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Retention models for the ion chromatographic separations of metals in the presence of complexing agents

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Abstract

Retention models for the separations of metal ions in the presence of complexing agents both on cation exchangers and on anion exchangers (in the form of anionic complexes) are presented. The following chromatographic systems were chosen as examples: the separation of divalent metal cations on cation exchangers with the aid of mobile phases containing tartaric or lactic acids and the separation of metal ions in the form of oxalic complexes on anion exchangers. Influences of the most important "side" equilibria (acid–base and complex-forming ones) on the analyte retention are discussed and the dependences of the capacity and separation factors on the ligand concentration and mobile phase pH are presented.

Keywords: Complexing agents; Retention models; Metal ions; Carboxylic acids

1. Introduction

Various ionic substances, including metal ions, can be separated and determined by ion chromatographic (IC) methods [1]. Except for a limited group of cations (alkaline metals, alkaline earth metals) an effective separation of di- and polyvalent metal cations is feasible only in the presence of complexing agents such as anions of di- and hydroxycarboxylic acids (oxalic, tartaric, lactic, citric, α-hydroxyisobutyric) [2,3]; the role of complex-forming equilibria in IC is discussed in reviews [4,5].

The complex formation for the metal cation, M^{x+}, and ligand, L^{y-}, can be described by Eq. 1:

$$M^{x+} + iL^{y-} \Leftrightarrow ML_i^{x-iy};\ \beta_i = \frac{[ML_i^{x-iy}]}{[M^{x+}]\,[L^{y-}]^i} \qquad (1)$$

where β_i are the overall stability constants. Weak carboxylic acids serving as complexing ligands undergo acid–base equilibria expressed by the following equations:

$$H_{i-1}L^{i-y-1} + H^+ \Leftrightarrow H_iL^{i-y};\ K_{Hi} = \frac{[H^iL^{i-y}]}{[H^+]\,[H_{i-1}L^{i-y-1}]} \qquad (2)$$

where K_{Hi} is the protonation constant. If we consider the distribution of analytes between the stationary and mobile phases as the main (primary) equilibrium, then the equilibria described by Eq. 1 and Eq. 2 are the most important side (secondary) equilibria taking place in IC of metal ions.

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 coexist in the mobile phase. Positively- and negatively-charged

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species can be retained by the ion-exchange mechanism on cation- and anion exchangers, respectively (ion-exchange chromatography, IEC).

The retention models for the IEC separations of metal ions in the presence of complexing agents are presented in this paper. The following model systems were chosen:

(1) Separation of divalent metal cations on the cation exchanger in the presence of tartrate anions.
(2) Separation of divalent metal cations on the cation exchanger in the presence of lactate anions.
(3) Separation of divalent metal cations in the form of anionic oxalate complexes on the anion exchanger.

An effect of the above-mentioned side equilibria on the analyte retention and separation is demonstrated. Some simplifying presumptions were adopted in derivations of the mathematical relationships between the retention and separation characteristics and the mobile phase composition:

- Only the ion-exchange retention mechanism was taken into account.
- The chromatographic process is considered as an equilibrium one, the side equilibria are sufficiently fast in comparison with the chromatographic migration.
- Only mononuclear complexes are formed in the system, preferentially with dissociated ligand; formation of hydroxocomplexes and mixed-ligand complexes is not taken into account.
- An eluting (driving) effect of the H^+ and OH^- ions is neglected in the considered pH range.
- The column parameters (capacity) do not depend on the mobile phase composition.

Employing experimental data obtained in the present and some previously published works [6–8] and using the derived relations the dependences of the capacity and separation factors on the ligand concentration and mobile phase pH are discussed.

2. Experimental

The liquid chromatograph consisted of two HPP 5001 high-pressure pumps (for pumping the mobile phase and the post-column derivatization agent), an LCI 30 injection valve with a 20-μl sampling loop, an RE-2M post-column reactor, a TZ 4261 chart recorder (all from Laboratorni Pøístroje, Prague, Czech Republic) and UV-Vis spectrophotometric detectors Model 832 870 (Knauer, Berlin, Germany) or LCD 2040 (ECOM, Prague, Czech Republic). The apparatus and the conditions of measurements are described in detail in Refs. [6–8].

The glass column (150×3 mm) packed with octadecyl-bonded silica gel, Separon SGX C_{18}, 5 μm, permanently coated with sodium dodecyl sulfate (SDS) was used for the metal separations in the presence of tartrate. The SDS-coated column exhibits properties of a strongly acidic cation exchanger. The preparation and properties of the column are described in detail elsewhere [9]. The separation of the metal cations in lactate medium was carried out on the glass column (150×3 mm) packed with the fixed-site cation exchanger with the silica gel matrix, Separon SGX CX, 7 μm. Anionic oxalate complexes were separated on the column (150×3 mm) packed with the strongly basic low-capacity anion-exchanger, Separon HEMA Q-L, 10 μm (all columns from Tessek, Prague, Czech Republic).

