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Review

Complex-forming equilibria in ion chromatography

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Abstract

The role of complex-forming equilibria in the separation of metal cations using the methods of ion chromatography (IC), in particular the ion-exchange chromatography and ion-interaction chromatography, is discussed. Relationships describing the dependence of analyte retention on the composition of the mobile phase containing complexing ligands in the mobile phase are presented and the possibility of using these relationships and IC methods for examining the properties of complexes (determination of stability constants) is outlined. In addition to more recent papers, some studies that appeared before the introduction of IC are considered; a number of them may be helpful in understanding the retention mechanism and for the separation of metals with the aid of IC methods.

Contents

1. Introduction	1
2. Cation-exchange chromatography	2
2.1. Systems with no cationic complexes in the mobile phase	2
2.2. Systems involving cationic complexes	5
2.3. Systems with eluting cations participating in complex-forming equilibria	5
3. Ion-interaction chromatography	6
4. Anionic systems	7
References	9

1. Introduction

Ion chromatography (IC) is a modification of the high-performance liquid (column) chromatography (HPLC), serving for the separation and determination of substances having ionic charac-

ter. It includes various separation methods such as ion-exchange chromatography, ion-interaction chromatography, ion-exclusion chromatography and some other combined techniques. Nowadays, almost 20 years after its introduction, IC is considered to be a standard method for the determination of anions and it is also being applied increasingly to the determination of metals. IC can advantageously be used in studies of metal speciation [1–4].

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Complex-forming equilibria play an important role in the analytical chemistry of metals. In IC, addition of complexing agents is often used to improve the separation of divalent and polyvalent metal cations [1,3,5] and less frequently for masking some metals [6]. This paper is devoted to the importance of complex-forming equilibria for IC methods, particularly ion-exchange chromatography (IEC) and ion-interaction chromatography (IIC). Methods in which metals are separated in the form of chelates with voluminous organic ligands will not be discussed here since, considering the mechanism of separation, they belong rather to the field of organic analysis. We have attempted not only to summarize the results of more recent studies but also to compare them with the results of some of the older work that may be an inspiration for the further development of IC.

2. Cation-exchange chromatography

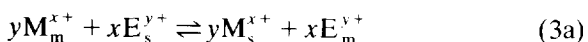
The separation of metal cations proceeds most frequently on strongly acidic cation exchangers with a sulphonic functional group. In the simplest case the mobile phase contains a driving cation (E) and an anion that may have complexing properties (L). After injection of an analyte (a metal cation, M) into the mobile phase, formation of complexes according to the following equations takes place (for simplicity the ionic charges are omitted):



In some cases also the driving cation may participate in the complexing equilibria:

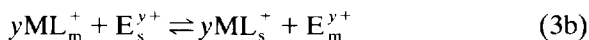


The retention of metal cations on a cation exchanger can be described by



where the subscripts m and s refer to the mobile

and stationary phases, respectively. The suggested retention model is demonstrated schematically in a paper by Haddad and Foley [7], where also the effect of pH on the given equilibria is discussed. In the cases when cationic complexes bearing a positive charge (e.g., of the ML^+ type) are formed, their retention on a cation exchanger according to Eq. 3b must also be considered:



Based on the above equations, it is possible to derive relationships between the retention of analytes and the composition of the mobile phase. Although a general solution is possible, it will be more reasonable to discuss hereafter some simplified cases based on real chromatographic conditions.

2.1. Systems with no cationic complexes in the mobile phase

Let us consider first as one of the commonest cases the separation of divalent metal cations M^{2+} in the presence of a complexing ligand L^{2-} . The analyte occurs in the mobile phase either in the form of a "free" cation or in the form of neutral or negatively charged complexes that do not take part in the complexing equilibria. We do not consider the formation of complexes of the driving cation with the ligand L^{2-} . The following relationship was derived [1,7] for the capacity factor:

$$k_M = \frac{\alpha_M w}{V_m} \cdot (K_M^E)^{1/y} \left(\frac{Q}{y}\right)^{x/y} [E^{y+}]_m^{-x/y} \quad (4)$$

where k_M is the capacity factor, w is mass of the stationary phase, V_m is volume of the mobile phase in the column (dead volume), Q is the column capacity and K_M^E is the equilibrium constant of reaction 3a (selectivity coefficient). The effect of complexing equilibria is expressed by a coefficient α_M , showing the share of the 'free' cation concentration $[M^{x+}]_m$ in the total concentration of the metal in the mobile phase, c_M :

$$\alpha_M = \frac{[M^{x+}]_m}{c_M} \quad (5)$$

Expressing α_M with the aid of the overall stability constants [8,9] β_1 - β_n , Eq. 4 may be rewritten [8,10] to give

$$k_M = \frac{w(K_M^E)^{1/y} \left(\frac{Q}{y}\right)^{x/y}}{V_M [E^{y+}]_m^{x/y} (1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n)} \quad (6)$$

