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## Review

# Retention models in ion chromatography: the role of side equilibria in ion-exchange chromatography of inorganic cations and anions

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### Abstract

Analyte ions (inorganic cations and anions) as well as eluent constituents, can participate in various equilibria in the mobile phase. An effective separation of many metal cations is possible only in the presence of complexing agents forming kinetically labile complexes with the separated ions. The retention and separation of inorganic anions as well as metal complexes may be influenced by employing dissociation/protonation equilibria of analyte species and eluent ions. The role of these equilibria (acid–base and complex-forming) in ion-exchange chromatography is discussed in the present paper. The retention models can be utilized for an optimization of separation and also for an estimation of physical constants. © 1997 Elsevier Science B.V.

*Keywords:* Retention models; Reviews; Stability constants; Equilibrium constants; Inorganic cations; Inorganic anions; Metal complexes

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## 1. Introduction

High-performance liquid chromatography (HPLC) is among the most effective and most frequently used tools for separations and determinations of organic substances (in reversed-phase systems, in the first place). Since the mid-1970s, however, HPLC methods have also played an important role in inorganic analysis. Inorganic compounds, as distinct from organic ones, are usually of ionic nature in solutions, which requires special separation procedures. Various HPLC methods serving for the separation of ionic or ionogenic substances are known under the name ion chromatography (IC) [1]. Three main mechanisms are employed for separations, namely ion-exchange chromatography, ion-interaction chromatography and ion-exclusion chromatography. The following discussion will be focused on the ion-exchange chromatography (IEC), although many conclusions may be generalized to the other IC modes.

Nowadays, many routine environmental, industrial and other analyses require determination of an increasing number of substances in a short time, often in complex matrixes and in a wide range of concentrations, which necessitates chromatographic systems with high separation efficiency. It is well known that the most effective way to influence the separation is to change the stationary phase. Unfortunately, this is not always possible because of a limited assortment and accessibility of chromatographic columns. Hence, a more practicable way is the optimization of the composition of the mobile phase—to change chromatographic ‘software’ instead of ‘hardware’.

Mobile phases in IEC are usually composed of diluted aqueous solutions of acids, bases or salts. Separated ions are retained by electrostatic forces on the surface of the stationary phase, where they compete with ions of the mobile phase bearing charge of the same sign for the active (ion exchange) sites. This distribution of analytes between the stationary and mobile phases is considered the main (primary) equilibrium, whereas equilibria taking place in the mobile phase (acid–base, complex-forming) are considered side (secondary) [2]. The role of the side equilibria in IEC will be discussed in this paper both for cation-exchange as well as for anion-exchange separations. Properties of the stationary

phase, such as column capacity, will be supposed constant (independent on the mobile phase composition), at least in the first approximation valid for strong exchangers, although some models considering e.g. dissociation of functional groups of the sorbent have been published [3] (a typical example is the dissociation of silanol groups of silica gel used as cation exchanger [4]).

## 2. Separation of metal cations

Typically, IC separations of metal cations are carried out on strong, low capacity, cation exchangers. While cations of alkaline and alkaline earth metals can be readily determined e.g. ‘standard cation IC’ [5] using diluted solutions of inorganic acids (nitric acid) as eluents, separations of other di- and polyvalent cations (transition and heavy metals) are almost impossible without presence of complexing agents in mobile phase. A role of complex-forming equilibria in IC of metal cations was discussed in reviews [6,7]. In recent time, a great attention has been paid to explain the relations between an analyte retention and a composition of mobile phases containing complexing agents. Retention models have been developed to describe the retention and separation of metals both on cation exchangers [8–11], as well as on anion exchangers [12–14] and even on mixed-bed resins [15].

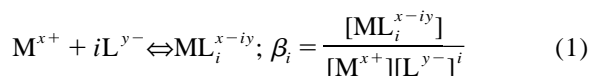
The ion-exchange equilibria on conventional resin-based exchangers in the presence of complexing agents (citric acid, lactic acid, nitrilotriacetic acid) were studied extensively dozens of years ago [16–19]. In modern IC, the relationships were derived between an analyte retention and a mobile phase composition both for cation-exchange [1,10,20–23] as well as for anion-exchange [1,12–14] separations of metals. Hence the development of the retention model for the separation of metal ions in the presence of complexing agents will be only shortly summarized here using a general theory of side equilibria.

The general theory of side equilibria was worked up by Foley and May [24], although some authors previously used a similar approach in reversed-phase liquid chromatography of ionogenic substances [25–27]. More recently, this concept was successfully

applied to the IC separations of metals in complexing media [2,14,23,28]. Jano et al. [29] used a general equation for calculating the dissociation constants of polyprotic acids and bases from retention indices measured in a reversed-phase chromatographic systems.

The development of the model is based on some simplifying assumptions listed in previous work [30]. Probably the most important of them is that the side equilibria are sufficiently fast in comparison with the chromatographic migration. Retention of cations is governed only by the ion-exchange mechanisms. Other presumptions are mentioned in the paper dealing with a computer simulation of ion-exchange chromatography [31].

The complex formation for the metal cation,  $M^{x+}$ , and ligand,  $L^{y-}$ , can be described by the following equation



where  $\beta_i$  are the overall stability constants. After injection of an analyte (metal cation) into the mobile phase containing complexing ligand the equilibrium according to Eq. (1) is established; hence the species carrying positive charge ('free' cations, cationic complexes), neutral complexes as well as negatively charged anionic complexes can co-exist in the mobile phase.

The capacity factor,  $k$ , of the metal cation co-existing in the forms of various complexes,  $ML_i$  in the mobile phase can be expressed as a sum [2]

$$k = \sum_{i=0}^n k_{ML_i} x_{ML_i} \quad (2)$$

where  $k_{ML_i}$  are the limiting capacity factors and  $x_{ML_i}$  are mole fractions of the respective species. Expressing  $x_{ML_i}$  with the aid of the overall stability constants,  $\beta_i$  one obtains (charges are omitted in Eqs. (2) and (3)):

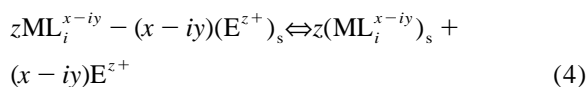
$$k = \frac{\sum_{i=0}^n k_{ML_i} \beta_i [L]^i}{\sum_{i=0}^n \beta_i [L]^i} \quad (3)$$

Eq. (3) is a general one, which holds true both for

cation- as well as for anion-exchange chromatography. It is worth noticing that a formally very similar equation is used to express an effective mobility in capillary electrophoresis (CE) [32].