The following stock solutions were prepared: 1 mol/l NaOH and LiOH, 0.1 mol/l oxalic, tartaric and lactic acids. The solution of lactic acid (Ciba, Basel, Switzerland) was purified by passing through a column with Dowex 50W-X8 cation exchanger in the H^+ form, the other chemicals were of reagent-grade purity (Lachema, Brno, Czech Republic) and were used without further purification. The concentrations of the stock solutions were checked with the aid of common titrimetric procedures. Mobile phases were prepared by mixing the stock solutions in a requisite ratio and adjusting (if necessary) the pH value with diluted $HClO_4$, the procedures are described in detail in previous works [6–8]. 0.2 mmol/l solution of 4-(2-pyridylazo) resorcinol (PAR) containing 1 mol/l acetic acid and 3 mol/l ammonium hydroxide served as the post-column derivatizing agent. Redistilled water was used for preparing the solutions.

TableCurve 3D software (Jandel Scientific, San Rafael, CA, USA) was used for the visualization of the dependences of the capacity and separation factors on the mobile phase composition.

3. Results and discussion

3.1. M^{2+}–tartrate system, cation-exchange separation

When the divalent metal cations interact with tartrate anions (L^{2-}) according to Eq. 1, the neutral and negatively charged complexes, ML ... ML_n^{2-2n}, are formed in the mobile phase. Then only free (uncomplexed) cation M^{2+} can participate in the cation-exchange process on the column. In this case the retention model presented by Haddad and Foley [10] may by adopted; the following relationship was derived for the dependence of the capacity factor (k) on the concentrations of eluting cation (E^{z+}) and ligand at constant pH [7]

$$k = \frac{w}{V_m} \frac{(K_M^E)^{1/z} \left(\frac{Q}{z}\right)^{2/z}}{[E^{z+}]^{2/z}(1+\beta_1[L^{2-}]+\beta_2[L^{2-}]^2+\cdots+\beta_n[L^{2-}]^n)} \quad (3)$$

where K_M^E is the selectivity coefficient, Q is the column capacity, w is the weight of stationary phase and V_m is the volume of mobile phase in the column. It is evident that if the separated cations have the same charge, their separation (separation factor) can not be affected by the change of the concentration of eluting cations. Therefore, the dependences of the capacity factors on the ligand concentration were studied in detail. In Fig. 1 experimentally obtained dependences are compared with those calculated according to Eq. 3. The experimental data were taken from Ref. [6], while the stability constants determined in Ref. [7] by the IC method were used for the calculations of the theoretical dependences. These calculations are based on the presumption that the examined metal cations have the same (or very close) selectivity coefficients, which holds true with an exception of the Mn^{2+} ions (Fig. 1a).

The concentration of the ligand L^{2-} and, subsequently, the eluting capability of the mobile phase can be effectively affected by the change of its pH value [10,11]. It holds for the total ligand concentration, c_L:

$$c_L = [H_2L] + [HL^-] + [L^{2-}] + [ML] + \cdots + [ML_n^{2-2n}] \quad (4)$$

Under common chromatographic conditions the injected amount of analyte is small in comparison with the amount of ligand and concentrations [ML] ... $[ML_n^{2-2n}]$ may be neglected in Eq. 4. Using the protonation constants Eq. 4 can be rewritten as follows:

$$c_L = [L^{2-}](1 + K_{H1}[H^+] + K_{H1}K_{H2}[H^+]^2) \quad (5)$$

On combining Eq. 3 and Eq. 5 one obtains the dependence of the capacity factor on the mobile phase pH. The dependence of the capacity factor of Co^{2+} ions on the mobile phase pH and total concentration of tartrate at constant concentration of eluting cations is shown in Fig. 2; published values of stability constants [7] and protonation constants ($\log K_{H1}=3.95$, $\log K_{H2}=2.85$ [12]) were used for calculations, the other parameters of the retention model were determined from experimental data [6]. With the aid of the mentioned relations also a dependence of the separation factor α ($\alpha_{2,1}=k_2/k_1$) on the mobile phase composition can be easily expressed; this dependence for Co^{2+} and Ni^{2+} ions (the separation factor as a function of the mobile phase pH and total concentration of tartrate) is shown in Fig. 3. It is clearly demonstrated that the separation of Co^{2+} and Ni^{2+} ions, which is nearly impossible without presence of complexing agents, can be accomplished after an addition of tartrate. Because of the dissociation of complexing agent the separation improves with increasing pH. The calculated dependences agree with those experimentally obtained in Ref. [13].

