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Short communication

Separation of metal–oxalate complexes on an anion-exchange column

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Abstract

Divalent metal cations (Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+}) were separated on HEMA Q-L anion exchanger in the form of their oxalate complexes. The mechanism of the retention of anionic complexes on an anion-exchange column is proposed using the general theory of side equilibria in liquid chromatography. Dependences of the analyte retention on the mobile phase composition were measured and evaluated with the aid of the derived relationships.

1. Introduction

Metal cations can be effectively separated by various ion chromatographic (IC) methods such as ion-exchange chromatography (IEC) and ion interaction chromatography (IIC). The most commonly employed approach is ion-exchange separation on low-capacity cation exchangers with mobile phases containing weak complexing agents, e.g., hydroxycarboxylic or dicarboxylic acids. One of the agents which can be used in both cation and anion-exchange separations of metals is oxalic acid. The IEC separation of divalent metal cations in the form of their anionic complexes has been reported [1,2], an excellent IIC separation of oxalate complexes of rare earth metal cations was achieved by Jones et al. [3] and a similar chromatographic system was applied also to the separation of divalent metal cations [4].

A retention model for the separation of anionic complexes by anion exchange was pre-

sented by Haddad and Jackson [5]; the derived relationships do not convey the experimental dependences very well, especially in those cases when the anion of mobile phase acts simultaneously as an eluting ion and a complexing agent [2].

In this paper, a retention model is suggested that describes the retention of divalent metal cations in the form of their anionic oxalate complexes on an anion-exchange column. The dependences of the analyte retention on the mobile phase composition were investigated for Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} ions.

2. Experimental

The liquid chromatograph consisted of an HPP 5001 high-pressure pump, an LCI 30 injection valve with a 20- μl sampling loop, an LCD 2040 UV-Vis spectrophotometric detector operating at 254 nm and a TZ 4620 chart recorder (all from

Laboratorní Přístroje, Prague, Czech Republic). Separations were carried out on a glass column (150 × 3 mm I.D.) packed with Separon HEMA Q-L (7 μm) sorbent (polymeric anion-exchange material based on a matrix of hydroxyethyl methacrylate copolymer with a low specific ion-exchange capacity).

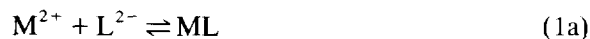
Stock solutions of 0.1 mol/l oxalic acid and sodium perchlorate were prepared. Mobile phases were prepared by mixing these stock solutions in the required ratios and adjusting their pH to 6 ± 0.1 with dilute sodium hydroxide solution. In addition, stock solution of 0.1 mol/l MnCl₂, CoCl₂, NiCl₂ and Cu(NO₃)₂ were prepared and subsequently diluted with the mobile phase to concentrations of 1 mmol/l (MnCl₂, CoCl₂ and NiCl₂) or 0.02 mmol/l (Cu²⁺ solutions) before measurements. All chemicals were of analytical-reagent grade (Lachema, Brno, Czech Republic) and solutions were prepared with redistilled water.

The mobile phases were deaerated in an ultrasonic bath before measurements. The mobile phase flow-rate was 0.3 ml/min. Measurements were carried out at laboratory temperature (22 ± 2°C).

Retention times of analytes were determined as an averages from at least triplicate injections of the respective metal solution and capacity factors were calculated by the usual method. The column dead volume (time) was assessed from disturbances on the chromatograms brought about by the injection of samples or redistilled water.