Eq. 6 describes the dependence of analyte retention on the composition of mobile phase; it expresses both the pushing effect of the driving cation and the pulling effect of the complexing anion. These relationships also enable one to express the separation characteristics for the separation of metals in the presence of complexing agents. For the simplest separation characteristic, the separation factor $\alpha_{2,1}$, it holds that

$$\alpha_{2,1} = \frac{k_{M2}}{k_{M1}} = \left(\frac{K_{M2}^E}{K_{M1}^E}\right)^{1/y} \times \left(\frac{1 + \beta'_1[L] + \beta'_2[L]^2 + \dots + \beta'_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n}\right) \quad (7)$$

where β_1 - β_n and β'_1 - β'_n are the stability constants of complexes of metals M_1 and M_2 . For analogous, but more general relationships, see also Refs. [11,12].

With appropriate experimental arrangement, Eq. 4 or 6 can be simplified. If the ligand concentration is kept constant (or equal to zero, as the case may be), we obtain a simple relationship usually presented in logarithmic form [1,7,13-17]:

$$\log k_M = C_1 - \frac{x}{y} \cdot \log [E^{y+}]_m \quad (8)$$

where all the constant terms are included in the constant C_1 . Linearity of the dependence of the logarithm of the capacity factor on the logarithm of the eluent concentration is usually considered to be a criterion when determining whether the

retention of analytes is controlled by the ion-exchange mechanism [18]. The slope of this dependence is given by the ratio of charges of the analyte and the driving cation. Sevenich [19] studied the dependences of $\log k_M$ vs. $\log(\text{eluent concentration})$ in detail using the IC method on low-capacity cation exchangers. In some cases the values of the slopes of the dependences differed markedly from the theoretical values; possible reasons were discussed by Gjerde [17].

Provided that a free cation did not participate in the ion-exchange process, it is possible to calculate the charge of the respective species from the experimental values of the slope. This has been made use of very frequently when studying complexes with the aid of ion exchangers in the classical batch arrangement. In this case a similar relationship to Eq. 8 holds true, except that the distribution coefficient D_M [20,21] replaces k_M (a simple and well known correlation [1] exists between k_M and D_M). A survey of older original papers can be found in the book by Marcus and Kertes [21] or in a review [22]. Dependences of the retardation factor R_F (retention characteristic used in paper and thin-layer chromatography) on the composition of the mobile phase were derived [23] in a similar way to k_M and D_M . Paper chromatography on ion-exchange paper became an effective tool in the research of complexes particularly in the 1960s; papers of that period have been compiled by Lederer [24].

The concentration of the driving cation (in addition to the pH) can be kept constant with a proper arrangement of experiments when studying the dependence of analyte retention on ligand concentration [8,10]. Eq. 6 can then be rewritten in the following form:

$$\frac{1}{k_M} = C_2(1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n) \quad (9)$$

where again the constant quantities are combined in the constant C_2 . If only one type of complex is predominating in the mobile phase, Eq. 9 can be simplified further:

$$\frac{1}{k_M} = C_2(1 + \beta_n[L]^n) \quad (10)$$

A similar relationship has been presented by Starý [25] for the distribution coefficient of transplutonium elements separated on cation exchangers in the presence of complexing agents.