3.2. M^{2+}–lactate system, cation-exchange separation

Whereas tartrate belongs to the most frequently used complexing agents in IC and chromatographic systems employing tartaric acid and other dicarboxylic acids have been extensively studied, lactic acid has been used in IC quite rarely [14]. In the past it was used in ion-exchange separations of lanthanides and actinides [15,16].

In addition to neutral and negatively charged complexes also positively charged complexes of the ML^+ type may by formed by the reaction of lactate

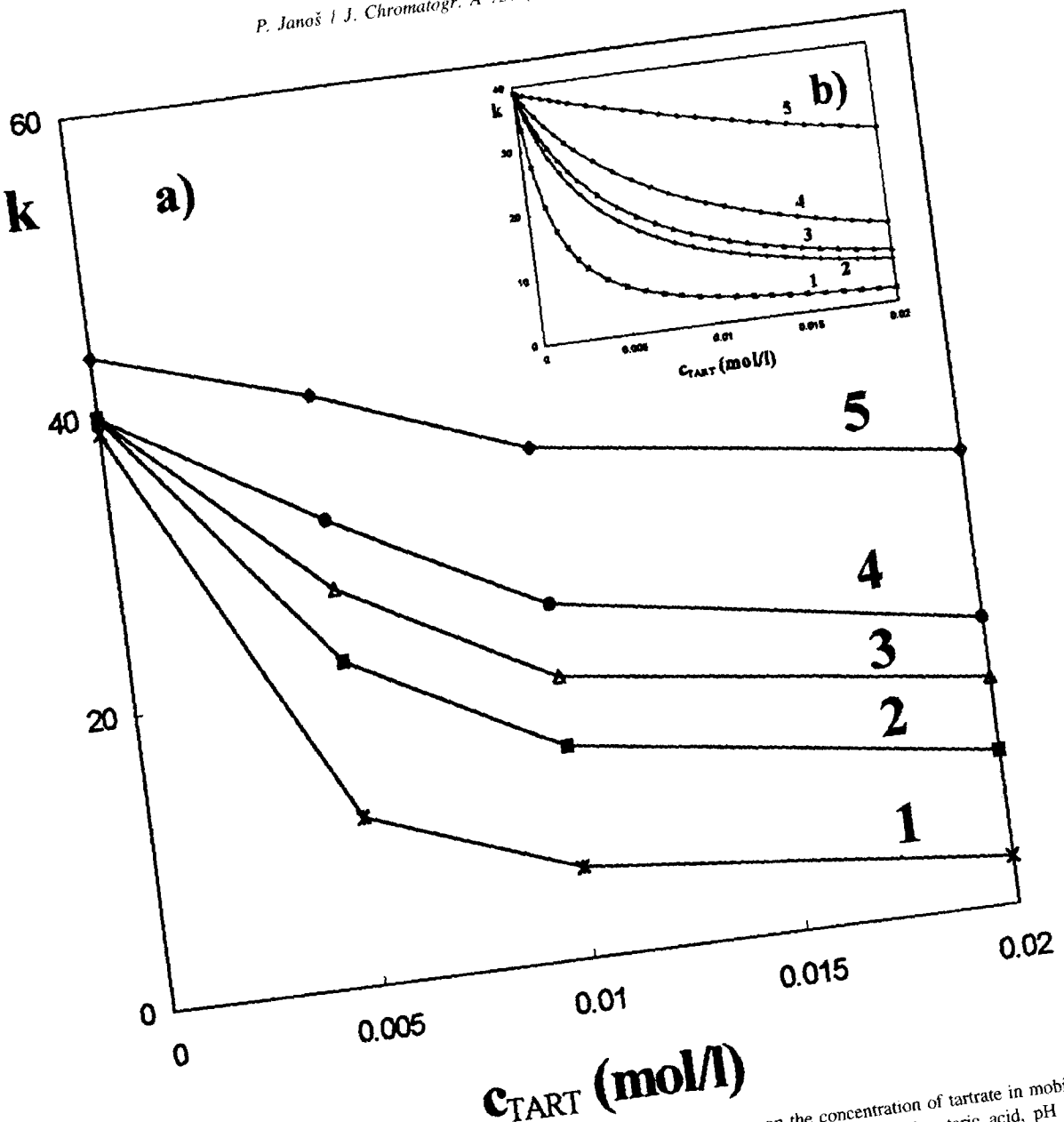

Fig. 1. Comparison of experimental (a) and calculated (b) dependences of capacity factors on the concentration of tartrate in mobile phase. Column 150×3 mm, Separon SGX C_{18}, coated with SDS. Mobile phase 0.04 mol/l LiOH–0–0.02 mol/l tartaric acid, pH 3.6±0.05 adjusted with $HClO_4$. 1, Pb^{2+}; 2, Ni^{2+}; 3, Co^{2+}; 4, Cd^{2+}; 5, Mn^{2+}.

anion L^- with divalent metal cations. Hence both free cations M^{2+}, as well as cationic complexes ML^+ can participate in cation-exchange equilibria.

