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Determination of stability constants of metal complexes from ion chromatographic measurements

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ABSTRACT

Relations were derived between the retention of metal cations on a cation-exchange column and the composition of a mobile phase in the presence of complexing agents and, based on the derived relations, a method was suggested for measuring the stability constants of complexes of metal cations with anions of dicarboxylic (polycarboxylic) acids. The method was applied to the determination of the stability constants of complexes of some divalent cations (Zn^{2+}, Ni^{2+}, Co^{2+}, Cd^{2+}, Mn^{2+}, Fe^{2+} and Pb^{2+}) with the anions of oxalic, tartaric, citric, pyridine-2,6-dicarboxylic and malonic acids. The results are in good agreement with those obtained with other methods.

INTRODUCTION

The method of ion chromatography (IC) has been widely used for the separation and determination of metal cations. Complex-forming reactions in the mobile phase are often employed to improve the separation (see, for example, refs. 1–5) and a number of others as given in the review [6]). Although these methods are fairly common in analytical practice, comparatively few studies have been devoted to a systematic investigation of the effect of a complexing ligand on the separation of metal cations and to deriving relations between retention of the analytes and composition of the mobile phase [7–10]. Until now IC has been used, but to a lesser extent, for assessing physico-chemical characteristics.

Recently Lin and Horváth [11] published a paper dealing with the measurement of the stability constants of metal complexes, using the IC method. Independently of the mentioned work [11], we suggested in our preceding paper [12] the possibility of studying the composition and stability of complexes with the aid of the ion chromatographic method.

In the present paper relations are derived in greater detail, describing the retention of metal cations on cation exchangers in those cases when complex-forming reactions are taking place in the mobile phase. Based on the derived relations a method for measuring the stability constants of metal complexes is suggested. The method was adopted for measuring the stability constants of complexes of divalent metal cations with the anions of oxalic, tartaric, citric, pyridine-2,6-dicarboxylic (PDCA) and malonic acids.

EXPERIMENTAL

Apparatus

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-μm sampling loop, an RE 2M post-column reactor, a TZ 4261 strip-chart recorder (all made by

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Laboratorní přístroje, Prague, Czech Republic) and a Model 832 870 UV–VIS spectrophotometric detector (Knauer, Berlin, Germany) operated at a wavelength of 520 nm.

The mobile phases were deaerated in an ultrasonic bath prior to their use. The flow-rates of both the mobile phase and derivatization agent in the course of measuring were 0.3 ml min^{-1}. The capacity factors of analytes were calculated by a usual method. The column dead volume was assessed from disturbances on chromatograms, brought about by the injection of samples (injection or solvent peaks). The measurements were carried out at the room temperature, 22 ± 1°C.

Columns and chemicals

A glass column 150 × 3 nm packed with octadecyl-bonded silica Separon SGX C_{18}, 5 μm, coated for 2 h with 5 mmol l^{-1} sodium dodecyl sulphate (SDS) at a flow-rate of 0.1 ml min^{-1}, was used for the separation of metal ions. A more detailed description of the preparation of columns and of their properties is given in ref. 13. It was found that the separation on a column modified in this way is controlled by an ion-exchange mechanism [13]. A saturation column, 30 × 3 mm packed with the Separon SGX 7-μm silica, was connected between the pump and the sampling loop (all columns were supplied by Tessek, Prague, Czech Republic).

The 5 mmol l^{-1} SDS solution was prepared from research-grade-quality reagent (Serva, Heidelberg, Germany).

In addition, the following stock solutions were prepared: 1 mol l^{-1} sodium hydroxide and 0.1 mol l^{-1} solutions of oxalic, tartaric, citric and malonic acids. The 1 mmol l^{-1} solution of PDCA (Merck, Darmstadt, Germany) was prepared by dissolving in 0.1 mol l^{-1} sodium hydroxide. Concentrations of the stock solutions were checked using conventional titrimetric (acidimetric or alkalimetric) methods. The mobile phases were prepared by combining the sodium hydroxide stock solution with the solution of each acid at requisite ratios so that the mobile phases should always contain equal quantity of Na^+ and required amount of the complexing ligand. The mobile phase pH was adjusted to a required constant value by adding dilute perchloric acid.

