

CHROM. 13,028

## SEPARATION OF METAL IONS ON ION-EXCHANGE RESIN WITH ETHYLENEDIAMINE FUNCTIONAL GROUPS

E. MARTON-SCHMIDT\*, J. INCZÉDY, Z. LAKI and Ö. SZABADKA

*Department of Analytical Chemistry, University of Veszprém, H-8201 Veszprém (Hungary)*

---

### SUMMARY

The complexation and protonation of a chelating ion-exchange resin containing ethylenediamine functional groups have been studied. The apparent stability constants of the copper(II), nickel(II), zinc(II) and cadmium(II) complexes have been determined. The resin has also been used for the column chromatographic separation of the above metal ions.

---

### INTRODUCTION

The stability constant of chelating ion-exchange resins have been studied extensively by a various workers using several methods. The methods applied can be roughly divided into two groups. In one, two ligands (an immobilised and a freely moving bulky solution phase ligand) are in competition for a metal ion of the solution; these are the so-called ligand-competition methods, introduced by Loewenschuss and Schmuckler<sup>1</sup>. The other procedures are based on competition for a fixed, resin-phase ligand either between two metal ions or between a metal ion and the proton; the former method is called metal competition<sup>2</sup> and the latter proton competition<sup>3</sup>. The Bjerrum method used by Eger *et al.*<sup>4</sup> and the method of the complex-decomposition pH introduced by Hering<sup>5</sup> are also based on the proton competition.

This paper is concerned with the determination of the stability constants of the complex-forming resin containing ethylenediamine functional groups (ED-resin) with copper, nickel, zinc and cadmium ions. The experimental and calculation procedures were carried out by the method of Hering<sup>5</sup>.

### THEORETICAL

The concept of the complex-decomposition pH is defined in the following way. If a metal-form chelating resin is eluted by a strong acid and the pH of the effluent is measured and plotted against its volume, then a curve is obtained that usually has a range where the pH remains constant. Under well defined conditions this pH is reproducible and is considered as the complex-decomposition pH (DpH).

For the calculation of the stability constant ( $K_{MR}$ ) of the 1:1 metal–chelating resin complexes the following equation was suggested by Hering<sup>5</sup>:

$$\log K_{MR} = \log \beta'_j - n \cdot \text{DpH} \quad (1)$$

where  $\beta'_j$  is the apparent cumulative protonation constant of the ligand and  $n$  is the number of protons bound to the ligand. In order to calculate  $K_{MR}$  the protonation constants and the DpH values should be measured.

For the determination of the protonation constant of an immobilized base, the following general equation was derived by Szabadka and Inczédy<sup>6</sup>:

$$\sum_{j=0}^n (\alpha - n + j) \beta'_j(\text{H})^j = 0 \quad (2)$$

where  $\alpha$  is the molar fraction of the non-protonated base and  $\cdot(\text{H})$  is the hydrogen ion activity in the resin phase. The  $\text{p}(\text{H})$  inside an ED-resin is defined as follows:

$$\text{p}(\text{H}) = \text{pH}_{\text{soln.}} + \log \left[ \frac{a_{\text{Cl}^-(\text{resin})}}{a_{\text{Cl}^-(\text{soln.})}} \right] \quad (3)$$

If this general equation is applied to the calculation of the  $K_1$  and  $K_2$  protonation constants of the ED-resin being studied, then eqn. 2 takes the following simpler form:

$$\frac{2 - \alpha}{(\alpha - 1)(\text{H})} = K_1 + \frac{\alpha(\text{H})}{\alpha - 1} \cdot K_1 K_2 \quad (4)$$

If, therefore,  $\alpha$  and  $(\text{H})$  are obtained from the experimental data, then  $K_1$  and  $K_2$  can be calculated from eqn. 4.

## EXPERIMENTAL

### *Preparation of the resin*

The ED-resin was synthesized in our laboratory and its properties have been described by Szabadka and Inczédy<sup>7</sup>. Prior to the experiments it was treated with 0.1 mol/dm<sup>3</sup> hydrochloric acid, whereby the protonated form of the base ( $\text{H}_2\text{ED}^{2+} \cdot 2\text{Cl}^-$ ) was obtained. The capacity was checked by several methods. On the basis of the nitrogen (Kjeldahl), chloride (argentimetric) and dissociable proton (acid–base) content measurements the capacity was found to be 4.3 mmol of functional group per gram of dry ED-resin.

