partially dissociated mono- and divalent organic ions (acetic, lactic, succinic, malic, tartaric and oxalic acids).

3.1. Apparatus

We employed a Shimadzu ion chromatograph consisting of a basic module (HIC-6A) equipped with a manual valve injector (20-μl sample loop) and monopiston pump (LP-6A), temperature control oven for column and detector (CTO-6AS), ion conductivity detector (CDD-6A) and recorder–integrator (C-R6A Chromatopac) for signal processing. pH measurements were performed using a Crison Digilab 517 pH meter.

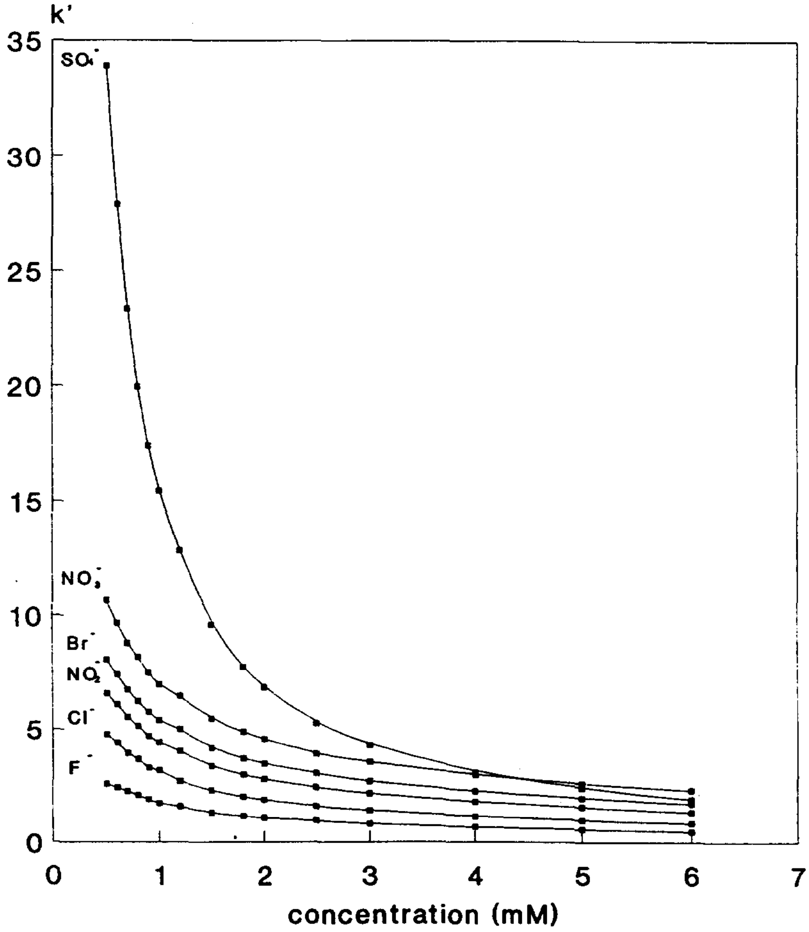

Fig. 1. Variation of k' with phthalic acid concentration with inorganic anions as sample.

3.2. Stationary phase

A Shimpack IC-AI column (100 × 4.6 mm I.D.) filled with quaternary ammonium polymethacrylate (particle size 12.5 μm; mass W = 0.92 g dry resin) was used. This was a low-capacity organic polymer column ($Q = 0.050$ mequiv./g), capable of supporting maximum pressures of 25 kg/cm^2, with an operating temperature of up to 50°C and a wide pH range (2–12).

3.3. Reagents and materials

Phthalic acid was prepared in ultrapure water (Nanopure II, Barnstead), adjusting the pH with tris(hydroxymethyl)aminomethane to limit the increase in background conductivity. Filtering was performed through 0.45-μm membranes with vacuum–ultrasound degasification. The mobile phase flow-rate was 1.5 ml/min; at 40°C, the dead time was 0.82 min, corresponding to the time to the peak injection exit.