### 2.1. Cation exchange chromatography

A retention of positively charged species (cationic complexes as well as free metal cations) on a cation exchange column can be described as follows



where  $E^{z+}$  is the eluting cation and the subscript  $s$  refers to the stationary phase. The equilibrium constant for Eq. (4) (selectivity coefficient) is:

$$K_{ML_i}^E = \frac{[ML_i^{x-iy}]_s^z [E^{z+}]^{x-iy}}{[ML_i^{x-iy}]^z [E^{z+}]_s^{x-iy}} \quad (5)$$

Ion-exchange sites on the stationary phase are occupied with the eluting cations and the analyte species. As the amount of the analyte injected on the column is small, the column capacity can be expressed by the simple relation:

$$Q = z[E^{z+}]_s \quad (6)$$

The limiting capacity factor for the species  $ML_i$  is defined as the ratio of its amount in the stationary phase to that in the mobile phase [27]:

$$k_{ML_i} = \frac{w}{V_m} \frac{[ML_i^{x-iy}]_s}{[ML_i^{x-iy}]} \quad (7)$$

$w$  is the mass of stationary phase and  $V_m$  is the volume of mobile phase in the column. When combining Eqs. (3) and (5) with Eq. (7) we obtain after rearrangement:

$$k = \frac{w}{V_m} \frac{\sum_{i=0}^n (K_{ML_i}^E)^{1/z} \left(\frac{Q}{z}\right)^{(x-iy)/z} [E^{z+}]^{(iy-x)/z} \beta_i [L^{y-}]^i}{\sum_{i=0}^n \beta_i [L^{y-}]^i} \quad (8)$$

The general Eqs. (3) and (8) may be simplified for many real chromatographic systems. Most frequently used complexing ligands for separations of divalent

metal cations are anions of weak di- and polycarboxylic acids, such as tartaric, citric, oxalic and pyridine-2,6-dicarboxylic. In those systems, cationic complexes are not formed in the mobile phase (only neutral and negatively charged ones), and the only analyte species taking part in a cation-exchange process is the metal cation. Then  $K_{ML_i}^E = 0$  for  $i > 0$  and Eq. (8) can be written in a more simple form [1,7,10]

$$k = \frac{w(K_M^E)^{1/z} \left(\frac{Q}{z}\right)^{x/z}}{V_m[E^{z+}]^{x/z} (1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n)} = \frac{\alpha_M w}{V_m} (K_M^E)^{1/z} \left(\frac{Q}{z}\right)^{x/z} [E^{z+}]^{-x/z} \quad (9)$$

where  $\alpha_M$  is the coefficient of side equilibria showing the share of the free metal concentration in the total concentration of the metal in the mobile phase,  $c_M$ :

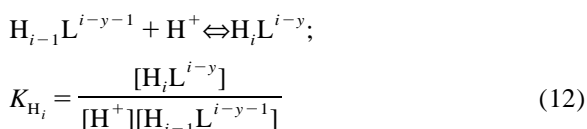
$$\alpha_M = \frac{[M^{x+}]}{c_M} \quad (10)$$

Eq. (9) is often presented in its logarithmic form [8–10,33].

In the case of the separation of divalent metal cations in the presence of monovalent ligands, such as anions of lactic or  $\alpha$ -hydroxyisobutyric acids (HIBA), the cationic complexes of the  $ML^+$  type can be formed in the mobile phase. The following relationship was derived for those systems [22]:

$$k = \frac{w(K_M^E Q^2 + K_{ML}^E Q[E^+]\beta_1[L])}{V_m[E^+]^2(1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n)} \quad (11)$$

Complexing agents employed in this kind of separations are usually weak organic acids, which undergo dissociation (protonation) according to the following equations



where  $K_{H_i}$  are the protonation constants. As the amount of ligand bound to the complexes is small in

comparison with the total amount of ligand in the mobile phase, the total ligand concentration,  $c_L$ , can be expressed:

$$c_L = \sum_{i=0}^y H_i L^{i-y} = [L^{y-}] \sum_{i=1}^y K_{H_i} [H^+]^i \quad (13)$$

On combining Eq. (13) with some of Eqs. (8) and (9) or Eq. (11) we can describe the dependence of an analyte retention on all principal parameters in the cation-exchange chromatography—the concentration of the eluting cation, the concentration and kind of the complexing ligand and the mobile phase pH.

The derived relations can be used for a prediction and optimization of separations and also for an examination of complex-forming equilibria taking place in the mobile phase. Before that, however, it is useful to obtain some additional information on the retention mechanism in the respective system.

### 2.1.1. Study of the retention mechanism

It is reasonable to start an investigation of the separation of metal cations on ion exchangers with measurements of the dependence of an analyte retention on the concentration of an eluting cation. If the side equilibria do not play role in the chromatographic system, the dependence of the logarithm of the capacity factor on the logarithm of the concentration of an eluting ion is a straight line with a slope given by the ratio of the charges of an analyte and eluting ions, as is well known from literature [1,33] and as may be readily derived from Eqs. (8), (9), (11):

$$\log k = C_1 - \frac{x}{z} \log[E^{z+}] \quad (14)$$

The constant  $C_1$  incorporates the column parameters ( $w$ ,  $V_m$ ,  $Q$ ) and the selectivity coefficient  $K_M^E$ . An applicability of Eq. (14) was verified many times [8,34–37] and the linearity of the  $\log k$  vs.  $\log$  (eluent concentration) plots is considered a confirmation that the retention is governed by an ion exchange mechanism. In extensive measurements of Sevenich [38] on low capacity ion exchangers, the slopes of the  $\log$ – $\log$  dependencies differed in some cases significantly from the theoretical values according to Eq. (14). Deviations from theory depend on the diameter of the hydrated cation in the order

$\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$ . According to Gjerde [33], the large radius of the hydrated cations may prevent from penetrating the ion exchanger and exchanging with an equivalent number of functional groups.

It should be noted that many common anions added into the mobile phase to adjust its pH or ionic strength may have a complexing ability, too (e.g. sulfate or chloride), which can also cause deviations from the theoretical dependence predicted by Eq. (14). The effect of the presence of chloride ions was observed in [39] and explained in [28].

Eq. (8) or Eq. (11) can be transformed into the linear logarithmic form even in the presence of complexing agent on condition that the only one kind of analyte species takes part in the ion-exchange process and the ligand concentration is kept constant [30]. The dependencies of  $\log k$  vs.  $\log [\text{E}^{z+}]$  were measured at a constant non-zero concentration of ligand (and at constant pH) only for a limited number of systems [29,40,41]. In Fig. 1, the dependencies of the logarithms of capacity factors on the logarithms of the  $\text{Na}^+$  concentration are presented for some divalent metal cations in the presence of 0.02 M lactate. The measurements were carried out on a  $\text{C}_{18}$  column permanently coated with

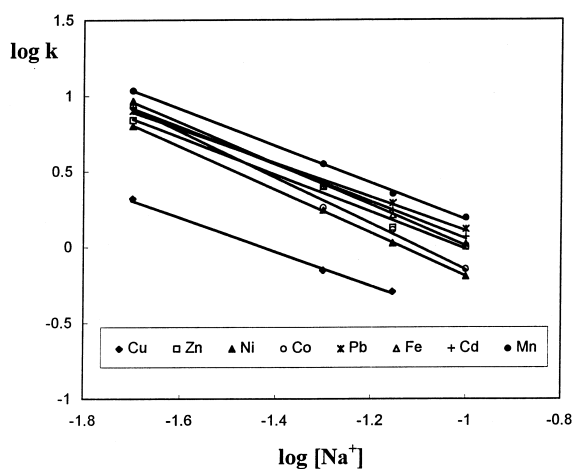


Fig. 1. Dependence of logarithms of capacity factors on logarithms of concentration of eluting cation ( $\text{Na}^+$ ). Column Separon SGX  $\text{C}_{18}$ ,  $30 \times 3$  mm,  $7 \mu\text{m}$ , permanently coated with dodecylsulfate. Mobile phase 0.02–0.1 M  $\text{Na}^+$  + 0.02 M lactic acid (pH  $6 \pm 0.1$ ) adjusted with perchloric acid. Experimental data from [40].