Stock solutions of the examined cations were prepared from the nitrates, chlorides or sulphates and diluted to a constant concentration within the 0.01–0.1 mmol l^{-1} range for each run of the measurements.

A 0.2 mmol l^{-1} solution of 4-(2-pyridylazo)resorcinol (PAR) containing 1 mol l^{-1} acetic acid and 3 mol l^{-1} ammonium hydroxide served as the post-column derivatizing agent.

Unless stated otherwise all the reagents used were analytical grade (Lachema, Brno, Czech Republic). Redistilled water was used for preparing the solutions.

RESULTS AND DISCUSSION

With the experimental arrangement described in the preceding section the mobile phase contains, in the first place, the eluting cation E^{z+}, a complexing anion (ligand, L) and perchlorate ions supplied by adjusting pH with the aid of perchloric acid. In the present derivation we will not consider (unlike Lin and Horváth [11]) the participation of H^+ in the ion-exchange equilibria. We are assuming that the pH value is sufficiently high that the H^+ concentration may be neglected. (Provided that the concentration of the eluting ion is, for example, 0.1 mol l^{-1}, as shown below, this assumption holds true within almost the full range of commonly employed pH values.) At the same time we assume that the prevailing form of ligands in the solutions at the given pH is the anion L^{2-} (dissociation to the second degree). After the injection of analyte (metal cation, M^{2+}) into the mobile phase formation of complexes occurs according to:

$$M^{2+} + L^{2-} \rightleftarrows ML \tag{1a}$$

$$ML + L^{2-} \rightleftarrows ML_2^{2-}\text{ , etc.} \tag{1b}$$

The separated metals are present in the form of free cations or in the form of neutral or negatively charged complexes that do not take part in the ion-exchange processes taking place on the column. The retention of analytes is described by:

$$zM_m^{2+} + 2E_s^{z+} \rightleftarrows zM_s^{2+} + 2E_m^{z+} \quad (2)$$

The indexes m and s refer to mobile and stationary phases, respectively. The equilibrium constant of eqn. 2 (selectivity coefficient) is given as

$$K_M^E = \frac{[M^{2+}]_s^z[E^{z+}]_m^2}{[M^{2+}]_m^z[E^{z+}]_s^2} \quad (3)$$

The sorbent capacity, Q, is expressed as a sum

$$Q = z[E^{z+}]_s + 2[M^{2+}]_s \quad (4)$$

while the second term on the right-hand side usually may be neglected and it is possible to write:

$$[E^{z+}]_s = Q/z \quad (5)$$

It holds for the capacity factor k_M:

$$k_M = q\frac{[M^{2+}]_s}{c_M} \quad (6)$$

where q is the phase ratio and c_M is total concentration of metal in the mobile phase as given by the sum (for simplicity the ionic charges are omitted):

$$c_M = [M]_m + [ML]_m + [ML_2]_m + \cdots + [ML_n]_m \quad (7)$$

Eqn. 7 can be rewritten using the overall stability constants β_1–β_2:

$$c_M = [M]_m(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n) \quad (8)$$

On combining the eqns. 3, 5, 6 and 8 and rearranging, we obtain:

$$k_M = q\frac{(K_M^E)^{1/z}\left(\frac{Q}{z}\right)^{2/z}}{[E^{z+}]^{2/z}(1 + \beta_1[L] + \beta_2[L]^2 + \cdots \beta_n[L]^n)} \quad (9)$$

expressing both the pushing effect of eluting cation and the pulling effect of complexing anion. Usually eqn. 9 is presented in logarithmic form and the effect of complexing equilibria is expressed by means of the side equilibria coefficient α_M [7,8,10].

To be able to examine experimentally the influence of complexing equilibria on the retention of analytes, we had to vary the concentration of ligand in the mobile phase and, at the same time, keep all the other variables in the mobile phase constant, particularly the concentration of eluting ion and pH. Lin and Horváth [11] used ethylene diamine and tartaric acid as the main components of the mobile phase; the concentration of the ethylenediammonium cation was kept constant, the tartrate anion concentration was varied within 0.2–5 mmol l^{-1} and the constant value of pH was adjusted by adding either sodium hydroxide or nitric acid. Thus the mobile phase contained, in addition to the main components, an undefined amount of other ions (Na^+, NO_3^-). Their influence, however, is likely to be negligible.