Some papers have considered the linear dependence of the logarithm of the capacity factor or logarithm of the distribution coefficient on the logarithm of ligand concentration [26]. It follows clearly from the detailed derivation by Tikhonova [27] that such a relationship is a kind of simplification; it may also be arrived at from Eq. 10 on the assumption that $1 \ll \beta_n[L]^n$, which condition is satisfied in a number of real systems. Eq. 10 is then transformed into

$$-\log k_M = \log C_2 + \log \beta_n + n \log [L] \quad (11)$$

Smith and Hoffman [28] studied the separation of lanthanoids and actinoids on a column with the cation exchanger Dowex 50-X4 with the aid of a solution of the ammonium salt of α -hydroxyisobutyric acid (HIBA). They found, among others, a linear dependence between the logarithm of the “peak position” (expressed in “free column volumes” units, obviously corresponding to the capacity factor) and the logarithm of the HIBA concentration within the concentration range ca. 0.05–0.3 mol l⁻¹. If we consider the values of the stability constants of the Ln–HIBA complexes formed to be at the level $\beta_1 \approx 10^3$ – 10^4 [29], then the above simplification is justified and, in agreement with experimental results, a linear logarithmic dependence may be expected.

It follows clearly from Eqs. 9–11 that the retention of metal cations declines with increasing stability of the complexes. Timerbaev and Bonn [30] reported a linear dependence $\log k_M$ on $\log \beta_n$ for the separation of the cations Mn^{2+} , Cd^{2+} , Co^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} and Fe^{2+} in the presence of citric and oxalic acids. This linear dependence (Eq. 11) obviously holds for complexing agents that are sufficiently “strong” and/or for high ligand concentrations. When weaker complexes are formed as, e.g., Mn^{2+} ions, with the given ligands the simplification used in deriving Eq. 11 is not justified. The published diagrams [30,31] indicate that the values for the

Mn^{2+} ions deviate slightly from a linear dependence of $\log k_M$ vs. $\log \beta_n$.

It is possible to obtain information on the composition and stability of complexes formed in the mobile phase by an analysis of the dependence of the capacity factors on the concentration of ligands (provided that the other mobile phase parameters remain constant). Lin and Horváth [32] were the first to apply the IC method to the measurement of the stability constants of tartrate complexes (we also pointed out such a possibility independently [8]); they used a relationship analogous to Eq. 10. Their derivation, however, is more complex and more general than that suggested in this paper. The stability constants of complexes of several divalent cations with anions of tartaric, oxalic, citric, malonic and pyridine-2,6-dicarboxylic acids have also been measured [10] and subsequently [33] the method was applied to some inorganic complexes. It turned out that in most cases it is possible to use the simplified Eq. 10 for $n = 1$ and to calculate the stability constant simply as the ratio of the slope and the y-axis intercept of the (linear) dependence $1/k_M$ vs. ligand concentration.

It should be mentioned that the history of the study of metal complexes with the aid of ion exchangers is long and rich [34]. Günther-Schulze [35] was the first to study the composition and stability of complexes (divalent metal cations with halides) using inorganic ion exchangers. His results were not reliable, however, because of instability of the ion exchangers used and other factors. Most of the ensuing studies were made with resin ion exchangers (as compiled by Marcus and Kertes [21]). (Recently attention has notwithstanding been attracted to investigations of ion-exchange equilibria on zeolites in the presence of complexing agents, in connection with the application of zeolites in phosphate-free washing powders [36].) Eq. 9 and methods based on it represent in fact a special case of the well known Schubert method [37,38] based on the determination of distribution coefficients at different (at least two) ligand concentrations. It is interesting that the conditions as set up by Schubert for the application of his

method (low metal concentration, excess of ligand, constant pH, roughly constant ionic strength, etc. [37]) are also common in modern IC or can be arrived at comparatively easily [10]). The relationship in question is most frequently presented in the form [21]

$$\frac{(D_M^0/D_M)}{c_L} = \beta_1 + \beta_2 c_L + \dots + \beta_n c_L^{n-1} \quad (12)$$

which can easily be transformed into an equation of the type of Eq. 9 (c_L being the ligand concentration). There are many examples of the application of Schubert's method (e.g., Refs. [39–41]) and others were compiled by Marcus and Kertes [21]. Usually the experiments were carried out with a batch arrangement under static conditions, but in some studies the stability of complexes was assessed under dynamic conditions using ion-exchange chromatography [27,42].

2.2. Systems involving cationic complexes

Monovalent anions of the L^- -type, e.g., inorganic anions or the commonly applied HIBA, often participate in the complexing equilibria. In these cases it is usually not possible to disregard the formation of cationic complexes bearing a positive charge and it is necessary that the retention model should include also Eq. 3b (and others, as the case may be).