Table 1

Slopes of plots of  $\log k$  vs.  $\log [\text{Na}^+]$

Metal cation	Slope	Metal cation	Slope
$\text{Ni}^{2+}$	-1.42	$\text{Pb}^{2+}$	-1.12
$\text{Zn}^{2+}$	-1.23	$\text{Cd}^{2+}$	-1.24
$\text{Cu}^{2+}$	-1.14	$\text{Fe}^{2+}$	-1.36
$\text{Co}^{2+}$	-1.52	$\text{Mn}^{2+}$	-1.22

Column Separon SGX  $\text{C}_{18}$ ,  $30 \times 3$  mm,  $7 \mu\text{m}$ , permanently coated with dodecylsulfate. Mobile phase  $\text{Na}^+$  + 0.02 M lactic acid (pH  $6 \pm 0.1$ ) adjusted with perchloric acid. Data from [40].

dodecylsulfate; the column exhibits properties of a strong acidic cation exchanger [39]. The slopes of the  $\log k$  vs.  $\log [\text{Na}^+]$  dependence in Table 1 suggest that the separated cations are, at least in some cases, retained on the column in the form of the  $\text{ML}^+$  complexes, which prevail in the mobile phase under given conditions. Similar results were obtained also on a fixed-site cation exchanger for the  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  ions [30]. Alumaa and Pentšuk [41] measured dependence of the adjusted retention times of divalent metal cations ( $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ) on the concentration of eluting cation (ethylenediamine) at the constant concentration of complexing agent (0.006 M tartrate or 0.005 M citrate). The logarithmic plots were straight lines with almost the same slopes for all the metals investigated; the slope for  $\text{Pb}^{2+}$  was estimated at  $\sim -1.85$ , the slopes measured in the presence of citrate were markedly higher in absolute values.

In cases where the logarithmic plot is not linear, it is possible to construct the dependence of the capacity factor on a reciprocal value of the eluting ion concentration and from this dependence one can judge a type and stability of complexes formed in the mobile phase. However, a reliable evaluation of the dependence requires a sufficient number of experimental data. It is not easy to find a suitable experimental arrangement and this kind of dependence is not commonly measured in IC.

### 2.1.2. Prediction of the retention and separation

The goal of every chromatographic process is to gain a sufficient separation of analytes within a reasonable time. A suitable criterion of the quality of separation of two adjacent peaks is a resolution,  $R$  [42]:

$$R = \frac{\sqrt{n}}{4} \frac{\alpha - 1}{\alpha} \frac{k_2}{1 + k_2} \quad (15)$$

$n$  is the number of theoretical plates of the column,  $\alpha$  is the separation factor and  $k_2$  is the capacity factor of the latterly eluted peak. Dependence of capacity factor on a mobile phase composition can be estimated from the retention model using the above presented relationships. Also the separation factor can be readily calculated as a ratio of the capacity factors of the respective peaks. When estimate a column efficiency from several experiments one can predict also the dependence of the resolution on the eluent composition (providing that the column efficiency do not change with the eluent composition).

The principal mobile phase parameters in cation-exchange separations of metal cations, which may be varied independently to the certain degree, are: the concentration of eluting cation, the concentration of complexing ligand and the mobile phase pH. It is commonly accepted in ion-exchange separations of metal cations with non-complexing eluents that the separation factor of cations bearing the same charge does not depend on the concentration of the eluting cation [1]. This also holds true in complexing media on condition that the separated metals are retained on the column in the same form (e.g. either as  $M^{2+}$  or as  $ML^+$  in the case of the separation of divalent cations), which is probably satisfied in many chromatographic systems. An experimental confirmation was accomplished in [41] for tartrate and citrate media and in [40] for the separations of divalent metal cations in the presence of lactate. According to the theory, the resolution decreases slightly with increasing concentration of the eluting cation (decreasing retention). An experimentally assessed decline, however, was not very pronounced in the system with  $Na^+$  as an eluting cation and lactate [40] or HIBA [43] as complexing agents. It is evident that there is not much opportunity to enhance separation by varying the concentration of the eluting cations.

An addition of complexing ligand into the mobile phase decreases the retention of metal cations on a cation exchange column. If the complexes of separated metals with the anions of mobile phase have different compositions and/or stability then the separation improves. The dependence of the capacity factors on the concentration of complexing agent

have been measured in the presence of tartrate [20,41,44,45], citrate [41], lactate [40] and HIBA [23,43]. Orlov et al. [45] have found a linear dependence between the logarithm of the capacity factor and the logarithm of the stability constant of complexes formed in the mobile phase. This linear dependence can be derived e.g. from Eq. (9) under some simplifying presumptions—formation of sufficiently strong complexes and high concentrations of ligands [7,46]. Dependence of the separation factor on the ligand concentration were studied for the separation of lanthanides in the presence of nitrilotriacetic acid (NTA) [47]. The respective relationships were derived in [1,7,47]. Liu and Wang [47] used a generalized equation for the separation factor to optimize the separation of six heavy metals with the aid of a complex ternary eluent containing sodium citrate, sodium tartrate and sodium chloride. Inczédy [48] suggested a calculation method by which the retention and separation characteristics can be predicted from equilibrium constants (ion exchange, protonation and complex formation) in gradient cation exchange chromatography. In [30], the experimentally assessed dependence of capacity factors on the ligand concentration were compared with those predicted from the retention model for the  $M^{2+}$ -tartrate and  $M^{2+}$ -lactate systems.

The dependence of the separation factor for some divalent metal cations separated on a strongly acidic cation exchanger, Separon SGX CX, in the presence of HIBA are shown in Fig. 2. Theoretical dependencies (solid lines) were calculated from the retention model using stability constants measured in [23]. As can be seen, the calculated curves are slightly shifted in comparison with the experimental points, but trends of the dependence are related. The dependence for the  $Zn^{2+}/Ni^{2+}$  pair passes through the maximum, which is typical for the pairs forming different kinds of complexes; it follows from the values of stability constants [23] that  $Zn^{2+}$  ions exhibit a more pronounced tendency to form the higher complexes.

The analyte retention can be effectively governed also by the change of the pH value of the mobile phase. This way is often more convenient than the change of the total ligand concentration. In general, the dissociation of complexing agent increases with increasing pH value and subsequently its complexing

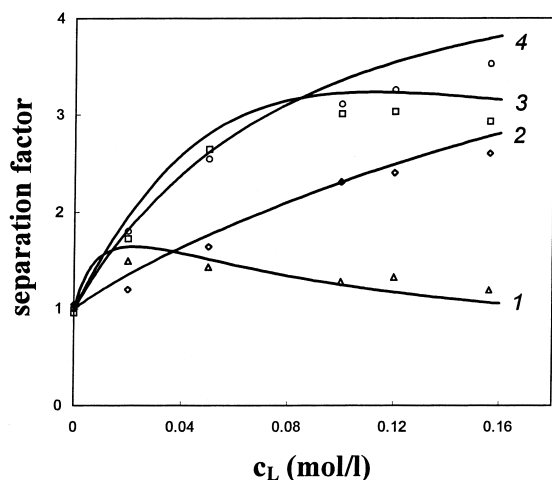


Fig. 2. Dependence of separation factors on total concentration of HIBA. Comparison of predicted dependence (solid lines) with experimental data (points). Column  $150 \times 3$  mm, Separon SGX CX, mobile phase  $0.15$  M NaOH and HIBA ( $\text{pH } 6 \pm 0.05$ ) adjusted with perchloric acid. Experimental data from [43]. 1 =  $\text{Ni}^{2+}/\text{Zn}^{2+}$ , 2 =  $\text{Co}^{2+}/\text{Ni}^{2+}$ , 3 =  $\text{Cd}^{2+}/\text{Co}^{2+}$ , 4 =  $\text{Mn}^{2+}/\text{Co}^{2+}$ .

