

## Short Communication

# Study of complex-forming equilibria between divalent metal cations and some inorganic anions using ion chromatography

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### ABSTRACT

Complex-forming equilibria between some divalent metal cations ( $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ) and inorganic anions ( $SCN^-$ ,  $SO_4^{2-}$ ) were studied using ion chromatography on a column packed with octadecyl-bonded silica permanently coated with dodecyl sulphate. Relationships were derived describing the retention of metal cations in the presence of complexing agents. Stability constants of the complexes formed in the mobile phase were assessed from the dependences of the analyte capacity factors on ligand concentration in the mobile phase.

### INTRODUCTION

Ion chromatography (IC) is frequently used for the determination of ionic substances, particularly inorganic ions. To improve the separation of metal cations, advantage is taken of complexing reactions in the mobile phase [1,2]. Relationships between the analyte retention and the composition of the mobile phase in the presence of complexing agents were derived in previous papers [3,4]; these relationships can be employed for studying the composition and stability of complexes by IC.

A detailed description of the principle of stability constant measurement was given previously and the respective mathematical relationships were derived [4]. The method was applied to the determination of the stability constants of complexes of divalent metal cations ( $Zn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Fe^{2+}$ ,  $Cd^{2+}$ ,  $Mn^{2+}$ ) with the anions

of simple di- and polycarboxylic acids (oxalic, tartaric, citric, pyridine-2,6-dicarboxylic and malonic). It follows from the published values of the stability constants [5] and from our previous observations [6] that some inorganic anions may also participate in the complexing reactions taking place in the mobile phase (and thus influence the retention). In this work, IC was used for studying the complex-forming equilibria between selected divalent metal cations and some inorganic anions ( $SCN^-$ ,  $SO_4^{2-}$ ); a more general retention model was elaborated and the respective mathematical relations were derived for this purpose.

### EXPERIMENTAL

#### Apparatus

The measurements were conducted on the apparatus and under the conditions described in

detail previously [3,4]. The separations were carried out on a Separon SGX C<sub>18</sub> (5 μm) column (Tessek, Prague, Czech Republic) dynamically coated for 2 h with a 5 mmol l<sup>-1</sup> solution of sodium dodecyl sulphate (SDS) at a flow-rate of 0.1 ml min<sup>-1</sup>. The preparation and properties of the separation column were described previously [6]. The measurements were carried out at room temperature (22 ± 1°C).

### Chemicals

SDS solution (5 mmol l<sup>-1</sup>) was prepared from the research-grade reagent (Serva, Heidelberg, Germany). NaOH, H<sub>2</sub>SO<sub>4</sub> and NaSCN stock solutions (1 mol l<sup>-1</sup>) were prepared. The mobile phases were prepared by combining these stock solutions in appropriate proportions and by adjusting the pH (when necessary) to 6 ± 0.05 using dilute perchloric acid.

Perchlorate solutions of the cations examined were prepared using a conventional cation-exchange column and prior to the measurements these were diluted with the mobile phase to concentrations in the range 0.01–0.1 mmol l<sup>-1</sup> (constant for each run of measurements).

A 0.2 mmol l<sup>-1</sup> solution of 4-(2-pyridylazo)resorcinol (PAR) containing 1 mol l<sup>-1</sup> acetic acid and 3 mol l<sup>-1</sup> ammonia served as the postcolumn derivatizing agent.

Unless stated otherwise, all reagents were of analytical-reagent grade (Lachema, Brno, Czech Republic). Doubly distilled water was used for preparing the solutions.

### RESULTS AND DISCUSSION

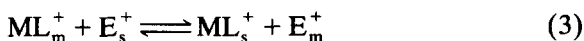
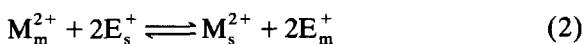
It follows from our previous work [3,4,6] that the retention of metal cations on an SDS-coated C<sub>18</sub> column is controlled by an ion-exchange mechanism. A retention model for metal cations participating simultaneously in the ion-exchange and complex-forming equilibria has been described, *e.g.*, by Haddad and Foley [7]; the relationships derived in our work [3,4] are also based on that model. According to that model, only “free” metal cations take part in the ion-exchange processes on the column while the remaining part of the metal in the mobile phase is present in the form of neutral or negatively

charged complexes not retained by the cation exchanger. This is true with most common systems where divalent cations are separated and anions of di- or polycarboxylic acids serve as the complexing agents.