Stock standard solutions (1000 mg/l) of the anions were prepared in ultrapure water, using appropriate amounts of the sodium or potassium salts of the inorganic ions or the organic free acids. Dilutions of this stock solution were prepared for both individual and mixed injection. The anion concentrations were 200 mg/l for the

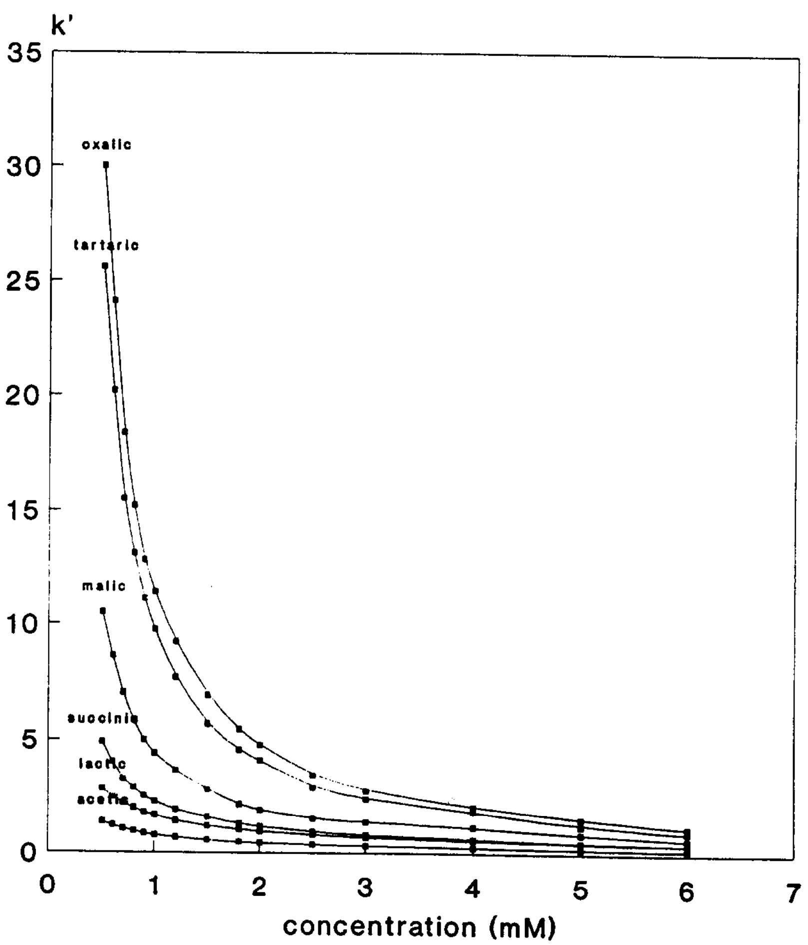

Fig. 2. Variation of k' with phthalic acid concentration with organic anions as sample.

organic ions and 20, 40, 60, 40, 120 and 160 mg/l for F^-, Cl^-, NO_2^-, Br^-, NO_3^- and SO_4^{2-}, respectively.

Table 1 shows the accumulated (40°C) protonation constants of the sample and eluent acids [14].

4. Results and discussion

We have developed a general equation for polyanionic samples and eluents that relates the capacity factor, k', to a number of different variables pertaining to the eluent (pH, C), resin phase (V_0, W, Q) and the eluent (β_i) and sample (β_j) protonation constants. The equation is thus able to determine the retention times of any ion-exchange process as a function of any of these variables.

4.1. k'(C) curves

At constant pH, pairs of values (k', C) are obtained that, when applied to the general equation, provide the selectivity coefficients, E_i, and contributions made by each ion-exchange reaction in the total process.

This method was applied to elutions with phthalic acid ($n = 2$) at pH 4.2 over the concentrations range 6–0.5 m*M*. The capacity factors of each of the anions tested were determined. The corresponding values are shown in Figs. 1 and 2 for inorganic and organic species, respectively.

Monoanionic sample anion

The inorganic anions were evaluated (including SO_4^{2-}, presuming the contribution of HSO_4^- to be negligible), together with acetic and lactic acid. In this case, involving only two unknowns ($n = 2$ and $x_1 + x_2 = 1$), Eq. 16 becomes

$$k' = \frac{P}{C^{\left[i\left(\frac{x_1}{1}+\frac{x_2}{2}\right)\right]}} = \frac{P}{C^{\left(i-\frac{x_2}{2}i\right)}} \tag{16a}$$