In the present study we used a weaker driving cation, Na^+, at a higher concentration. Mobile phases were prepared by combining sodium hydroxide solution with solutions of each acid (oxalic, tartaric, etc.) so that the Na^+ concentration was constant while only the ligand concentration was varied. Constant pH value was adjusted with the aid of perchloric acid. Therefore, the mobile phase composition was exactly defined and the measurements were carried out at almost constant ionic strength (*ca.* 0.1 mol l^{-1} sodium perchlorate). Perchlorate anions take part neither in complexing nor in ion-exchange reactions in the system under consideration. The measurements were carried out at a pH value at which the examined dibasic acids are almost fully dissociated [14] (oxalic and tartaric acids and PDCA at pH 6 and malonic acid at pH 6.5). For measurements in the citrate medium the pH value of 5.5 was adopted, at which the prevailing form in the solution is a HL^{2-} anion (the formal charge is −2.156 [14]).

Provided that, with a proper arrangement of experiments, we can consider the concentration of the eluting cation E^{z+} as being constant, eqn. 9 may be rewritten in the following form:

$$\frac{1}{k_M} = A(1 + \beta_1[L] + \beta_2[L]^2 + \cdots + \beta_n[L]^n) \quad (10)$$

where the constant A is given as:

$$A = \frac{[E^{z+}]^{2/z}}{q(K_M^E)^{1/z}\left(\frac{Q}{z}\right)^{2/z}} \quad (11)$$

Eqn. 10 expresses the dependence of the capacity factor on the concentration of ligand in a mobile phase or, on the other hand, makes it possible to determine stability constants from experimentally assessed dependences $1/k_M$ *vs.* ligand concentration.

An example of the experimentally assessed dependence of the reciprocal value of capacity factors on the concentration of a ligand in the mobile phase in the case of tartrate complexes is shown in Fig. 1. As may be seen from that diagram, the obtained dependences are linear within the examined concentration range. This means that we may neglect the quadratic and higher terms in brackets on the right-hand side of eqn. 10. Then the stability constants can be

TABLE I

STABILITY CONSTANTS OF METAL COMPLEXES

Ions	Log β_1	
	This work	Published values [references]
Oxalate complexes		
Zn^{2+}	4.07 ± 0.06	3.88 [15]; 4.87 [2]
Ni^{2+}	4.69 ± 0.46	5.16 [15]
Co^{2+}	4.08 ± 0.04	3.25 [15]
Cd^{2+}	3.35 ± 0.01	2.75 [15]
Mn^{2+}	3.35 ± 0.01	3.2 [15]; 3.20 [2]
Fe^{2+}	3.64 ± 0.03	3.05 [15]
Pb^{2+}	4.12 ± 0.57	3.32 [15]
Tartrate complexes		
Zn^{2+}	2.44 ± 0.06	2.29 [12][a]; 2.75 ± 0.03 [11][b]; 3.82 [15]
Ni^{2+}	2.41 ± 0.07	2.39 [12][a]
Co^{2+}	2.24 ± 0.01	2.36 [12][a]; 2.48 ± 0.02 [11][b]; 3.225 [16][c]
Cd^{2+}	2.15 ± 0.03	2.04 [12][a]; 2.27 ± 0.01 [11][b]; 2.913 [16][c]
Mn^{2+}	1.94 ± 0.02	1.35 [12][a]; 1.89 ± 0.04 [11][b]; 2.49 [15]
Fe^{2+}	2.11 ± 0.01	2.29 [12][a]; 2.17 ± 0.01 [11][b]; 2.2 [15]
Pb^{2+}	2.43 ± 0.04	2.93 [12][a]; 2.60 [15]
Citrate complexes (HL^{2-})		
Zn^{2+}	4.18 ± 0.11	4.27 [15]; 4.98 [2]
Co^{2+}	4.48 ± 0.02	5.00 [15]
Cd^{2+}	3.32 ± 0.05	3.15 [15]
Mn^{2+}	3.50 ± 0.09	4.15 [15]; 3.70 [2]
Fe^{2+}	3.75 ± 0.07	4.4 [15]
Pb^{2+}	4.10 ± 0.06	4.34 [15]
PDCA complexes		
Mn^{2+}	4.66 ± 0.13	5.01 [2]
Malonate complexes		
Zn^{2+}	2.81 ± 0.03	2.96 [15]
Ni^{2+}	3.19 ± 0.10	3.24 [15]
Co^{2+}	3.01 ± 0.06	2.97 [15]
Cd^{2+}	2.75 ± 0.06	1.92 [15]
Mn^{2+}	2.71 ± 0.06	3.28 [15]
Fe^{2+}	2.85 ± 0.08	