The relationship between the capacity factor and th mobile phase composition was derived for simil chromatographic systems in Ref. [17]:

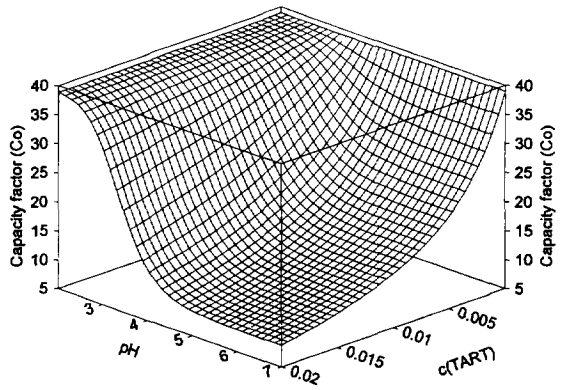

Fig. 2. Dependence of the capacity factor of Co^{2+} ions on pH and total concentration of tartrate at a constant concentration of Li^{+} ions (0.04 mol/l).

$$k = \frac{w}{V_m} \frac{K^E_M Q^2 + K^E_{ML} Q [E^+]}{[E^-]^2 (1 + \beta_1 [L^-] + \beta_2 [L^-]^2 + \cdots + \beta_n [L^-]^n)} \quad (6)$$

Previously published results [17] suggest that the only one kind of positively charged species predominantly takes part in an ion-exchange process on the cation-exchange column, i.e., one of the terms in the denominator on the right-hand side of Eq. 6 may be neglected. If the dependence of the capacity factor on the concentration of eluting cation is studied at constant concentration of ligand, Eq. 6 can be rewritten after simplification into the logarithmic form:

$$\log k = C_1 - z \log [E^+] \quad (7)$$

where z is the charge of the analyte species participating in ion-exchange and the constant C_1 includes column parameters, selectivity coefficient, ligand concentration and stability constants. These logarithmic dependences have been very often measured for zero concentrations of ligands [1]. In this work the dependences of the logarithm of the capacity factors on the logarithm of the concentration of eluting cation (Na^+) were assessed at constant pH and in the presence of non-zero concentration of lactate (0.056 mol/l). The experimental dependences in Fig. 4 comply with Eq. 7, and from the magnitudes of their slopes, which approach -1 (-1.14 and -1.03 for Ni^{2+} and Cu^{2+}, respectively), one can deduce that the separated cations are retained in the

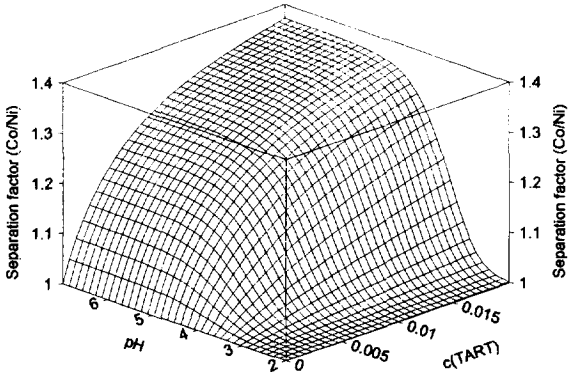

Fig. 3. Dependence of the separation factor of Co^{2+} and Ni^{2+} ions on pH and total concentration of tartrate at constant concentration of Li^{+} ions.

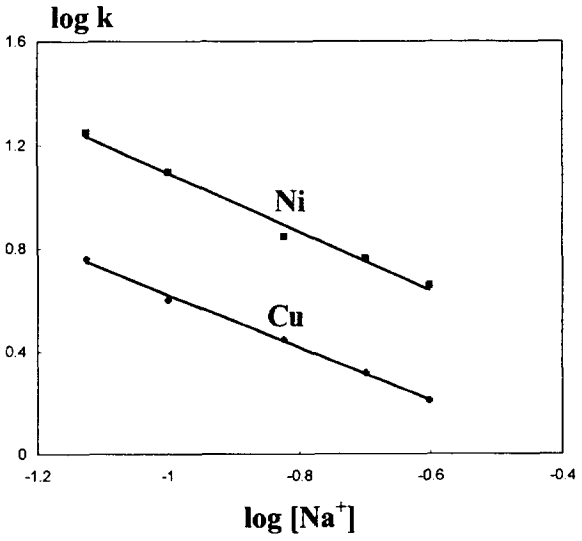

Fig. 4. Dependence of $\log k$ on the logarithm of concentration of eluting cation (Na^+) at a constant concentration of lactate in the mobile phase. Column 150×3 mm, Separon SGX CX. Mobile phase 0.075–0.25 mol/l NaOH–0.056 mol/l lactic acid, pH 6.0±0.1 adjusted with $HClO_4$.