which may be linearized, yielding

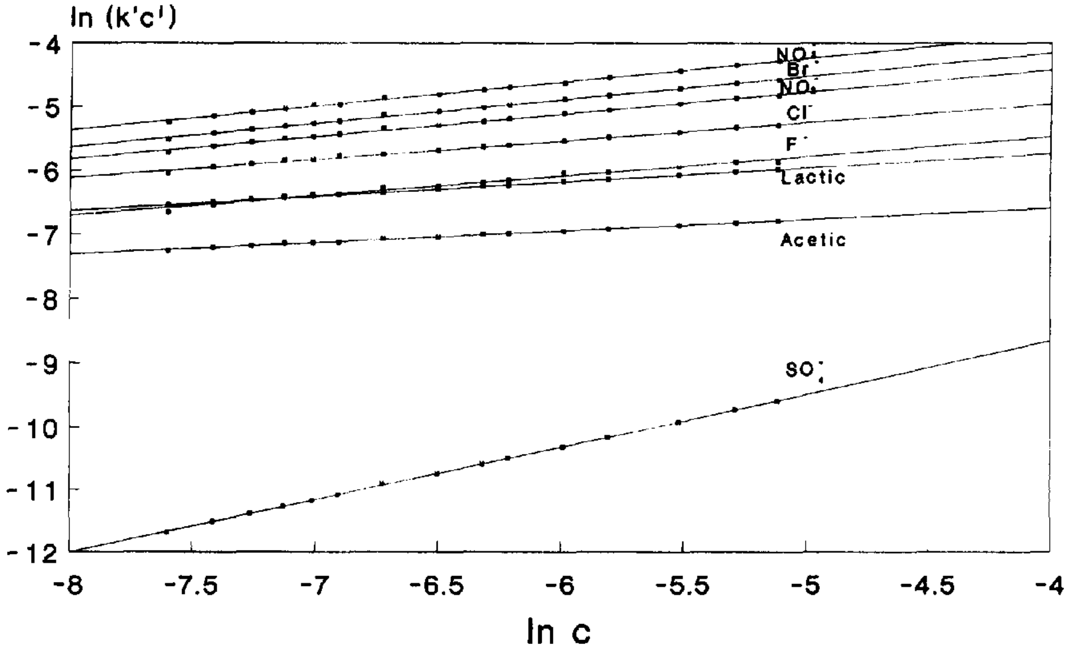

Fig. 3. Plot $\ln(k'c^j)$ vs. $\ln c$; $j = 2$ for sulfate and $j = 1$ for the other anions.

$$\ln(k'C^j) = \ln P + \left(\frac{jx_2}{2}\right) \ln C \qquad (25)$$

where $j = 2$ for sulfate and $j = 1$ for the remaining monoanions (Fig. 3). The linearity resulting in all cases shows the process to be an ion exchange.

This expression is then used to calculate the contribution, x_i, of each exchange reaction, along with the corresponding global selectivity coefficient, E_0, of each component. Table 2 shows the results obtained, which were used to plot the k'(pH) curves for comparison with the respective experimental curves.

The linearity obtained corroborates the validity of the model when applied to dianionic eluents; in the case of the monoanionic ions, it moreover leads to the expression commonly described in the literature.

Dianionic sample anion

When working with succinic, malic, tartaric and oxalic acids, we apply Eq. 23, which requires the application of a fitting method to calculate the parameters implied, since linearization is not possible. By applying the Marquard algorithm [15] we obtain the contributions of the different specimens to the ion-exchange equilibrium, and also the corresponding selectivity coefficients