3. Results and discussion

After injection of an analyte (metal cation, M²⁺) into the mobile phase containing oxalate anions (L²⁻), formation of complexes according to the following equations takes place:



A general theory of secondary equilibria can be used for the description of the retention of

analytes which can exist in more than one form in the mobile phase [6]. The capacity factor of the metal co-existing in equilibrium with complexes ML₁ . . . ML_n in solution can be expressed as a sum of weighted average capacity factors for each analyte form [7,8]:

$$k = k_M F_M + k_{ML} F_{ML} + k_{ML_2} F_{ML_2} + \dots + k_{ML_n} F_{ML_n} \quad (2)$$

where $k_M \dots k_{ML_n}$ are the limiting capacity factors and $F_M \dots F_{ML_n}$ are mole fractions of the analyte in each of its forms. It holds for the mole fractions that

$$F_{ML_i} = \frac{[ML_i]}{c_M} = \frac{\beta_i [L]^i}{1 + \sum_{i=1}^n \beta_i [L]^i} \quad (3)$$

where β_i are overall stability constants and [L] is the concentration of ligand in the mobile phase (charges of the species are omitted for simplicity). On combining Eqs. 2 and 3, one obtains

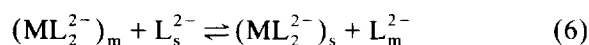
$$k = \frac{k_M + \sum_{i=1}^n k_{ML_i} \beta_i [L]^i}{1 + \sum_{i=1}^n \beta_i [L]^i} \quad (4)$$

Eq. 4 can be applied both to cationic systems (metal cation separations on cation exchangers) and to anionic systems (separations of metals in the form of anionic complexes on anion exchangers). The magnitude of the k_{ML_i} coefficients expresses the ability of the respective complexes to be retained on the stationary phase surface. We assume that only negatively charged species are retained on the anion-exchange column. k_M expresses the retention of a free (uncomplexed) cation and it is equal to zero; likewise k_{ML} expresses the retention of the neutral complex. Taking into account that the highest complex in the M²⁺-oxalate system of ML₂ type, we can rewrite Eq. 4 as follows:

$$k = \frac{k_{ML_2} \beta_2 [L]^2}{1 + \beta_1 [L] + \beta_2 [L]^2} \quad (5)$$

The coefficient k_{ML_2} involves the mass of station-

any phase, m , the volume of mobile phase in the column, V_M , the column capacity, Q , the concentration of the eluting cation and the equilibrium constant of the ion-exchange reaction taking place on the column. When the mobile phase contains only oxalate anions acting simultaneously as complexing agent and eluting (driving) anion, the analyte retention can be expressed by the equation



where the subscripts m and s refer to the mobile and stationary phases, respectively. The limiting capacity factor for the ML_2 species is given as the ratio of its amount in the stationary phase to that in the mobile phase:

$$k_{\text{MM}_2} = \frac{m}{V_M} \cdot \frac{[\text{ML}_2]_s}{[\text{ML}_2]_m} \quad (7)$$

The column capacity is expressed as a sum:

$$Q = 2[\text{L}]_s + 2[\text{ML}_2]_s \quad (8)$$

while the second term on the right-hand side of Eq. 8 may be neglected under common chromatographic conditions. Then, using the relationship for the equilibrium constant of Eq. 6 (selectivity coefficient, $K_{\text{ML}_2}^{\text{L}}$) and combining with Eqs. 7 and 8, we obtain

$$k_{\text{ML}_2} = \frac{m}{V_M} \cdot \frac{K_{\text{ML}_2}^{\text{L}} Q}{2[\text{L}]} \quad (9)$$

Substituting into Eq. 5, we obtain a rather complicated dependence of the capacity factor on the ligand concentration:

$$k = \frac{mK_{\text{ML}_2}^{\text{L}} Q \beta_2 [\text{L}]}{2V_M (1 + \beta_1 [\text{L}] + \beta_2 [\text{L}]^2)} \quad (10)$$

The stability constants for the oxalate complexes of the metals investigated are typically in the range 10^3 – 10^5 . Hence for ligand concentrations greater than ca. 10^{-3} mol/l the numeral 1 may be neglected with respect to the other terms in parentheses in the denominator on the right-hand side of Eq. 10. After simplification and rearrangement, we obtain

$$\frac{1}{k} = C_1 \left(\frac{\beta_1}{\beta_2} + [\text{L}] \right) \quad (11)$$

where the constant C_1 involves the column parameters (m , V_M , Q) and the selectivity coefficient $K_{\text{ML}_2}^{\text{L}}$.