(pulling) ability increases, too, which causes decreasing the analyte retention. It was shown [23] that the dependence of  $\log(\text{capacity factor})$  vs. pH can be substituted by two (or more) straight lines with an intersect at the pH value corresponding to the dissociation constants of the complexing agent. This kind of dependence was measured for divalent metal cations in the presence of tartrate [41] and HIBA [23] and also for lanthanides in the presence of HIBA [49]. The dependence of the separation factor of divalent metal cations on pH were studied on silica-based and polymer based cation exchangers in the presence of tartrate [50].

In Fig. 3, the dependence of both calculated and measured separation factors and resolution on the mobile phase pH are shown for the  $\text{Zn}^{2+}$  and  $\text{Ni}^{2+}$  ions in the presence of HIBA together with the dependence of the capacity factors on pH. The stability constants and other model parameters were taken from [23]. An agreement between the calculated and measured dependence is satisfactory. The trends are similar to those published in [50]. Since the resolution yields relatively complete and quite useful information on the analyte separability, the dependence of this characteristics on the most important parameters of the mobile phase (pH, total

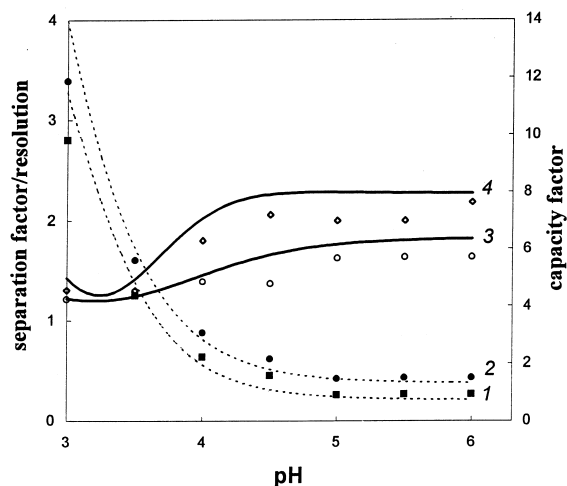


Fig. 3. Dependence of capacity and separation factors and resolution on the mobile phase pH. Column as in Fig. 2, mobile phase  $0.2$  M NaOH and  $0.15$  M HIBA, pH adjusted with perchloric acid. (1) dependence of capacity factor on pH for  $\text{Zn}^{2+}$  ion (2) dependence of capacity factor on pH for  $\text{Ni}^{2+}$  ion (dashed lines calculated from the retention model) (3) dependence of separation factor on pH for the  $\text{Ni}^{2+}/\text{Zn}^{2+}$  pair (4) dependence of resolution on pH for the  $\text{Ni}^{2+}/\text{Zn}^{2+}$  pair (solid lines calculated from the retention model). Experimental data from [43].

concentration of HIBA) was calculated (Fig. 4). In the absence of the complexing agent, or at low pH values when the ligand is present in its undissociated form, the separated metals exhibit an identical retention and the resolution is equal to zero. High

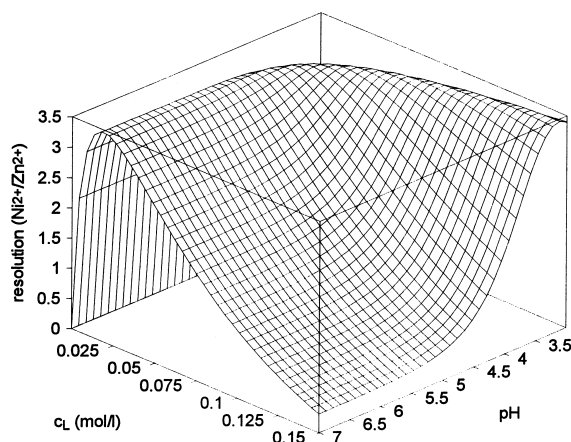


Fig. 4. Dependence of resolution of  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions on pH and total concentration of HIBA at constant concentration of  $\text{Na}^+$  ions.

concentrations of complexing agent, on the other hand, cause decreasing the retention. The analyte peaks come closer and the resolution tends towards zero again.

Relationships between retention and separation characteristics and parameters of the chromatographic system enable optimization of the chromatographic separation. Many chromatographers, however, prefer a 'visual inspection' of chromatograms when assessing the quality of separation. The chromatographic elution curve may be expressed, in the first approximation, by the superimposition of Gaussian distribution curves. With the aid of the retention model the elution curve (chromatogram) can be calculated employing the respective physical constants ( $\beta_i$ ,  $K_{H_i}$ ) and a relatively small amount of experimental data needed for an estimation of parameters of the chromatographic system. In Fig. 5, the calculated chromatogram is compared with an experimentally obtained one for the separation of divalent metal cations in the presence of HIBA. The theoretical curve was calculated for the equimolar mixture of the test metals provided that all the cations produce an equal detector response. However, this was not entirely satisfied in the given detection system, where the post-column derivatization with 4-(2-pyridylazo) resorcinol (PAR) was utilized. The stability constants from [23] were used for the calculations except of that for  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  ions, which were taken from [51] and corrected to the actual ionic strength. The experimental chromatogram was measured in [43]. The peak of the  $\text{Fe}^{3+}$  ion, not involved in the computer simulation, can also be seen in the experimental chromatogram. The agreement between the measured and simulated chromatograms is very good. The quality of the prediction depends on the quality (availability) of the physical constants used for the simulation.

As evident from the above paragraphs, one can obtain valuable information on the separability of metals from the relatively simple retention model. Furthermore, the retention model provides data that can be used to develop a procedure for preconcentrating trace amounts of metals, as suggested by Sarzanini et al. [11].

### 2.1.3. Measurements of stability constants

Ion exchangers have been playing an important

role in investigations of complex-forming equilibria for a very long time. Gunther-Schultze [52] was the first to study the composition and stability of complexes (divalent metal cations with halides) using inorganic ion exchangers. Most of measurements were made with resin-based ion exchangers both in batch as well as in column (gravity-feed) arrangements, as compiled in many reviews and monographs [19,53–55]. Schubert's [56,57] and Fronaeus [58–60] works have laid the foundations for a large amount of ensuring studies devoted to the examination of the properties of metal complexes with the aid of ion exchangers. Relations of modern IC methods to 'classical' ion-exchange investigations are emphasized in the review in [7].

Lin and Horváth [61] first applied the IC method to the measurement of the stability constants of tartrate complexes. Independently of the mentioned work, the possibility of studying the composition and stability of complexes with the aid of the IC method was suggested in [20]. The determinations of the stability constants are based on the measurements of the dependence of capacity factors on the ligand concentration, while the concentration of an eluting cation and pH are kept constant. Under these conditions, Eq. (9) can be rearranged as follows [20–23]

$$\frac{1}{k} = C_2(1 + \beta_1[\text{L}] + \beta_2[\text{L}]^2 + \dots + \beta_n[\text{L}]^n) \quad (16)$$

where all the constant terms are included in the constant  $C_2$ . An experimental arrangement, which enables work at almost constant ionic strength, is described in detail in [21,22]. Papoff et al. [62] studied an effect of the ionic strength on the ion exchange mechanism and applied the IC method to studying the  $\text{Cd}^{2+}-\text{Cl}^-$  and  $\text{Cd}^{2+}-\text{NO}_3^-$  systems.