[a] IC method, ionic strength *ca.* 0.04 mmol l^{-1} lithium perchlorate pH 3.60 ± 0.05.

[b] IC method, 30°C, ionic strength *ca.* 1–13 mmol l^{-1}.

[c] Capillary isotachophoresis method.

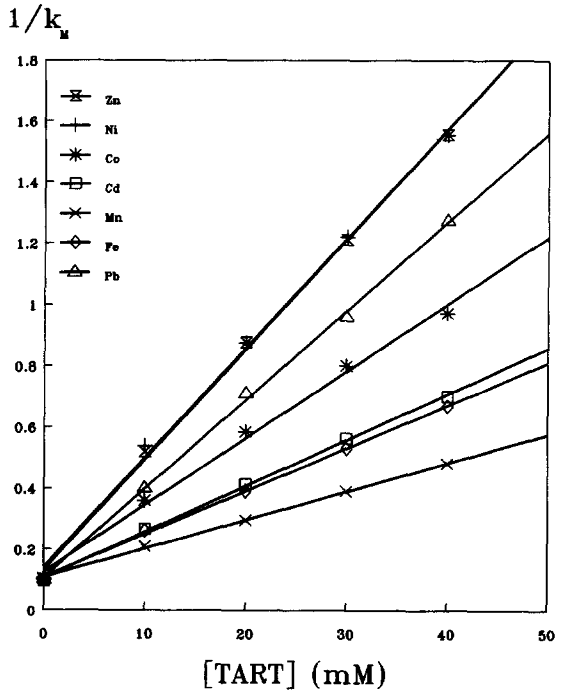

Fig. 1. Dependence of reciprocal value of the capacity factor on tartrate concentration in mobile phase. Column: 150 × 3 mm, Separon SGX C_{18}, 5 μm, SDS coated. Mobile phase: 0.1 mol, l^{-1} Na^+ + tartrate, pH 6.00 ± 0.05 adjusted with perchloric acid.

calculated simply as the quotient of the line slope and the y-axis intercept of the linear dependence.

In Table I the values of the stability constants as obtained by the described method are presented and compared with the corresponding published data. In most cases the agreement between our results and the literature may be considered comparatively good. The differences are caused by different experimental methods, particularly by different conditions in the course of the measuring proper (temperature, ionic strength, etc.); these conditions are not always specified in the cited papers.

CONCLUSIONS

The method of IC enables the stability constants of metal cation complexes with anions of simple dicarboxylic or polycarboxylic acids to be measured in a simple way. In the case of complexes with larger organic ligands the possibility of more complex mechanisms of retention has to be considered. The accuracy of the stability constant determination depends, in the first place, on the accuracy of measuring the analyte retention characteristics. In the chosen system the conditions of the measurement can be optimized by changing either the mobile phase composition or, as the case may be, the column capacity (see ref. 13). A disadvantage of the column used is that it is not possible to measure at higher pH values because of the damage to the silica gel matrix of the column packing.

It has been shown that by a detailed analysis of the experimental dependences $1/k_M$ *vs.* ligand concentration, and using eqn. 10, the stability constants of higher complexes is certain systems may be obtained (provided that such complexes are formed under the given conditions) [17].

The relations derived in the present work may be used not only for calculating the stability constants from chromatographic measurements but also for optimizing the process of separation on the basis of published values of the stability constants.

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