### *Determination of protonation constants*

For a detailed description of this measurement, the reader is referred to a related paper<sup>8</sup>. We mention here only that the fully protonated  $\text{H}_2\text{ED}^{2+} \cdot 2\text{Cl}^-$  form of the resin was titrated with carbonate-free 0.1 mol/dm<sup>3</sup> potassium hydroxide solution at 25°C and the ionic strength was adjusted to 1 with potassium chloride. The titration curve is shown in Fig. 1, where the  $\text{p}(\text{H})$  is plotted against the molar fraction of the non-protonated base ( $\alpha$ ).

The logarithms of the protonation constants calculated from the data of the above curve by eqn. 4 are  $\log K_1 = 9.80$  and  $\log K_2 = 7.10$ .

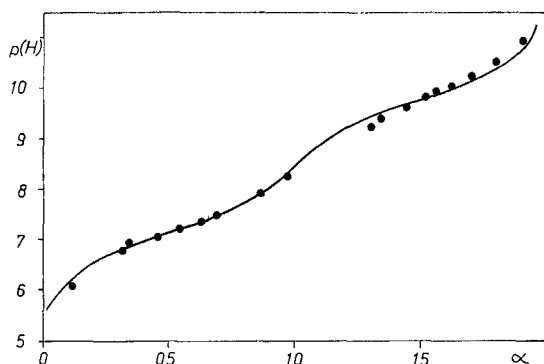


Fig. 1. Titration curve for the  $H_2ED^{2+} \cdot 2Cl^-$  form of the resin. The variables on the axes are calculated according to refs. 6 and 8.

#### Determination of the complex-decomposition pH

About 3 g of an air-dry sample of the resin was weighed into an ion-exchange column (13 mm I.D.). The column was treated with acetic acid–sodium acetate buffer and 0.4–1 mmol of the metal ion being investigated was applied on the top of the column. The sample was then eluted with 0.1–0.5 mol/dm<sup>3</sup> hydrochloric acid and 15–15-cm<sup>3</sup> fractions of the effluent were collected. The pH was measured and the metal ion content in each fraction was determined by complexometric titration<sup>9</sup>. The metal ions studied and further details are given in Table I.

In order to obtain the DpH values for the systems studied, the metal content and the pH of each fraction were plotted against the volume of the effluent (Fig. 2).

TABLE I  
EXPERIMENTAL DATA USED FOR THE DETERMINATION OF DpH VALUES

Parameter	$Cu^{2+}$	$Ni^{2+}$	$Zn^{2+}$	$Cd^{2+}$
pH of the effluent buffer before the application of the metal ion	4.7*	5.6*	8.9**	8.9**
Amount of metal (mmol)	0.4	0.4	1.0	1.0
Eluent (HCl) concentration (mol/dm <sup>3</sup> )	0.5	0.1	0.1	0.1

\* Acetic acid–sodium acetate buffer.

\*\* 0.2 mol/dm<sup>3</sup> sodium acetate solution.

#### Elution experiments

The same column was also used to separate mixtures containing given pairs of metal ions (Table II).

#### RESULTS AND DISCUSSION

From the curves in Fig. 2 the following complex-decomposition pH values were obtained:  $DpH(Cu^{2+}) = 3.65$ ,  $DpH(Ni^{2+}) = 4.40$ ,  $DpH(Cd^{2+}) = 5.25$  and  $DpH(Zn^{2+}) = 5.35$ .

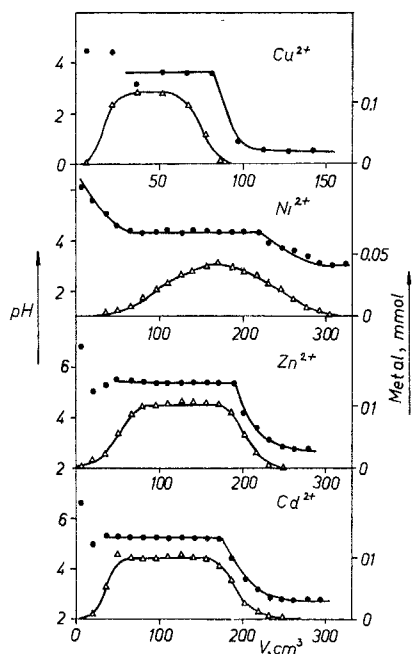


Fig. 2. Change in the pH (●) and the metal content (Δ) of the collected fractions as a function of the volume of the eluate.