The dependences of the analyte retention on the oxalate concentration were investigated at pH 6, where oxalic acid was fully dissociated. As can be seen from Fig. 1, the experimentally assessed dependences are in good agreement with Eq. 11. The slopes of the straight lines depend on (in addition to the column parameters) the selectivity coefficients of the respective anionic complexes. It can be expected, for example, that the selectivity coefficient of MnL_2^{2-} and CoL_2^{2-} complexes will be similar. Separation of these complexes is permitted by different values of the stability constants. It follows from Eq. 11 that the ratio of the intercept on the ordinate to the slope of the respective dependence is equal to the β_1/β_2 ratio [i.e. $\log \beta_1 - \log \beta_2 = \log(\text{intercept/slope})$]. These values are compared in Table 1. The agreement of the experimental results with theory is satisfactory only

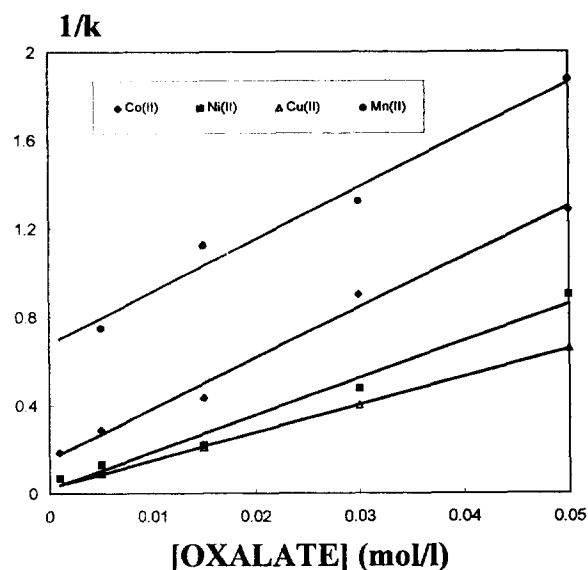


Fig. 1. Dependence of reciprocal of capacity factor on oxalate concentration in the mobile phase. Column, 150×3 mm I.D., Separon HEMA Q-L, $7 \mu\text{m}$; mobile phase, 0.001–0.05 mol/l sodium oxalate (pH 6.0 ± 0.1 , adjusted with NaOH).

Table 1

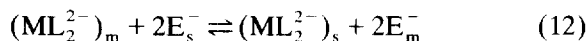
Stability constants of metal–oxalate complexes and log(intercept/slope) values calculated from experimental dependences in Fig. 1

Metal cation	Log β_1	Log β_2	$\Delta \log \beta$	Log $\left(\frac{\text{intercept}}{\text{slope}}\right)$
Mn ²⁺	3.2	4.4	-1.2	-1.54
Ni ²⁺	4.05	6.01	-1.96	-2.91
Cu ²⁺	4.87	9.21	-4.37	-2.71
Co ²⁺	3.25	5.60	-2.35	-2.17

Stability constants of Ni²⁺-oxalate complexes from Ref. [9] ($I = 0.5$, 25°C), others from Ref. [10] ($I = 0.1$, 25°C for Mn²⁺ and $I = 1$, 25°C for Cu²⁺ and Co²⁺ ions).

in some cases; however, the limited number of experimental data do not allow us to draw definite conclusions concerning the validity of the retention model.