A classical solution for the case of a divalent cation, monovalent anion and a cationic complex ML^+ was suggested by Fronaeus [43], and later this model was generalized to be applicable to other types of complexes also [44]. Fronaeus's approach has been used by a number of workers for studying the formation of complexes and measuring the stability constants (e.g., Refs. [45,46]). Maslova *et al.* [47] applied a similar model in studies of the separation of cations of the rare earth elements using ion-exchange chromatography in the presence of lactic acid.

A model of the retention of divalent cations including the sorption of ML^+ -type complexes has been developed in IC [33] and the following relationship was derived for the capacity factor:

$$k_M = \frac{w(K_{ML}^E Q [E^+]_m \beta_1 [L] + K_M^E Q^2)}{V_m [E^+]_m^2 (1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n)} \quad (13)$$

Earlier experience showed that the sorption of cationic complexes must not be neglected, particularly in the case of trivalent cations (sorption of the ML^{2+} complexes) [44,48]. When studying thiocyanate complexes using the IC method it was demonstrated that the sorption of the ML^+ complexes may be neglected, which is somewhat controversial with batch method measurements [49]. There are, however, still only a few data obtained by the IC method for a comparison of the two procedures.

Complexing equilibria are playing a particularly important role in the separation of lanthanoids, which problem has been studied very intensively. Citric acid was used as the driving agent [50] (Ketelle and Boyd [51] also presented an equation describing the dependence of the distribution coefficient on citric acid concentration) but later lactic acid [52] and especially HIBA [53,54] proved to be more effective; the latter is becoming more commonly and successfully used in IC [55,56].

2.3. Systems with eluting cations participating in complex-forming equilibria

In real chromatographic systems, driving cations can also participate in complexing equilibria (Eqs. 2a, 2b, etc.). Such cases are not unusual; typical examples are mobile phases containing $CuSO_4$ or $CuCl_2$ that are often used in the separation of cations with indirect photometric detection [57,58].

If complexes are formed between the driving cation and ligand, then the total concentration of the eluent, c_E , is given by (for simplicity ionic charges are omitted)

$$\begin{aligned} c_E &= [E]_m + [EL]_m + [EL_2]_m + \dots + [EL_n]_m \\ &= [E]_m (1 + \beta'_1 [L] + \beta'_2 [L]^2 + \dots + \beta'_n [L]^n) \end{aligned} \quad (14)$$

where β'_1 – β'_n are the stability constants of complexes of a cation E with a complexing ligand L. On combining Eqs. 6 and 14, rearranging and transforming into logarithmic form, we obtain

$$\log k_M = C_3 - \log C_E + \log \left(\frac{1 + \beta'_1[L] + \beta'_2[L]^2 + \cdots + \beta'_n[L]^n}{1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n} \right) \quad (15)$$

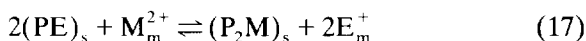
It is obvious that when both the driving cation and the cations being separated form complexes of a similar type and stability with anions of the mobile phase, the last term on the right-hand side of Eq. 15 tends to zero and the effect of complexing equilibria is not detectable. Such was the case with the separation of divalent metal cations by means of a mobile phase containing CuSO_4 or CuCl_2 [59] and, therefore, the slopes of the dependences of $\log k_M$ vs. logarithm of eluent concentration were near to the theoretical values as calculated according to Eq. 8.

3. Ion-interaction chromatography

In ion-interaction chromatography, the separation of analytes proceeds on non-polar stationary phases (e.g., C_{18}) and the retention of substances of an ionic nature is made possible by addition of suitable ionogenic agents to mobile phase. In the separation of cations the mobile phase contains three constituents, an ion-interaction (ion-pair) agent (e.g., octylsulphonate, P^-), a driving cation and an anion that may have complex-forming properties. There are several models describing the retention of ionic substances on the surface of a non-polar stationary phase (e.g., ion-pair model, dynamic ion-exchange model) [1]; currently the most commonly used is the ion-interaction model. According to this, two main equilibria predominate in the retention: sorption of the ion-interaction agent on the surface of the stationary phase and ion exchange between ions of the analyte and the driving ions [60,61]. Relationships were derived between the retention of analytes and the mobile

phase composition [60,61]; as in IEC, the effect of complexing equilibria can be expressed with the aid of the coefficient α_M [1].