form of the ML^+ complexes on the column. Obviously the concentration of free metal cations can be neglected in an excess of ligand. On the other hand, when the dependences of the capacity factors on the ligand concentration at constant concentration of eluting cations (an experimental arrangement is described in detail in [6,7]) are studied, then after the above-mentioned simplifications (an omission of the first term in the denominator of Eq. 6 and an omission of the concentration of free cations M^{2+}) Eq. 6 can be rearranged into the form

$$\frac{1}{k} = C_2 \left(1 + \frac{\beta_2}{\beta_1} [L^-] + \cdots + \frac{\beta_n}{\beta_1} [L^-]^{n-1} \right) \quad (8)$$

where the constant terms are again combined into the constant C_2. The experimental dependences presented in Fig. 5 for the Ni^{2+} and Cu^{2+} ions comply with Eq. (8). The ratios of stability constants β_2/β_1 ... β_n/β_1 can be calculated from the dependences of $1/k$ vs. $[L^-]$. The comparison of the experimentally assessed values with those taken from literature is given in Table 1. An agreement with the theory is satisfactory for the β_2/β_1 ratios, but not for the β_3/β_1 ratios. It should be noted that some stability constants, especially for higher complexes, are branded as less reliable in the literature [12].

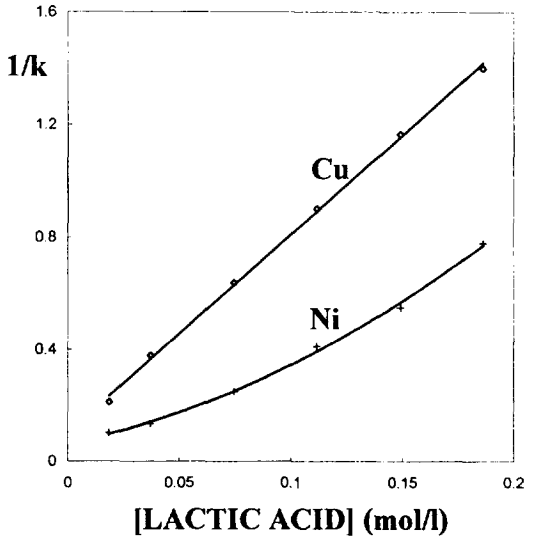

Fig. 5. Dependence of $1/k$ on the lactate concentration at constant concentration of eluting cation. Column as in Fig. 4. Mobile phase 0.2 mol/l NaOH–0.019–0.187 mol/l lactic acid, pH 6.0±0.1 adjusted with $HClO_4$.

Table 1
Stability constants of lactate complexes and values of the β_2/β_1 and β_3/β_1 ratios for the Cu^{2+} and Ni^{2+} ions

	Cu^{2+}	Ni^{2+}
$\log \beta_1^a$	2.45	1.64
$\log \beta_2^a$	4.08	2.76
$\log \beta_3^a$	4.7	3.1
$\log (\beta_2/\beta_1)^b$	1.63	1.12
$\log (\beta_2/\beta_1)^c$	1.84	1.44
$\log (\beta_3/\beta_1)^b$	2.25	1.46
$\log (\beta_3/\beta_1)^c$	0	2.26

[a]Data form Ref. [12].
[b]Calculated from published values.
[c]Calculated from experimental dependences in Fig. 5.

Similar to the case of tartrate complexes, also in the M^{2+}–lactate system the retention of metal ions can be influenced by the change of the mobile phase pH. It holds for the total lactate concentration:

$$c_L = [L^-](1 + K_{H1}[H^+]) \quad (9)$$

On combining Eq. 9 with Eq. 6, or, as the case may be, with simplified Eq. 8, we obtain the dependence of the capacity factor on the concentration of mobile phase and its pH. The dependence of the capacity factor of the Ni^{2+} ions on the lactate concentration and mobile phase pH at constant concentration of eluting cations is shown in Fig. 6. The given value of the protonation constant of lactic acid ($\log K_{H1} = 3.66$ [12]) was used for the calculation, the other system parameters were determined from the experimental

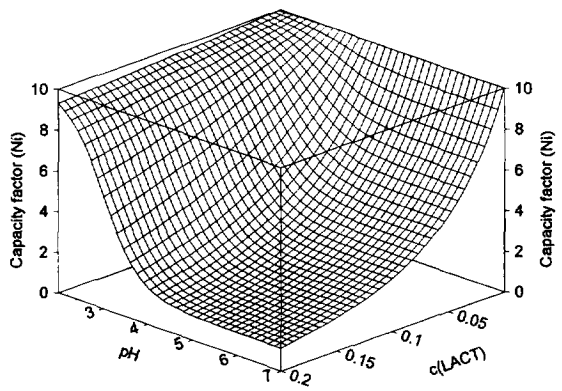

Fig. 6. Dependence of the capacity factor of Ni^{2+} ions on pH and total concentration of lactate at constant concentration of Na^+ ions (0.2 mol/l).