The retention of anionic complexes on an anion-exchange column can be effectively influenced by the addition of other eluting anion; a powerful and frequently used eluting agent is perchlorate anion. When the mobile phase contains two or more eluting anions, the entire retention model (dual eluent species approach) is rather complicated. For simplicity, we will assume further that perchlorate anions play the main role in the analyte elution (dominant equilibrium approach). The analyte retention can be then expressed as



where E⁻ is perchlorate anions. The relationship for k_{ML_2} can be derived in a similar way to that shown above. In this case

$$k_{\text{ML}_2} = \frac{m}{V_M} \cdot \frac{K_{\text{ML}_2}^{\text{E}} Q^2}{[\text{E}^-]^2} \quad (13)$$

Substituting into Eq. 5, we obtain

$$k = \frac{mK_{\text{ML}_2}^{\text{E}} Q^2 \beta_2 [\text{L}]^2}{V_M [\text{E}]^2 (1 + \beta_1 [\text{L}] + \beta_2 [\text{L}]^2)} \quad (14)$$

Dependences of the retention of oxalate complexes on the perchlorate concentration were investigated at constant concentration of oxalate anions in the mobile phase. Under given conditions the dependences can be expressed with

the aid of a commonly used logarithmic relationship:

$$\log k = C_2 - 2 \log [\text{E}] \quad (15)$$

where the constant C_2 involves the column parameters, selectivity coefficient, ligand concentration and stability constants. Experimentally assessed dependences (Fig. 2) satisfy Eq. 15 comparatively well, but the slopes are smaller (ca. 0.6–0.8) than those predicted by Eq. 6. This may be caused by the above-mentioned simplification of the retention model. Mn²⁺ ions exhibit a low retention with the mobile phase containing

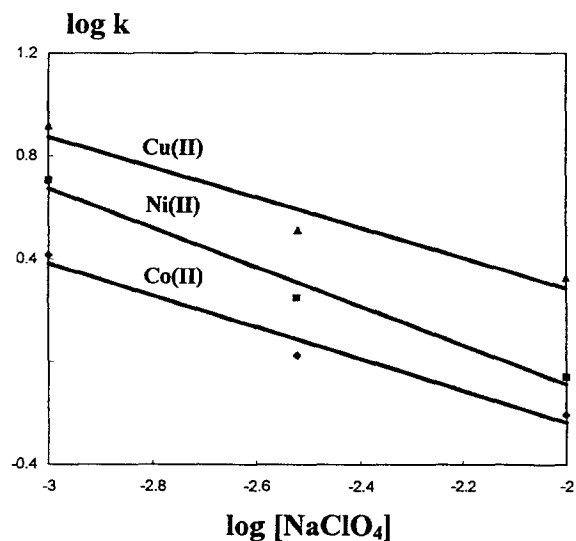


Fig. 2. Log k vs. log $[\text{NaClO}_4]$ plots. Column as in Fig. 1; mobile phase, 0.005 mol/l sodium oxalate + 0.001–0.01 mol/l sodium perchlorate (pH 6.0 ± 0.1 , adjusted with NaOH).

perchlorate ions and therefore retention data are not presented in Fig. 2.

The pH of the mobile phase significantly affects the retention of analytes in the system examined. The effect of pH can manifest itself particularly in two ways: the degree of dissociation of the mobile phase components (oxalic acid) and hence the eluting capability increase with increase in pH, and the pH influences the course of complex-forming reactions, the composition (net charge) of complexes and thus the ability of the complexes to be retained on the column. It was demonstrated in our previous work [2] that the analyte retention decreases with increasing pH within the range 3–7; obviously the first of the above-mentioned effects predominates. Similar dependences were also observed in an analogous IIC system [4].

Sorption of metals both on cation exchangers and on anion exchangers has frequently been employed for investigations of the composition and stability of metal complexes [11,12]. The possibilities of using these “classical” approaches (Fronaeus, Marcus and Coryell, Kraus and Nelson approaches [11,12]) in ion chromatography were pointed out in a review [13], but anion-exchange chromatography has not yet been applied. Future work will be aimed at investiga-

tions of complex-forming equilibria with the aid of IC in the anion-exchange mode.

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