The published relationships hold exactly only for monovalent ions. However, complexing equilibria work particularly in the separation of polyvalent cations. Let us consider further a simple case, fairly common in practice, viz., the separation of divalent cations on a non-polar stationary phase in the presence of octylsulphonate as the ion-interaction agent, a monovalent driving cation E^+ (e.g., Na^+ ion) and a divalent complexing anion (e.g., oxalate). Retention of the analytes is described, analogously with [1,60,61], by the following equations:



where A_s corresponds to free adsorption sites on the surface of stationary phase. Complexing equilibria are described by Eqs. 1a, 1b, etc. The capacity factor is given by

$$k_M = \frac{w}{V_m} \cdot \frac{(\text{P}_2\text{M})_s}{c_M} \quad (18)$$

The column capacity is given by the sum

$$Q = \text{A}_s + (\text{PE})_s + 2(\text{P}_2\text{M})_s \quad (19)$$

where the last term on the right-hand side can be neglected; this assumption is common in IEC and its validity for IIC was confirmed experimentally [61] (retention being independent of analyte concentration). On expressing c_M by means of the stability constants and ligand concentration and solving the set of equations, we obtain

$$\frac{1}{k_M} = \frac{(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n)w}{V_m Q^2 K_2} \times \left(\frac{1}{K_1 [\text{P}^-]_m} + [\text{E}^+]_m \right)^2 \quad (20)$$

where K_1 and K_2 are the equilibrium constants of eqns. 16 and 17. Eq. 20 reveals a comparative complex dependence of the capacity factor on ligand concentration. Moreover, the more complete and more general models could include

also the retention of cationic complexes (analogously to IEC as is indicated in Section 2.2). An example of when the presence of cationic complexes must not be neglected is the IIC separation of transition metals, lanthanoids and actinoids in the presence of HIBA, mandelic acid or lactic acid [62–64]. Detailed retention models for these cases, however, have not yet been worked out.

If we confine ourselves to an examination of the effect of a complexing agent on analyte retention, i.e., if the concentrations of both the ion-interaction agent and the driving cation (as well as pH) are kept constant, Eq. 20 can be rewritten as

$$\frac{1}{k_M} = C_4(1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n) \quad (21)$$

this form being formally identical with Eq. 9. Eq. 21 can be further simplified (Eq. 9) and applied to the measurement of stability constants [65]. The results of measurements of the stability constants of oxalate complexes using the IEC and IIC methods are given in Table 1. In the case of IIC the chromatographic system is more complex than it is with IEC, and particularly when more voluminous organic ligands are used, other retention mechanisms may also be effective. This has to be considered when interpreting the results obtained by the IIC method.

In the IIC separation of polyvalent metal

cations the same complexing agents are used as in IEC, i.e., mainly the anions of tartaric, citric and oxalic acids. IIC determinations of metals are less usual than those using IEC methods but there exist a number of successful and useful examples of such determinations, e.g., in Ref. [1].

4. Anionic systems

Some metals can be separated and determined in the form of their anionic complexes using both ion-exchange and ion-interaction chromatography. Platinum group metals were separated in the form of cyano or chloro complexes [66–68], and complexes with ethylenediaminetetraacetic acid (EDTA) and similar agents are also frequently used [69,70]. Anion-exchange chromatography can be used for separating complexes with comparatively simple ligands such as oxalates [71,72] and also those with voluminous organic ligands such as 4-(2-pyridylazo)resorcinol (PAR) [73]. The addition of a suitable complexing agent to the mobile phase and separation of metals in the form of anionic complexes is one of the methods employed in simultaneous determinations of anions and cations by means of IC [74].

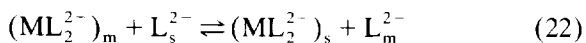
Most metals can be separated both on cation exchangers and on anion exchangers; the sequence of peaks, however, is usually reversed. A good example is the separation of rare earth elements where in the case of cation-exchange separation the order of peaks is from Lu to La, whereas on anion exchangers (e.g., in the form of oxalate complexes) the order is the opposite [74]. The same is true with similar ion-interaction systems. In some cases it is possible to use the same complexing agent in both the cationic and anionic systems. Divalent metal cations were separated by the IIC method on a C₁₈ column in the presence of octylsulphonate and oxalate ions (cationic system, order of peaks Cu²⁺, Ni²⁺, Co²⁺, Mn²⁺) [65] or on the same column in the presence of the tetrabutylammonium cation (anionic system, order of peaks Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺) [75].

Table 1
Stability constants of oxalate complexes

Ion	Log β_1	
	IEC method [10] ^a	IIC method [65] ^a
Zn ²⁺	4.07 ± 0.06	3.78 ± 0.03
Ni ²⁺	4.69 ± 0.46	4.07 ± 0.01
Co ²⁺	4.08 ± 0.04	3.86 ± 0.03
Cd ²⁺	3.35 ± 0.01	3.34 ± 0.05
Mn ²⁺	3.35 ± 0.01	3.38 ± 0.02
Fe ²⁺	3.64 ± 0.03	3.32 ± 0.04
Pb ²⁺	4.12 ± 0.57	3.85 ± 0.02

^a Ionic strength ca. 0.1 mol l⁻¹ sodium perchlorate, 22 ± 1°C.

When separating metals on ion exchangers or using the corresponding IIC systems, the respective complexes can be prepared either before the analysis proper (complexing agent is not present in the mobile phase; precolumn derivatization) or complexes can be formed only after injecting the sample into mobile phase containing a complexing agent (on-column derivatization). The same relationships as in the anionic IC separation of anions hold true in the former case; it is possible to assess the charge of the complex from the dependence of $\log k_M$ on the logarithm of the eluting anion concentration. In the latter case, when the ligand is acting simultaneously as a complexing agent and driving anion, the relationship between analyte retention and mobile phase composition may be more complex. Let us consider further the separation of divalent metal cations on an anion exchanger in the presence of divalent anions capable of forming complexes of the ML_2^{2-} type (e.g., oxalates). The retention of analytes can be described by



The relationship for k_M can be derived in the usual way:

$$k_M = \frac{wQ\beta_2[L]}{V_m K_{ML_2}^L (1 + \beta_1[L] + \beta_2[L]^2)} \quad (23)$$

In this case the formation of higher complexes and their contribution to the retention of analytes were not considered; basically it is analogous to Fronaeus's approach [76]. Fronaeus and other workers who continued with the development of his method [77,78] measured the dependences of distribution coefficients on ligand concentration (in the batch arrangement) and, based on an analysis of these dependences, assessed the characteristics of the complexes. It was demonstrated that on certain assumptions there is a linear dependence between $\log D_M$ and the logarithm of the concentration (more precisely activity) of the ligand.

It may be assumed that under conditions normal in IC all the metal in the above chromatographic system is present in the form of an

ML_2^{2-} complex (excess of ligand). Eq. 23 can then be rearranged and rewritten as

$$\log k_M = C_5 - \log [L] \quad (24)$$

An analogous relationship was presented by Vláčil et al. [79] for the separation of platinum metals in the form of chloride complexes.

The mobile phase composition can, of course, be more complex than in the given simple more or less model example. Other eluting anions are often present (phthalate anion [74], perchlorate [80]); additional terms then must be added to the right-hand side of Eq. 24. It is possible to expect generally a linear dependence between logarithm of the capacity factor and the logarithm of the driving anion concentration; the slope of these dependences is given by the ratio of charges of the complex and of the driving anion. This was very well confirmed [74] for metal complexes of EDTA, whereas deviations from the theory were ascertained in some cases with oxalate complexes [80]. A more complete and more detailed retention model for the separation of anionic EDTA complexes can be found in Ref. [81].

Complex relationships were derived for the separation of anionic complexes by the ion-interaction mechanism [75,82]. Experimentally assessed dependences of the capacity factor on mobile phase composition, however, are comparatively simple and they exhibit a similar character to those observed in the case of separation of simple inorganic anions in analogous ion-interaction systems [75].

One of a number of ion-interaction systems worth mentioning is the separation of metals in the form of oxalate complexes on common non-polar stationary phases (C_{18}) in the presence of tetrabutylammonium cation as the ion-interaction agent. An excellent example is the work by Jones et al. [83], in which all the rare earth elements were separated without using gradient elution. The method was applied to the determination of light rare earth elements in polishing powders [84]. It has been demonstrated [75] that the method is applicable more generally and that it can be used for the separation of a number of metal elements.

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