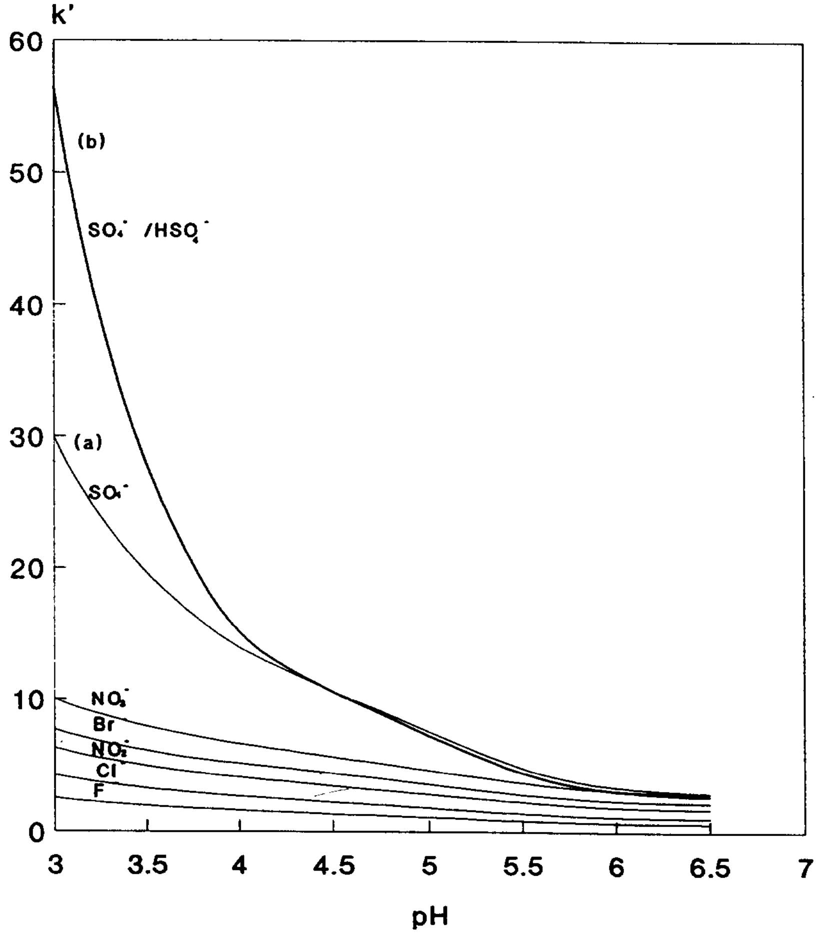

Fig. 4. Theoretical k'(pH) curves for inorganic anions as sample.

(Table 3). Analogously, these values may be used to derive the theoretical curves as a function of pH.

4.2. *k'(pH) curves*

In these cases we plot *k'* versus pH for a constant eluent concentration (1.2 m*M*) (Fig. 4).

Inorganic anions

The corresponding curves are in good agreement with the experimental curves (Fig. 5), with the exception of sulfate (Fig. 4, curve a), which exhibits the greatest deviation. As this cannot be due to having neglected the presence of HSO_4^-, we treat SO_4^{2-} as a dianionic species, obtaining Fig. 4, curve b as a result. This curve is much more similar to the corresponding experimental curve.

Organic anions

The theoretical curves of these acids are shown in Fig. 6. In general, the theoretical curves agree with the corresponding experimental curves (Fig. 7), except for those obtained with the oxalic anion at low pH, where some differences are observed. Likewise, at pH higher than 6 where all anions elute very close together, some changes were detected in the elution order. In these cases other mechanisms besides ionic