In most systems investigated the dependence of  $1/k$  vs. ligand concentration were straight lines, which suggests that the only one kind of complex predominates in the mobile phase. Then the stability constants can be simply calculated as a quotient of the line slope and the y-axis intercept. An example of the experimentally assessed dependence of the reciprocal values of capacity factors on the ligand concentration is shown in Fig. 6 for the mobile phase containing malonate as complexing agent (data were taken from [21]). Similar plots were measured and used for calculations of the stability constants of



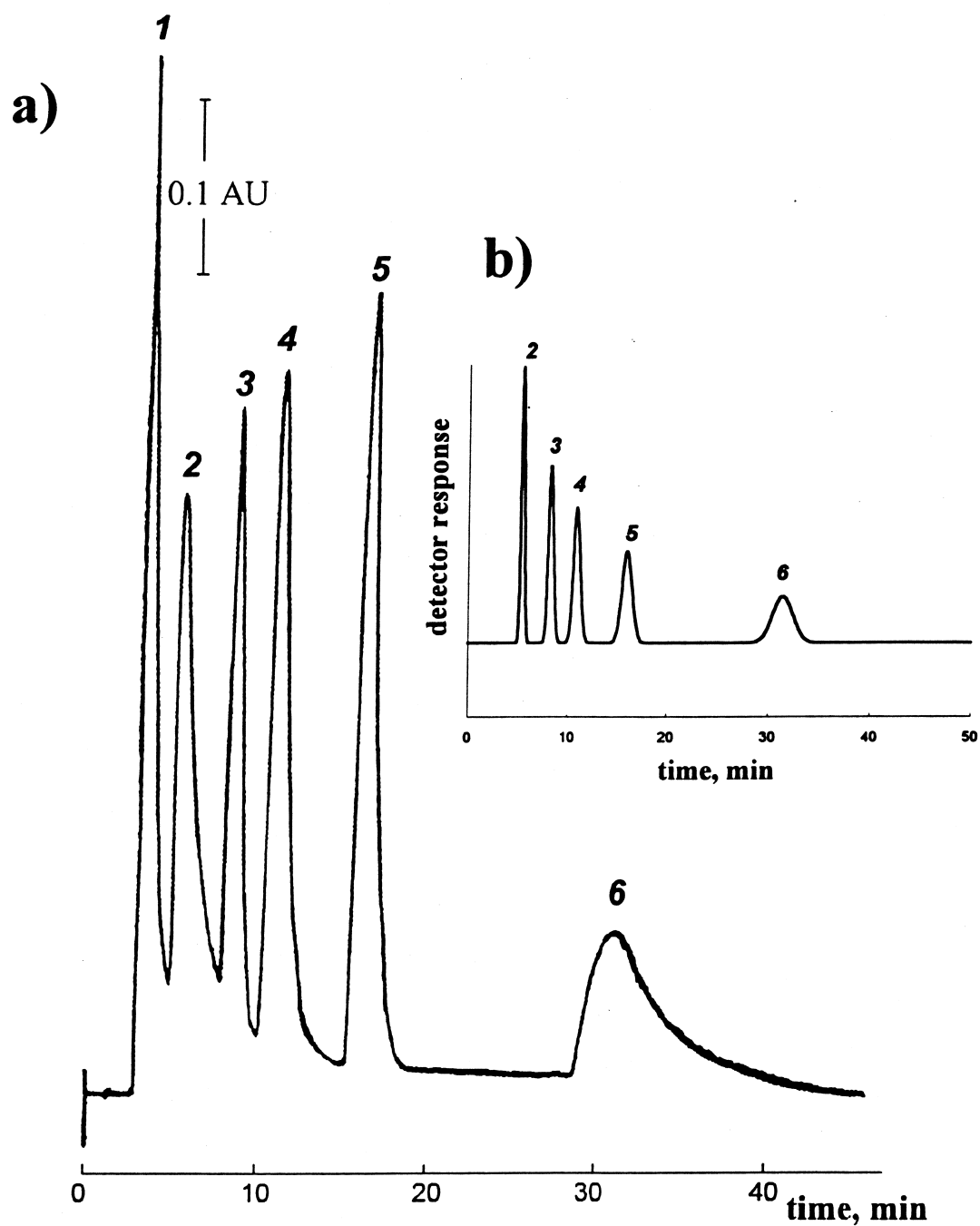


Fig. 5. Separation of the model mixture of cations (0.5 mM each). (a) Experimental chromatogram (from [43]). Column as in Fig. 2, mobile phase 0.15 M NaOH and 0.15 M HIBA (pH 4.97). Photometric detection at 520 nm using post-column derivatization with PAR. (b) Theoretical elution curve calculated from the retention model. 1 =  $\text{Fe}^{3+}$ , 2 =  $\text{Cu}^{2+}$ , 3 =  $\text{Zn}^{2+}$ , 4 =  $\text{Ni}^{2+}$ , 5 =  $\text{Co}^{2+}$ , 6 =  $\text{Pb}^{2+}$ .

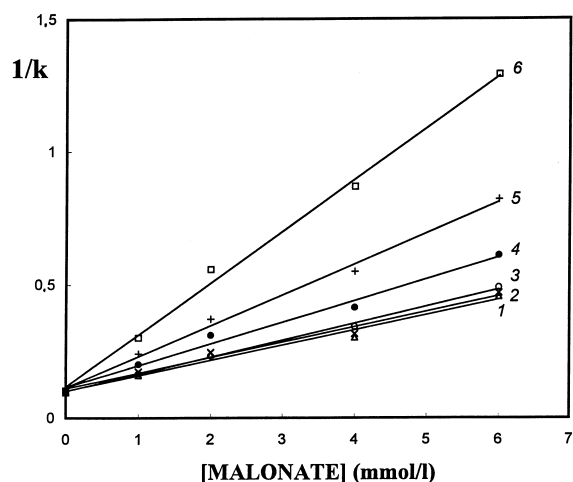


Fig. 6. Dependence of reciprocal value of capacity factors on malonate concentration in mobile phase. Column Separon SGX C<sub>18</sub>, 150×3 mm, 7 μm, permanently coated with dodecylsulfate. Mobile phase 0.1 M Na<sup>+</sup> + malonate (pH 6.5±0.05) adjusted with perchloric acid. 1=Cd<sup>2+</sup>, 2=Mn<sup>2+</sup>, 3=Zn<sup>2+</sup>, 4=Fe<sup>2+</sup>, 5=Co<sup>2+</sup>, 6=Ni<sup>2+</sup>.

metal ions with tartrate, citrate [21,41], oxalate, malonate, pyridine-2,6-dicarboxylate [21], sulfate, thiocyanate [22] and HIBA [23]. The stability constants determined by the IC method for the metal–tartrate complexes in several works are listed in Table 2. Unfortunately, direct comparison is not entirely possible, because the measurements were performed under different conditions (pH, temperature, ionic strength) and in some instances, the exact description of an experimental procedure is not

Table 2

Determination of stability constants of metal–tartrate complexes by IC methods

Ions	log β <sub>1</sub>			
	Ref. [61] <sup>a</sup>	Ref. [20] <sup>b</sup>	Ref. [21] <sup>c</sup>	Ref. [41] <sup>d</sup>
Zn <sup>2+</sup>	2.75±0.03	2.29	2.44±0.06	3.10±0.07
Ni <sup>2+</sup>		2.39	2.41±0.07	3.02±0.10
Co <sup>2+</sup>	2.48±0.02	2.36	2.24±0.01	2.77±0.15
Cd <sup>2+</sup>	2.27±0.01	2.04	2.15±0.03	2.66±0.02
Mn <sup>2+</sup>	1.89±0.04	1.35	1.94±0.02	2.32±0.04
Fe <sup>2+</sup>	2.17±0.0	2.29	2.11±0.01	
Pb <sup>2+</sup>		2.93	2.43±0.04	3.31±0.16

<sup>a</sup> Ionic strength ~1–13 mM, 30°C.