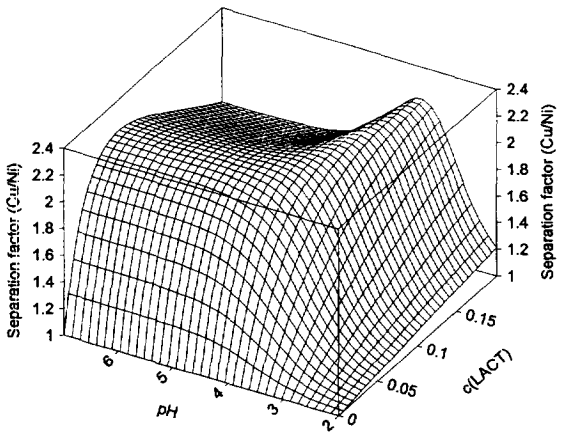

Fig. 7. Dependence of the separation factor of Cu^{2+} and Ni^{2+} ions on pH and total concentration of lactate at constant concentration of Na^{+} ions.

dependences in Fig. 4 and Fig. 5. The dependence of the separation factor for the Cu^{2+}/Ni^{2+} pair is demonstrated in Fig. 7. As can be seen the dependences are not monotonous, which is characteristic for systems where metal ions form complexes of different kinds (see Fig. 5).

3.3. M^{2+}–oxalate system, anion-exchange separation

It is well known from "classical" applications of ion exchangers, as well as from IC that a number of metal ions can be successfully separated on anion exchangers in the form of their anionic complexes [1,18]. One of the agents which have been used in separations of anionic complexes of transition and heavy metals is oxalic acid [8,19,20]. A general description of the chromatographic system may by rather complicated in this case. Let us suppose for simplicity that the highest complex formed by the reaction of the divalent metal cation M^{2+} with ligand L^{2-} (and the only complex which can be retained on the anion-exchange column) is that of the ML_2^{2-} type. Oxalate acting simultaneously as an eluting anion and complexing agent may be present in two forms having an eluting capability; as anions HL^- and L^{2-}. A similar situation occurs often in IC of common anions and there are a few approaches to solve this problem (dual eluent species approach, dominant equilibrium approach [1]). The solution, which is quite satisfactory for the separations of inorganic, as well as organic anions with the aid of polyvalent eluents, was derived recently by Mongay et al. [21]. Using their approach to the separation of oxalate complexes we can express the ion-exchange equilibrium on the anion-exchange column by the summary equation:

$$2\,[ML_2^{2-}]_m + L_s^{2-} + 2\,HL_s^- \Leftrightarrow 2\,[ML_2^{2-}]_s + L_m^{2-} + 2\,HL_m^- \quad (10)$$

The global selectivity coefficient is given:

$$K_{ML}^{L} = \frac{[ML_2^{2-}]_s^2\,[L^{2-}]_m\,[HL^-]_m^2}{[ML_2^{2-}]_m^2\,[L^{2-}]_s\,[HL^-]_s^2} \quad (11)$$

The subscripts m and s refer to the mobile and stationary phases, respectively. It is assumed further [21] that the concentrations of the individual eluent species in the stationary phase are proportional to their concentration in the mobile phase and to their charge:

$$\frac{[L^{2-}]_s}{[HL^-]_s} = \frac{2\,[L^{2-}]_m}{[HL^-]_m} \quad (12)$$

It holds for the column capacity

$$Q = 2\,[L^{2-}]_s + [HL^-]_s + 2[ML_2^{2-}]_s \quad (13)$$

where the last term on the right-hand side may be neglected. The capacity factor is given as the ratio of the amount of an analyte in the stationary phase to that in the mobile phase:

$$k = \frac{w}{V_m}\frac{[ML_2^{2-}]_s}{c_M} \quad (14)$$

The total concentration of metal in the mobile phase can be expressed as a sum:

$$c_M = [M^{2+}]_m + [ML]_m + [ML_2^{2-}]_m = [ML_2^{2-}]_m\left(1 + \frac{\beta_1}{\beta_2[L^{2-}]_m} + \frac{1}{\beta_2[L^{2-}]_m^2}\right) \quad (15)$$

On combining Eqs. 11–15 and rearranging we obtain the relationship for the capacity factor:

$$k = \frac{w}{V_m} \frac{(K^1_{ML})^{1/2} Q^{3/2}}{2\left(2[L^{2-}]_m + \frac{1}{2}[HL^-]_m\right)^{3/2} \left(1 + \frac{\beta_1}{\beta_2[L^{2-}]_m} + \frac{1}{\beta_2[L^{2-}]_m^2}\right)} \quad (16)$$

We can express the concentrations $[L^{2-}]_m$ and $[HL^-]_m$ using the total concentration and the respective protonation constants; in this way we obtain the dependence of the capacity factor on the mobile phase pH.