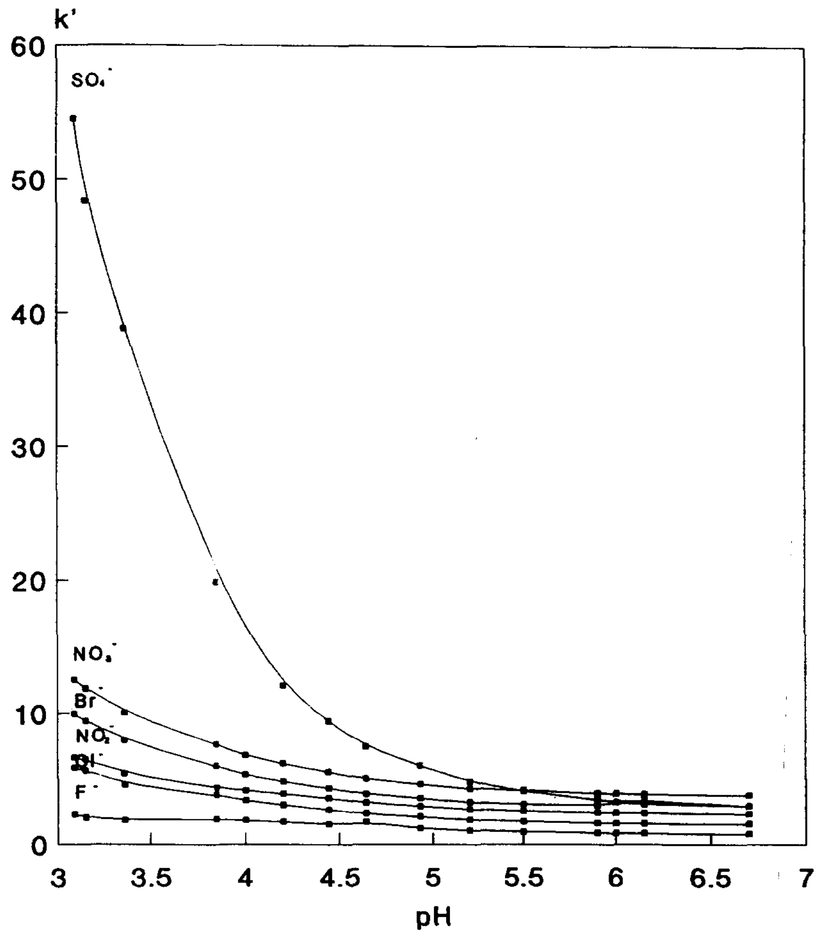

Fig. 5. Experimental *k'*(pH) curves for inorganic anions as sample.

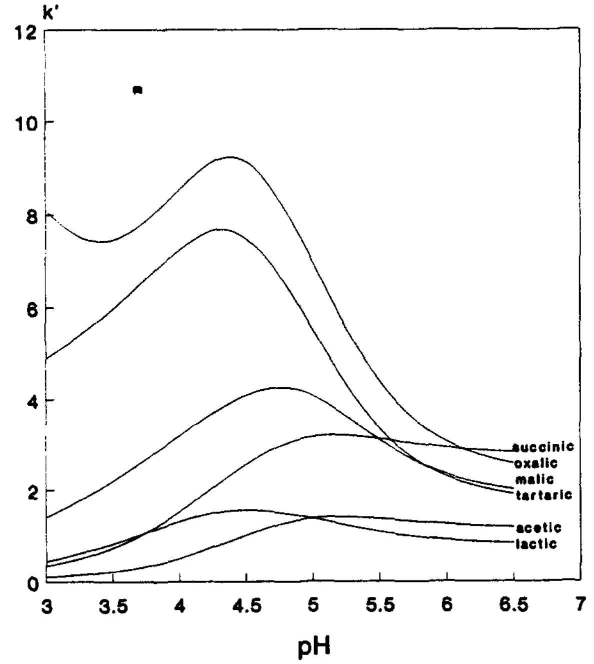

Fig. 6. Theoretical k'(pH) curves for organic anions as sample.

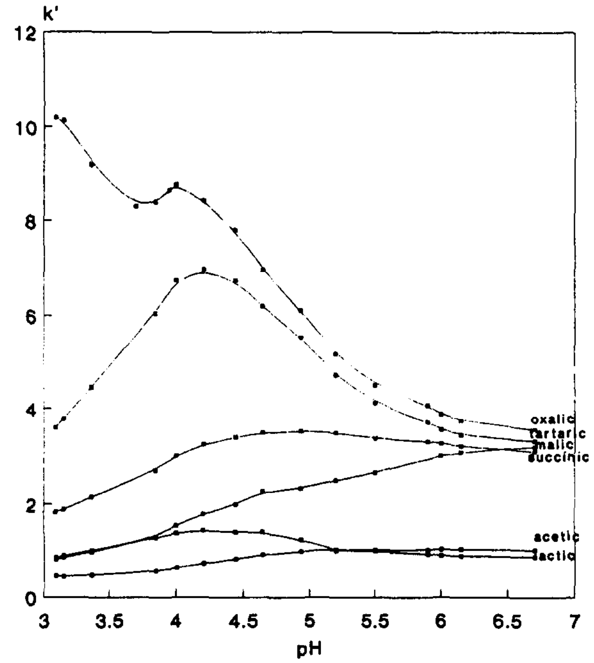

Fig. 7. Experimental k'(pH) curves for organic anions as sample.

exchange are implicated. The non-polar interactions, such as exclusion, are dependent on the size of the substrate cavity and the volume of the sample molecules. It is possible that the selection process by size takes place fundamentally at low pH values, where the concentrations of both the eluent and the sample ions are decreased.

This acceptable agreement between the theoretical and experimental curves for both mono- and dianionic samples allows us to predict the behaviour of the different species through ion chromatography when eluted with polyvalent mobile phases.

For a determinate system, the non-fitting of the model can indicate the existence of non-polar interactions between the substrate, eluent and sample.

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