<sup>b</sup> Ionic strength ~0.04 M LiClO<sub>4</sub> (pH 3.6±0.05), 22±1°C.

<sup>c</sup> Ionic strength ~0.1 M NaClO<sub>4</sub> (pH 6.0±0.05), 22±1°C.

<sup>d</sup> Ionic strength ~6–15 mM, 22–25°C.

given. Despite this, IC methods seem to provide comparable results. For the system M<sup>2+</sup>–HIBA, the dependencies were non-linear because of the presence of more kinds of complexes; the stability constants β<sub>1</sub>, and β<sub>2</sub> were calculated using a method of non-linear regression.

The IC methods in an ion-exchange mode seem to be a powerful tool for the determination of stability constants especially in those systems, where only one kind of complex predominates. A similar experimental arrangement was used also in ion-interaction chromatography for an investigation of the metal–oxalate complexes [63].

## 2.2. Metal separations on anion exchangers

Characteristic for many metals is the formation of anionic complexes, which can be retained on anion exchangers. In ‘classical’ separations of metals on open columns, anion exchangers were perhaps even more frequently used than cation exchangers. Both inorganic (halides, sulfates, carbonates, phosphates and even nitrates) as well as organic (tartrates, lactates, HIBA, NTA, etc.) ligands have been used for separations and/or preconcentrations of di- and polyvalent metal cations in the form of their anionic complexes [64,65].

In modern IC, platinum group metals and other noble metals have been determined in the form of their cyano and chloro complexes [66–68]. The separation of anionic complexes with ethylenediaminetetraacetic acid (EDTA) [69,70] and some related complexometric agents, such as 1,2-diaminocyclohexanetetraacetic acid (DCTA), ethylene glycol bis (2-aminoethyl ether) tetraacetic acid (EGTA) or diethylenetriaminopentaacetic acid (DTPA) [71] is very popular. Complexation with EDTA or other complexing agent (pyromellitate [72]) also allows simultaneous determination of metal ions and inorganic anions [13,73]. It is possible, for example, to distinguish between oxidation states of chromium—Cr(VI) is retained as chromate or dichromate anion, whereas Cr(III) is retained as anionic complex with DCTA [74] or EDTA [75].

The general equation derived above (Eq. (3)) holds true also for the anion exchange separation of metal complexes. However, a detailed description of the retention mechanisms is more complicated espe-

cially in those cases where the ligand acts simultaneously as complexing agent and eluting (driving) anion. Very often, the mobile phase is rather complex as it can contain the ligand and/or eluting anion in their various protonated forms. For example, the mobile phase used for the separation of anionic metal–EDTA complexes consisted of the carbonate buffer with pH ~10–11, where three kinds of eluting anions are effective— $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$ ; a sophisticated retention model for this kind of separations worked up Hajós et al. [12,13] using, in principle, a multiple eluent species approach (this concept, together with other related ones, will be discussed later in paragraphs dealing with the anion separations). The dependence of the analyte retention on the mobile phase composition (pH, eluent concentration) were similar to those for simple inorganic anions in the pH range examined by Hajós et al. [12,13]—the retention decreases monotonously with increasing the eluent concentration and pH.

One of the agents that can be used in both cation and anion exchange separations of metals is oxalic acid. Separation of metal–oxalate complexes was studied in [14,76,77], the retention model was developed in [7,14,30]. Under some simplifying presumptions, a mathematical model has been proposed describing the anion exchange separation of oxalate complexes; the derived relationships are rather complex. The computer simulation is presented in [30]. The dependence of the analyte retention on the eluent concentration and pH pass through the maximum. At low concentrations of complexing agent and at low pH values, where oxalic acid is not dissociated, the metal–oxalate complexes cannot be formed and retained on the anion-exchange column. At high pH values, on the other hand, a driving effect of fully dissociated oxalate anions prevails and the retention decreases with increasing eluent concentration and pH. Similar dependencies were measured also for metal–EDTA [71] and metal–pyromellitate [72] complexes. Al-Shawi and Dahl [78] compared the cation-exchange separation of lanthanides in the presence of HIBA with the anion exchange separation of these elements in the form of their anionic oxalate complexes.

The anion-exchange retention mechanisms are rather complicated in real chromatographic systems serving for the separations of metals. Nevertheless,

they can be applied to optimize the separation and also to obtain some information on the composition of complexes from retention data [14]. Modern anion-exchange chromatography (unlike classical applications of anion exchangers [18,79]) is not commonly utilized for an investigation of complex-forming equilibria.

### 3. Separation of inorganic anions

Selectivity coefficients of common inorganic anions on strongly basic anion exchangers are sufficiently different [66,80] and the ‘standard anion IC’ [5] may be successfully applied to solve most of separation problems in an anion analysis. Therefore, there is a relatively little need to improve separations with the aid of interactions in mobile phase. An effect of the nature of the cation on the retention behavior of anions has been studied only rarely [81]. Complex-forming equilibria between the separated anions and the cations of mobile phase are not utilized systematically to influence the separation, except in the special cases of the IC determination of chelating ligands (EDTA, EGTA, DCTA, DTPA) [82] or the ligand-exchange chromatography of amino acids [83]. The separation of W(VI) and Mo(VI) oxoanions was improved using citric acid as an eluent, which was explained by the formation of W(VI)– and Mo(VI)–citrate complexes [84].

In anion-exchange chromatography, an analyte retention is governed mainly by an eluent concentration. The pH value, and thus acid–base equilibria, however, play an important role, too. Several retention models have been proposed to describe the analyte retention in the anion exchange chromatography.

#### 3.1. Retention models

##### 3.1.1. Monoanionic eluents

Some anion separations in IC use a mobile phase containing only one kind of an eluting anion that, moreover, do not participate in any side equilibria, such as dissociation/protonation. Then only one eluting species takes part in an anion exchange process. The dependence of the analyte retention on the eluent concentration is a straight line with a slope

give by the ratio of charges of analyte and eluting ions [1,85] (analogous to Eq. (14)). These dependencies have been measured in many works [1,86–89] and can be used also for an estimation of the charge of more complex ions, such as condensed phosphates [90]. It is also possible to construct the plot of the capacity factor vs. reciprocal of the eluting ion concentration to confirm whether the retention is governed solely by the ion-exchange mechanism [91]. Deviations from theory have been observed in systems with a more complex composition of mobile phase; the reasons will be discussed below.

### 3.1.2. Polyanionic eluents

Most eluents used in anion-exchange chromatography contain two or more eluting anions, e.g. phosphate buffer and a more efficient driving anion, such as perchlorate or sulfate. As was clearly demonstrated in [92], even in a simplified case when none of the eluting anions undergoes acid–base equilibria, the dependence between the capacity factor and eluent concentration cannot be transformed to a linear log–log form. Only when the concentration or eluting power of one eluting anion is negligible do we obtain a common linear dependence  $\log k$  vs.  $\log$  (eluent concentration).

Eluent anions often undergo the dissociation/protonation depending on the pH value, and thus can co-exist in various forms in the mobile phase. Typical example is phthalate eluent in a single-column (non-suppressed) IC. Standard anion carbonate/bicarbonate eluent for suppressed IC anion separations contains three eluting anions— $\text{CO}_3^-$ ,  $\text{HCO}_3^-$  and  $\text{OH}^-$ . Haldna [93] studied the concentrations of these anions sorbed on the anion exchange stationary phase, i.e. the fractions of the resin capacity occupied with the respective anions. Eluents containing either more kinds of eluting anions, or anions co-existing in more than one protonated forms, are called polyanionic [94]. Some of analyte anions (typically phosphate) can also exist in several forms capable to take part in an anion exchange process.