In Fig. 8 the experimental and calculated dependences of the capacity factors on the oxalate concentration are compared for Co^{2+} a Ni^{2+} ions at a constant pH value. The given values of the stability constants [12] were used in calculations, the other model parameters were determined from experimental data in Ref. [20]. The dependence of the capacity factor (for the Ni^{2+} ions) on the total concentration of oxalate and the mobile phase pH is shown in Fig. 9. Eq. (16) was used for calculations with the model parameters determined from the experimental data and the protonation constants of oxalic acid taken from literature ($\log K_{H1}=3.82$, $\log K_{H2}=1.04$ [12]). It can be seen that in the examined range the analyte retention decreases with increasing concentration of oxalate (driving effect of oxalate anions), whereas the dependence of the analyte retention on the pH value passes through a not very distinct maximum. At low pH values oxalic acid is not dissociated and

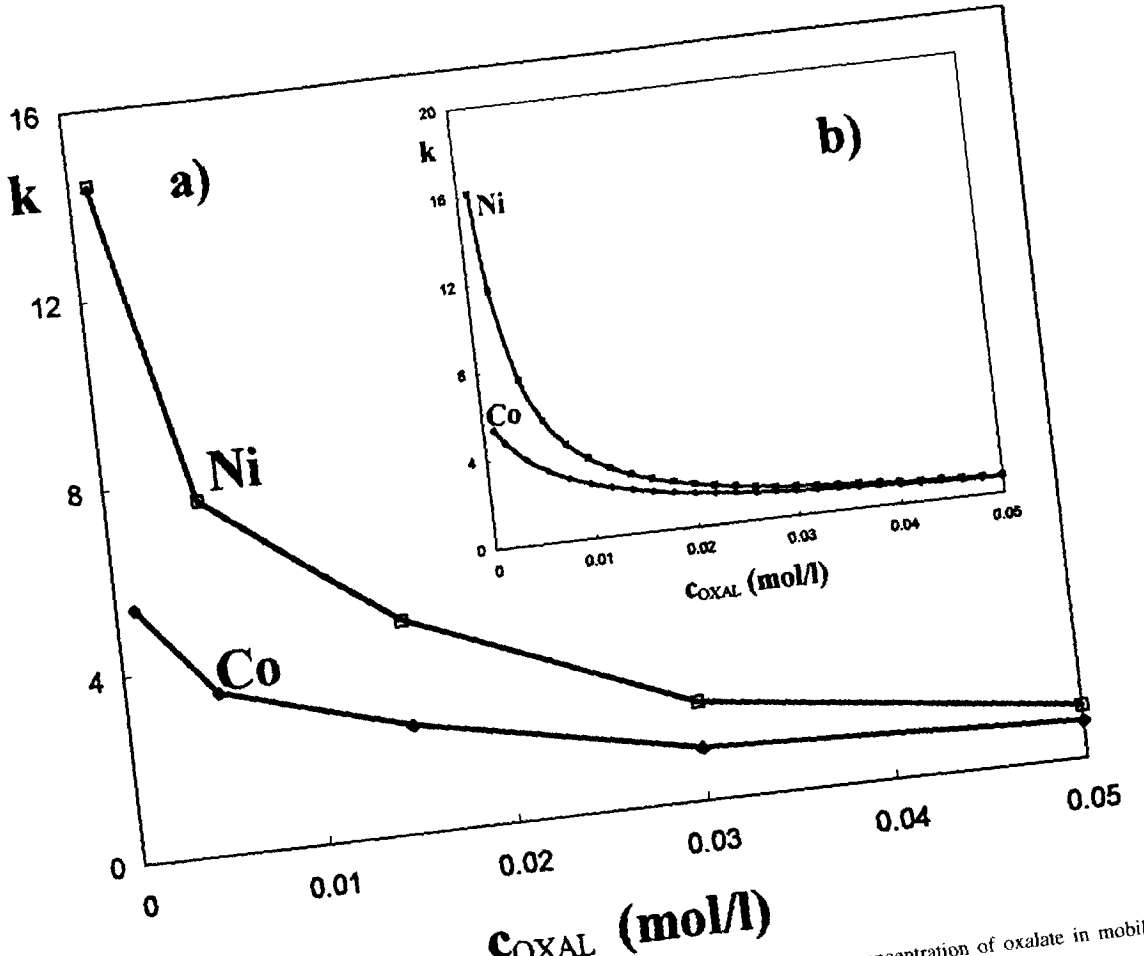

Fig. 8. Comparison of experimental (a) and calculated (b) dependences of capacity factors on concentration of oxalate in mobile phas
Column 150×3 mm, Separon HEMA Q-L, mobile phase 0.001–0.05 mol/l natrium oxalate, pH 6.0±0.1.