The influence of the presence of cationic complexes bearing a positive charge must not be neglected, however, in the reaction of divalent cations (M<sup>2+</sup>) with some inorganic anions (and also, *e.g.*, with the commonly used 2-hydroxyisobutyric acid, HIBA [8,9]). The formation of complexes with a ligand L<sup>-</sup> may be expressed by the following equations:



etc. It may be assumed in general that both the free (*i.e.*, non-bonded in a complex) cation M<sup>2+</sup> and the cationic complex ML<sup>+</sup> take part in the ion-exchange equilibria on a cation exchanger in accordance with



where E<sup>+</sup> is the eluting cation and the subscripts m and s refer to the mobile and stationary phase, respectively. The respective equilibrium constants (selectivity coefficients) are

$$K_M^E = \frac{[M^{2+}]_s [E^{+}]_m^2}{[M^{2+}]_m [E^{+}]_s^2} \quad (4)$$

$$K_{ML}^E = \frac{[ML^{+}]_s [E^{+}]_m}{[ML^{+}]_m [E^{+}]_s} \quad (5)$$

The capacity factor is given as the ratio of the amount of an analyte in the stationary phase to that in the mobile phase:

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

where *q* is the phase ratio and *c<sub>M</sub>* is the total concentration of metal in the mobile phase as given by the following relationships (for simplicity the ionic charges are omitted):

$$c_M = [M]_m + [ML]_m + [ML_2]_m + \dots + [ML_n]_m$$

$$= [M]_m(1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n)$$
(7)

The following sum holds true for the column capacity:

$$Q = [E^+]_s + [ML^+]_s + 2[M^{2+}]_s$$
(8)

which is usually rewritten as

$$Q = [E^+]_s$$
(9)

On combining eqns. 4–7 and 9 the rearranging, we obtain

$$k = q \cdot \frac{K_{ML}^E Q [E^+]_m \beta_1 [L] + K_M^E Q^2}{[E^+]_m^2 (1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n)}$$
(10)

If the eluting cation concentration is kept constant and provided that only one type of complex prevails in the mobile phase, eqn. 10 can be rewritten in the following form:

$$k = \frac{A[L] + B}{1 + \beta_n [L]^n}$$
(11)

where all the constant terms are summed in the constants  $A$  and  $B$ . In contrast to the previously published equations [3,4], however, this simplified form cannot be transformed to a linear function.

The dependence of the capacity factor on ligand concentration in the mobile phase at constant concentration of the eluting cation was examined in a similar way as in the previous work [3,4]. The thiocyanate anion was chosen as an example of such an inorganic ligand, with which the formation of  $ML^+$ -type complexes can be presumed [5,10–12]. The mobile phases were prepared by combining the NaOH and NaSCN stock solutions in appropriate proportions ratios and adjusting their pH to a constant value of  $6 \pm 0.05$  with dilute perchloric acid (perchlorate ions do not participate in either the complexing or the ion-exchange equilibria). On the assumption that  $n = 1$  and using eqn. 11 as the basis, the method of non-linear regression was employed to calculate the values of stability constants from the experimental dependences of capacity factors

TABLE I

STABILITY CONSTANTS (LOG  $\beta_n$ ) OF THIOCYANATE COMPLEXES

Metal ion	IC method <sup>a</sup>	IC method <sup>b</sup>	Published data [5]
Co <sup>2+</sup>	1.52 ± 0.04	1.51 ± 0.06	1.72
Ni <sup>2+</sup>	1.63 ± 0.07	1.62 ± 0.06	1.76
Fe <sup>2+</sup>	1.40 ± 0.02	1.44 ± 0.04	1.31
Cd <sup>2+</sup>	1.80 ± 0.08	1.79 ± 0.05	1.89
Mn <sup>2+</sup>	1.26 ± 0.03	1.31 ± 0.04	1.26

<sup>a</sup> Calculated by the non-linear regression method using eqn. 11.  $n = 7$ .