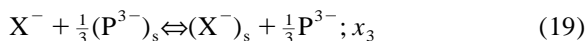
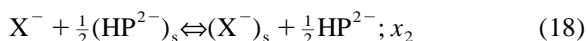
If a chromatographic system contains a polyanionic eluent and/or polyanionic analytes, then the analyte retention depends strongly on the pH value, in addition to the eluent concentration. An eluting capability of the mobile phase increases with increasing pH value (increasing dissociation) and conse-

quently the retention of the monoanionic anions (anions of strong inorganic acids— $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) decreases monotonously. On the other hand, the dependencies may be more complex for the polyanionic analytes, as have been observed for phosphate [95–98], selenite [92,99] and some anions of weak organic acids [94,98].

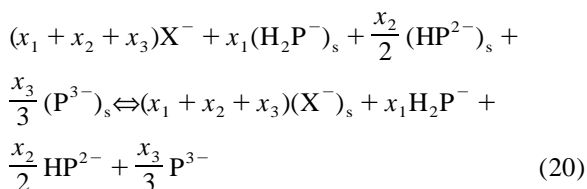
Haddad and Jackson [1] critically reviewed the retention models for the anion-exchange chromatography with polyanionic eluents. The retention models can be divided into three groups: the dominant equilibrium approach [100], the competing ion ‘effective charge’ approach [101–103] and the dual (multiple) eluent species approach. The most successful and generally applicable models are based on the multiple eluent species approach suggested by Hoover [104] and Jenke and Pagenkopf [105,106]. Hirayama and Kuwamoto [99,107] modified Jenke’s method by using the ‘elution system coefficient’ whereas Yamamoto et al. [108] introduced the concept of an ‘inter-eluent separation factor’ into the Hoover’s method. More recently, Jenke [109] modified his previously derived equations replacing the anion’s formal charge with its effective charge and using an empirical relationship between the selectivity coefficient and an analyte’s effective charge. The retention model developed by Mongay et al. [94] relates the capacity factors of analytes to stationary and mobile phase variables using the concept of the ‘global selectivity coefficient’; it was tested on the cases of separations of various inorganic and organic anions with phthalate eluent and an acceptable agreement between predicted and experimental dependencies was achieved. This approach was applied also to the separation of metals in the form of their anionic complexes on an anion-exchange column [30] with the aid of oxalate eluent.

Mongay’s approach seems to be most suitable for the mobile phases containing several ionic species of similar nature (different dissociated forms of the same eluting acid). As an example, the separation of singly charged anions,  $\text{X}^-$ , with an eluent consisting of phosphate buffer will be discussed here. (A more complex system employing mobile phase containing phosphate buffer together with perchlorate anion was evaluated elsewhere [92].) The phosphate-based eluent can contain the following anions:  $\text{PO}_4^{3-}$ ,  $\text{HPO}_4^{2-}$  and  $\text{H}_2\text{PO}_4^-$  (further denoted  $\text{P}^{3-}$ ,  $\text{HP}^{2-}$  and

$\text{H}_2\text{P}^-$ ). The partial ion exchange equilibria between eluting and analyte anions are described:



The subscript *s* refers to the stationary phase again,  $x_1$ – $x_3$  express the contribution of the respective partial reaction to the retention process. The global equilibrium on the column can be expressed:



Taking into account that  $x_1 + x_2 + x_3 = 1$ , the global selectivity coefficient is defined as the equilibrium constant of the global reaction Eq. (20):

$$K_{\text{P}}^{\text{X}} = \frac{[\text{X}^-]_s [\text{H}_2\text{P}^-]_s^{x_1} [\text{HP}^{2-}]_s^{x_2/2} [\text{P}^{3-}]_s^{x_3/3}}{[\text{X}^-] [\text{H}_2\text{P}^-]_s^{x_1} [\text{HP}^{2-}]_s^{x_2/2} [\text{P}^{3-}]_s^{x_3/3}} \quad (21)$$

The protonation of the eluent anion can be expressed by the equations similar to Eq. (12) (protonation constants  $K_{\text{H}1} \dots K_{\text{H}3}$ ). In general, also protonation of the analyte anion has to be taken into account (protonation constant  $K'_{\text{H}1}$ ). The capacity factor is given as the ratio of the amount of an analyte in the stationary phase to that in the mobile phase:

$$k = \frac{w}{V_{\text{m}}} \frac{[\text{X}^-]_s}{c_{\text{X}}} \quad (22)$$

It holds true for the total concentration of the analyte,  $c_{\text{X}}$ , in the mobile phase;

$$c_{\text{X}} = [\text{X}^-] + [\text{HX}] = [\text{X}^-](1 + K'_{\text{H}1}[\text{H}^+]) \quad (23)$$

whereas the total concentration of phosphate,  $c_{\text{P}}$ , is given:

$$c_{\text{P}} = [\text{H}_3\text{P}] + [\text{H}_2\text{P}^-] + [\text{HP}^{2-}] + [\text{P}^{3-}] \quad (24)$$

The column capacity is equal to:

$$Q = \sum_{i=1}^3 i[\text{H}_{3-i}\text{P}^{i-}]_s + [\text{X}^-]_s \quad (25)$$

The last term on the right-hand side of Eq. (25) may be neglected under common chromatographic conditions. In order to solve this set of equations we need two additional equations. Analogously to Mongay's approach [94] we adopt the assumption that the intensity of the bond between the eluting phosphate anion and the stationary phase is proportional to the charge of the anion. Then we can write:

$$\frac{[\text{HP}^{2-}]_s}{[\text{H}_2\text{P}^-]_s} = \frac{2[\text{HP}^{2-}]}{[\text{H}_2\text{P}^-]} \quad (26)$$

$$\frac{[\text{P}^{3-}]_s}{[\text{H}_2\text{P}^-]_s} = \frac{3[\text{P}^{3-}]}{[\text{H}_2\text{P}^-]} \quad (27)$$

On combining Eqs. (22)–(27) with Eq. (21) and expressing the terms  $\text{H}_{3-i}\text{P}^{i-}$  with the aid of the protonation constants and the total phosphate concentration we obtain

$$k = \frac{w}{V_{\text{m}}} \frac{K_{\text{P}}^{\text{X}} 2^{x_2/2} 3^{x_3/3} Q^{x_1 + x_2/2 + x_3/3}}{(1 + K'_{\text{H}1}[\text{H}^+]) C_{\text{P}}^{x_1 + x_2/2 + x_3/3}} \times \left( \frac{1 + K_{\text{H}1}[\text{H}^+] + K_{\text{H}1}K_{\text{H}2}[\text{H}^+]^2 + K_{\text{H}1}K_{\text{H}2}K_{\text{H}3}[\text{H}^+]^3}{9 + 4K_{\text{H}1}[\text{H}^+] + K_{\text{H}1}K_{\text{H}2}[\text{H}^+]^2} \right)^{x_1 + x_2/2 + x_3/3} \quad (28)$$

When the dependence of the capacity factors on the total phosphate concentration are studied at a constant pH value, Eq. (28) can be simplified and transformed into the logarithmic form, combining all the constant terms in a constant  $C_3$ :

$$\log k = C_3 - \left( x_1 + \frac{x_2}{2} + \frac{x_3}{3} \right) \log c_{\text{P}} \quad (29)$$

As  $x_1 + x_2/2 + x_3/3 < 1$ , the slopes of the log–log dependence are smaller (in absolute values) than those predicted for simple monoanionic eluents.