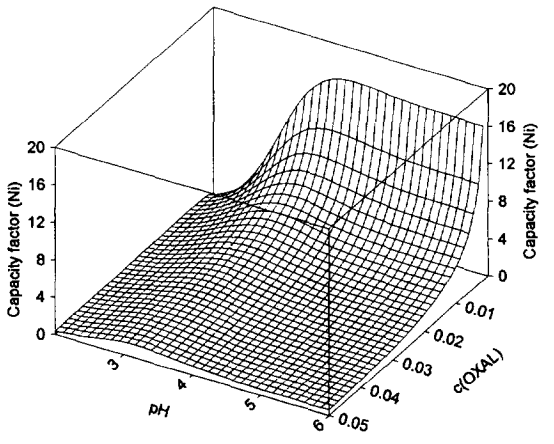

Fig. 9. Dependence of capacity factor of Ni^{2+} ions on pH and total concentration of oxalate.

metal–oxalate complexes, which could be retained on the anion-exchange column, can not be formed; at high pH values, on the other hand, a driving effect of fully dissociated oxalate anions prevails. The calculated dependences are in an agreement with those measured in [20] in the pH range 2–5. The dependence of the separation factor on the pH value and total oxalate concentration is demonstrated in Fig. 10 for the Ni^{2+}/Co^{2+} pair. The highest values of separation factor were reached at low oxalate concentrations, but this area has no importance for chromatographic separations, because the analyte retention is too small under these conditions. On the contrary, it is advantageous to work at higher pH values, when the retention and separation of analytes are sufficient.

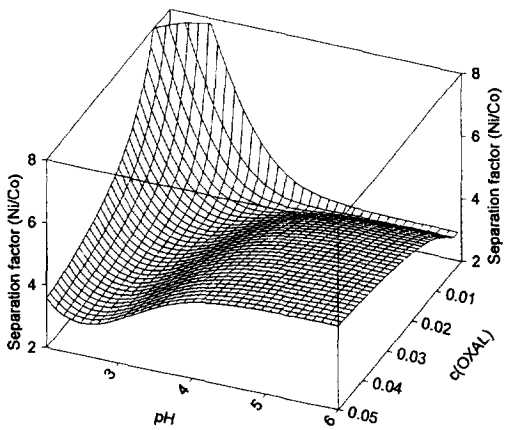

Fig. 10. Dependence of separation factor of Co^{2+} and Ni^{2+} ions on pH and total concentration of oxalate.

4. Conclusions

Retention characteristics of metal ions in IEC can be predicted with the aid of the relations derived in this work and also conditions for effective separations can be estimated. It is necessary to say that the separation factor as the simplest separation characteristic do not give full information about separability of analytes, at least the shapes of the peaks (peak width, asymmetry, tailing) must be taken into account. The peak width is given by the column efficiency in the first place and is related to the retention time [22]; therefore, it can be estimated from the presented relations. Using that, e.g., the resolution can be calculated. Other parameters, however, can not be determined from the equilibrium model presented here. Some of them likely depend on kinetics of the primary and/or secondary equilibria involved in the retention mechanism; these problems will be further investigated.

In the cation-exchange mode an addition of the suitable complexing agent reduces (not uniformly) the analyte retentions and simultaneously increases the separation factors. Somewhat stronger complexing agents, anions of di- and polycarboxylic acids such as tartrate, seem to be more convenient for the separations of divalent metal cations (heavy and transition metals). They are effective at concentrations of ca. 10^{-3}– 10^{-2} mol/l. Hydroxycarboxylic acids (lactic, α-hydroxyisobutyric) are less effective and have to be used at concentrations of 0.1 mol/l or even higher [14] to achieve a comparable effect. Their main role is in the separations of elements with very close properties such as lanthanides and actinides [2,3,16]. Many examples of the real separations can be found in the literature [1–3,14].

Separation of metals in the form of their anionic complexes is very promising. The retention mechanisms are more complicated in real chromatographic systems and will be further investigated.

5. List of symbols

α, $\alpha_{2,1}$	Separation factor
β_i	Overall stability constant
c_L	Total ligand concentration
E^{z+} (E^+)	Eluting (driving) cation in cation-exchange chromatography
k	Capacity factor
K_{Hi}	Protonation constant
K^E_M, K^E_{ML}, K^L_{ML}	Selectivity coefficients
L^{y-} (L^{2-}, L^-)	Complexing ligand
M^{x+} (M^{2+})	Metal (analyte) cation
Q	Column capacity
V_m	Volume of mobile phase in the column
w	Weight of stationary phase

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