<sup>b</sup> Calculated by the linear regression method using the simplified eqn. 13 for  $n = 1$ .  $n = 7$ .

on ligand concentration. The values obtained were converted to zero ionic strength with the aid of the Debye–Hückel relationship [5,12]; the results are presented in Table I.

A more detailed analysis of the experimental data showed that the term corresponding to the  $ML^+$ -type complex in eqns. 10 and 11 is not very significant. It is also possible to demonstrate by calculation that under the given experimental conditions (mobile phase composition, column capacity; see ref. 6) the ratio of the selectivity coefficients  $K_{ML}^E/K_M^E$  is *ca.*  $10^{-6}$ – $10^{-5}$ . This implies that the cationic complexes  $ML^+$  do not take part in ion-exchange processes on the column (analogously to neutral and anionic complexes). Therefore, the previously derived relationships [3,4] can be used for the treatment of the experimental data:

$$\frac{1}{k} = A'(1 + \beta_1 [L] + \beta_2 [L]^2 + \dots + \beta_n [L]^n)$$
(12)

On the assumption that only one type of  $ML_n$  complex is predominant in the mobile phase under certain conditions, eqn. 12 may be simplified further:

$$\frac{1}{k} = A'(1 + \beta_n [L]^n)$$
(13)

The dependences of the capacity factors on the thiocyanate concentration in the coordinates  $1/k$  vs.  $[L]$  (*i.e.*, for  $n = 1$ ) are presented in Fig. 1. As can be seen, the dependences are linear over a fairly wide concentration range and they confirm the correctness of the adopted simplifica-

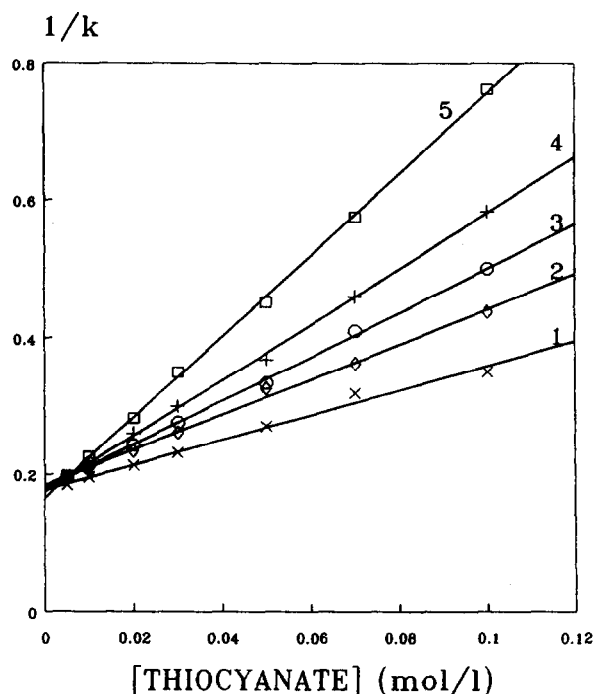


Fig. 1. Dependence of the reciprocal of the capacity factor on thiocyanate concentration in the mobile phase. Column  $150 \times 3$  mm I.D., Separon SGX  $C_{18}$ ,  $5 \mu\text{m}$ , SDS coated; mobile phase,  $0.1 \text{ mmol l}^{-1} \text{ Na}^+$  + thiocyanate ( $\text{pH } 6 \pm 0.05$ , adjusted with perchloric acid). 1 =  $\text{Fe}^{2+}$ ; 2 =  $\text{Mn}^{2+}$ ; 3 =  $\text{Cd}^{2+}$ ; 4 =  $\text{Co}^{2+}$ ; 5 =  $\text{Ni}^{2+}$ .

tions. These dependences served as the basis for calculating the stability constants  $\beta_1$ ; the results, converted to zero ionic strength, are presented in Table I.