As follows from the above derived equations, the magnitude of the log–log dependence changes with the pH value (fractions  $x_1 \dots x_3$  are pH-dependent). The dependencies of the logarithm of capacity factors on the logarithm of eluent concentration (total concentration of phosphate buffer) were measured for nitrite and nitrate anions at various pH values (5.5 and 7.5) [110] (see Fig. 7). The values of the respective slopes are listed in Table 3 and compared with those predicted with the aid of the dominant equilibrium approach and the effective

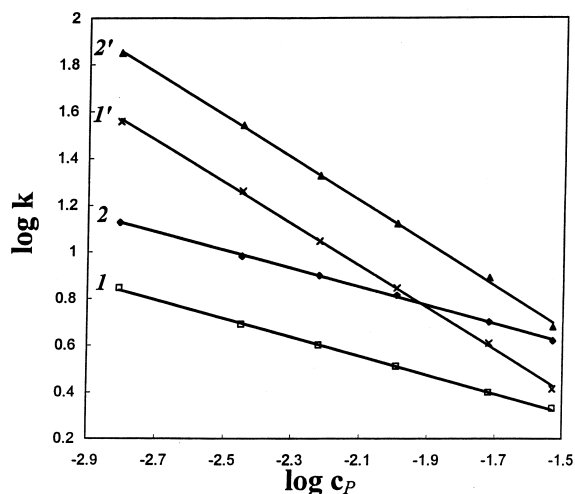


Fig. 7. Dependence of logarithms of capacity factors on logarithms of total concentration of phosphate buffer in mobile phase. Column 150×3 mm, Separon HEMA Q-L, 10  $\mu$ m, (anion exchanger containing triethylammonium groups) [110]. 1 and 1' = nitrites, 2 and 2' = nitrates, 1 and 2 at pH 7.5, 1' and 2' at pH 5.5.

charge approach. A similar comparison presented Haddad and Jackson [1] for phthalate eluents.

Eq. (28) allows prediction of the dependencies of the capacity factors on the main parameters of the mobile phase—total eluent concentration and pH—provided that the physical data (dissociation constants) are known and the other model parameters were estimated from a few initial experiments. In Fig. 8, the predicted dependence of capacity factors on pH are compared with the experimentally assessed ones for the nitrite and nitrate anions (anion exchange separation on the HEMA Q-L column with

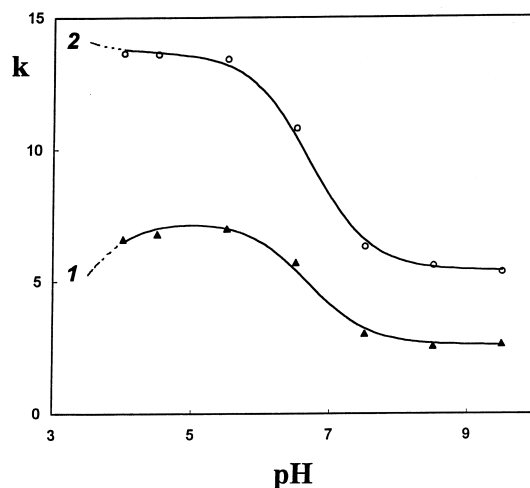


Fig. 8. Calculated dependence of capacity factors on pH of mobile phase (curves) together with experimental data (points). Total concentration of phosphate buffer in mobile phase 20 mM. (Dashed lines represent an extrapolation outside the examined pH range). Column as in Fig. 7 [110].

phosphate eluent) [110]. The dependence of the capacity and separation factors on both the principal parameters of mobile phase is shown in Fig. 9.

The retention models described above can be advantageously employed to optimize separations using a pH gradient elution [112] and they could be incorporated into ion chromatographic expert systems [113,114].

The relationships between an analyte retention and mobile phase parameters could be utilized for an estimation of physical constants, such as dissociation constants. This approach, however, has not been adopted very often in IC; Hirayama et al. [115]

Table 3

Mobile phase composition and slopes of the  $\log k$  vs.  $\log c_p$  dependencies for phosphate-based mobile phase [110]

pH of the mobile phase	Ionic species in the mobile phase (%)			Effective charge <sup>a</sup>	Theoretical slopes <sup>b</sup>		Observed slopes	
	H <sub>2</sub> P <sup>-</sup>	HP <sup>2-</sup>	P <sup>3-</sup>		DEA	ECA	Nitrite	Nitrate
5.5	98	2	$\sim 10^{-7}$	1.019	1	0.98	0.89	0.91
7.5	33	66	$\sim 10^{-3}$	1.676	0.5	0.59	0.41	0.30

<sup>a</sup> Ref. [111].

<sup>b</sup> Absolute values.

DEA = dominant equilibrium approach.

ECA = effective charge approach.

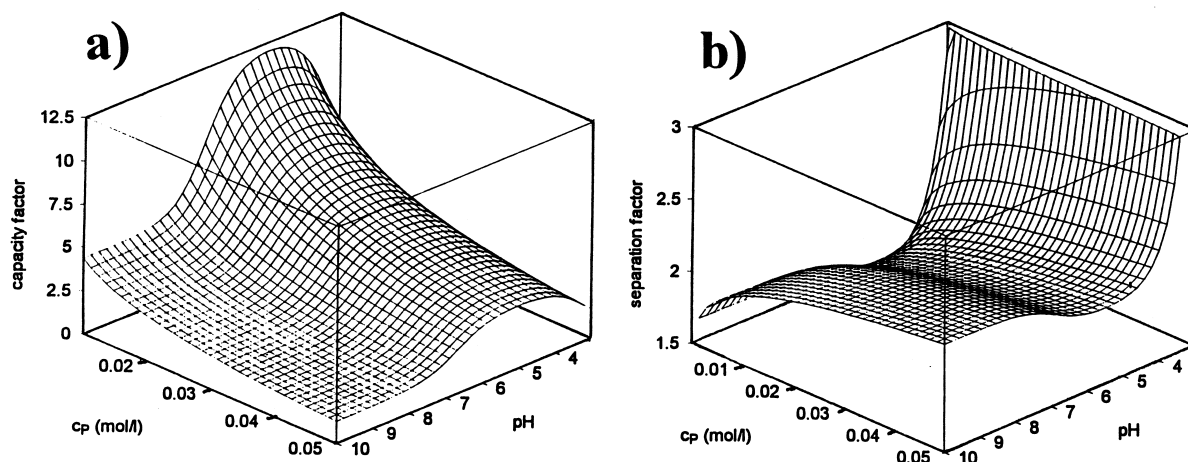


Fig. 9. Dependence of (a) capacity and (b) separation factors on total concentration of phosphate buffer and pH calculated for nitrite ion and nitrite/nitrate pair, respectively [110].

measured the dissociation constants of aromatic carboxylic acids by anion-exchange chromatography.

#### 4. Conclusions

The composition of the mobile phase provides a great flexibility for manipulating an analyte retention in order to achieve the desired separation. Relatively simple retention models enable prediction of the retention and optimization of the separation of inorganic ions in IC. The side equilibria in mobile phase can influence effectively both the retention properties of the analyte ions as well as the eluting capability of the competing ions. Of the various interactions in the mobile phase, the most important in chromatography of inorganic ions are acid–base and complex-forming equilibria. The separation of di- and polyvalent metal cations is almost impossible without the presence of complexing agents and their complexing ability depends strongly on the pH value. The eluting power of the eluents used in anion-exchange chromatography is also governed by their pH, when weak acids are employed. A further influence of eluent pH is on the formation of system peaks. This problem, very important in practice, has been studied extensively [116–120], but it was not dealt with in the present work.

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