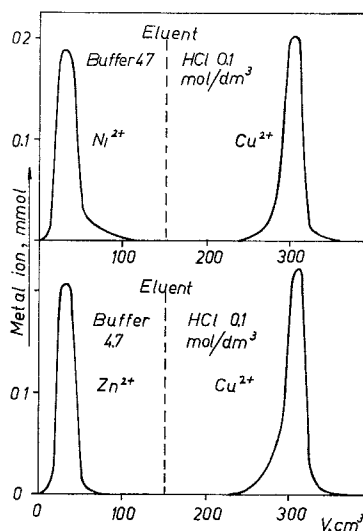


Fig. 3. Chromatographic separation of  $\text{Cu}^{2+}$ - $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$ - $\text{Zn}^{2+}$  ions on an ED-resin column. For details, see Table II.

TABLE II  
CONDITIONS OF THE SEPARATION EXPERIMENTS

<i>Ions to be separated</i>	<i>Pre-treatment of the column</i>	<i>Amount of metal ion applied (mmol)</i>	<i>Eluent</i>	<i>Metal recovered (mmol)</i>
$\text{Ni}^{2+}$	Buffer*, pH 4.7	0.390	Buffer*, pH 4.7	0.387
$\text{Cu}^{2+}$		0.390	0.1 mol/dm <sup>3</sup> HCl	0.382
$\text{Zn}^{2+}$	Buffer*, pH 4.7	0.400	Buffer*, pH 4.7	0.406
$\text{Cu}^{2+}$		0.400	0.1 mol/dm <sup>3</sup> HCl	0.392

\* Acetic acid-sodium acetate buffer.

The apparent stability constants of the metal-resin complexes studied calculated by means of eqn. 1 are given in Table III. In addition to the stability constants of the metal-fixed ligand complexes ( $K_{\text{MR}}$ ), the constants for the metal-water-soluble monomer ligand complexes ( $K_1$ ) are also given for purposes of comparison.

The data in Table III suggest that, with the exception of the zinc-cadmium pair, ED-resin can be used very advantageously for the separation of the metal ions

TABLE III

LOGARITHM OF APPARENT STABILITY CONSTANTS FOR SOME METAL-ED RESIN AND METAL-N-BENZYLETHYLENEDIAMINE COMPLEXES

Metal	Ligand	
	ED-resin	BED
Cu <sup>2+</sup>	log $K_{MR}$ = 9.6	log $K_1$ = 9.43 (ref. 10) log $K_1$ = 9.12 (ref. 11) log $K_1$ = 10.06* (ref. 12)
Ni <sup>2+</sup>	log $K_{MR}$ = 8.1	log $K_1$ = 7.17* (ref. 12)
Zn <sup>2+</sup>	log $K_{MR}$ = 6.2	log $K_1$ = 5.34* (ref. 12)
Cd <sup>2+</sup>	log $K_{MR}$ = 6.4	—

\* Values extrapolated to zero ionic strength;  $t = 30^\circ\text{C}$ ; in 50 vol.-% dioxane.

studied. Using the stability constant data, the experimental conditions for the separation can be optimized. An example of this practical application is illustrated in Fig. 3.

## REFERENCES

- 1 H. Loewenschuss and G. Schmuckler, *Talanta*, 12 (1964) 1399.
- 2 G. Schmuckler, *Talanta*, 10 (1963) 745.
- 3 C. Eger, W. M. Anspach and J. A. Marinsky, *J. Inorg. Nucl. Chem.*, 30 (1968) 1911.
- 4 C. Eger, W. M. Anspach and J. A. Marinsky, *J. Inorg. Nucl. Chem.*, 30 (1968) 1899.
- 5 R. Hering, *Chelatbildende Ionenaustauscher*, Academie Verlag, Berlin, 1967, p. 104.
- 6 Ö. Szabadka and J. Inczédy, *4th Symposium on Ion Exchange, 27-30 May, 1980, Siófok, Hungary*, Abstr. p. 33.
- 7 Ö. Szabadka and J. Inczédy, *Acta Chim. Acad. Sci. Hung.*, 99 (1979) 363.
- 8 E. Marton-Schmidt, Ö. Szabadka and J. Inczédy, *Acta Chim. Acad. Sci. Hung.*, in press.
- 9 A. I. Vogel, *Quantitative Inorganic Analysis*, Longmans, London, 1972.
- 10 L. G. Sillén and A. E. Martell, *Stability Constants of Metal-ion Complexes*, Chemical Society, London, 1964.
- 11 A. E. Frost and A. A. Carlson, *J. Org. Chem.*, 24 (1959) 1581.
- 12 D. E. Goldberg and K. C. Patel, *J. Inorg. Nucl. Chem.*, 34 (1972) 3583.