A similar procedure was adopted for the study of complexing reactions of divalent metal cations with sulphate anions. Under the given conditions we need not consider the formation of cationic complexes and, therefore, eqn. 12 or, as the case may be, eqn. 13 can be employed. As can be seen from Fig. 2, the plots of  $1/k$  vs. sulphate concentration are linear for  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  (and also for  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$ , not shown in Fig. 2). Stability constants of the sulphate complexes were calculated from these dependences and converted to zero ionic strength (Table II). For  $\text{Cu}^{2+}$ , the dependence in Fig. 2 is not linear. On the other hand, a linear dependence with a correlation coefficient close to unity ( $r = 0.992$ ) was found when using the

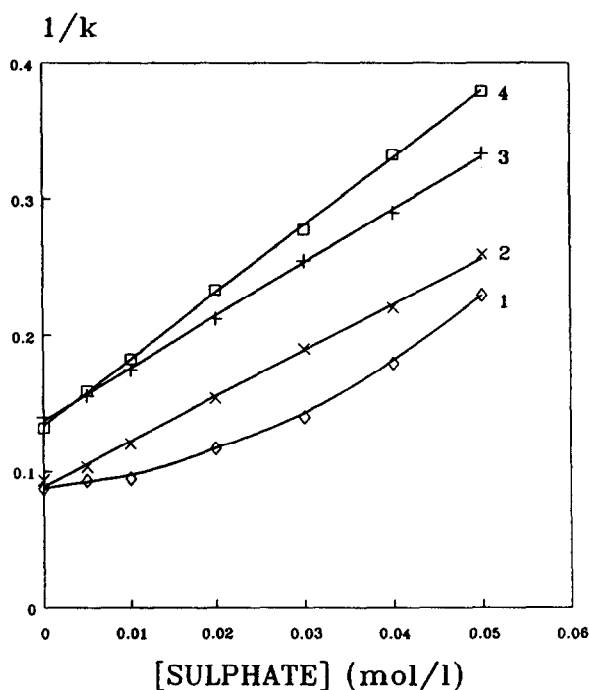


Fig. 2. Dependence of the reciprocal of the capacity factor on sulphate concentration in the mobile phase. Column as in Fig. 1; mobile phase,  $0.1 \text{ mol l}^{-1} \text{ Na}^+$  + sulphate (+ perchlorate). 1 =  $\text{Cu}^{2+}$ ; 2 =  $\text{Zn}^{2+}$ ; 3 =  $\text{Ni}^{2+}$ ; 4 =  $\text{Cd}^{2+}$ .

coordinates  $1/k$  vs.  $[\text{L}]^2$ . From this dependence the value of the stability constant  $\beta_2$  can be calculated ( $\log \beta_2 = 2.79$ ).

The values of the assessed stability constants of the thiocyanate complexes are in good agreement with those given in the literature. For the sulphate complexes the agreement between our results and the published data is also fairly good, except for the sulphate complexes of  $\text{Cu}^{2+}$ ,

TABLE II  
STABILITY CONSTANTS ( $\log \beta_1$ ) OF SULPHATE COMPLEXES

Metal ion	IC method	Published data [5]
$\text{Zn}^{2+}$	$2.29 \pm 0.04$	2.38
$\text{Co}^{2+}$	$2.19 \pm 0.04$	2.36
$\text{Ni}^{2+}$	$2.16 \pm 0.03$	2.32
$\text{Fe}^{2+}$	$2.20 \pm 0.04$	2.2
$\text{Cd}^{2+}$	$2.29 \pm 0.06$	2.46
$\text{Mn}^{2+}$	$2.17 \pm 0.03$	2.26

where our results differed markedly from those published; there are only data for  $\beta_1$  ( $\log \beta_1 = 2.36$  for  $I = 1$ ) in ref. 5. The reasons for this discrepancy are not clear and additional studies are needed concerning particularly those systems where higher complexes occur or where several types of complexes exist simultaneously in significant amounts.

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