

Immobilized Complexon Amides-Cation Exchangers of High Chelating Activity*

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Summary

Several complexon cation exchangers with EDTA or DTPA complexon groupings attached through the amide bond to the polymer matrix of bead cellulose or of the methacrylate type were prepared. The cation exchangers are comparatively stable to alkaline hydrolysis. Chelating ability of the sorbents was examined by measuring the distribution coefficients in Cu(II) and Ni(II) sorption from EDTA solutions. In spite of the low total capacity cation exchangers with immobilized DTPA have distribution coefficients higher by an order of magnitude than a commercial iminodiacetic resin.

Introduction

Scavenging of heavy metals from waste or technological liquors is often adversely affected by the presence of high concentrations of accompanying cations (Na, Mg) or by the presence of strong complexing agents (e.g. EDTA). Functional groups of both common and chelating cation exchangers do not possess sufficiently strong bonds with heavy metals which would guarantee an efficient sorption. Recently, a complexon cation exchanger based on bead cellulose with EDTA attached through ester linkage was prepared (KAHOVEC et al. 1980). The ion exchanger forms metal complexes of distinctly higher stability when compared with commercial iminodiacetic resins, but it is not stable in alkaline medium.

In this communication the original idea is further developed. To improve the hydrolytic stability an amide bond was used for the immobilization of complexons on the polymer carrier. To further enhance the stability of metal chelates, a complexon grouping of DTPA (diethylenetriaminepentaacetic acid) instead of that of EDTA was attached to the polymer matrix. Finally, polymethacrylate carriers were used along with bead cellulose.

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Experimental

Materials. Reactions of amine polymers with EDTA and DTPA dianhydrides (ECKELMAN et al. 1975) were performed similarly as reported earlier (KAHOVEC et al. 1980). The following polymer carriers were used for the immobilization of the complexons: 2-(4-aminophenylsulfonyl)ethyl derivative of bead cellulose ($\text{C-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$), 2-(4-aminophenylsulfonyl)ethyl derivative of macroporous poly [2-hydroxyethyl methacrylate-co-ethylene dimethacrylate] ($\text{S-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$, Spheron Ara 1000, Lachema Brno), ammonolyzed macroporous poly [glycidyl methacrylate-co-ethylene dimethacrylate] (G-NH_2 , SVEC et al. 1977), hexamethylenediamine-aminolyzed macroporous poly [glycidyl methacrylate-co-ethylene dimethacrylate] ($\text{G-NH(CH}_2)_6\text{NH}_2$, SVEC et al. 1977). For comparison, Lewatit TP 207 (Bayer), i.e. a macroporous iminodiacetic acid resin was employed. The properties of all polymers used are given in Table I.

TABLE I Characteristics of polymers used

Polymer	N content (%)	Total capacity ^a (mmol Cu(II)/ml)
$\text{C-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$	0.88	-
$\text{C-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH-EDTA}$	2.69	0.08
$\text{S-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH}_2$	0.72	-
$\text{S-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH-EDTA}$	2.85	0.19
G-NH_2	2.42	-
G-NH-DTPA	3.91	0.12
$\text{G-NH(CH}_2)_6\text{NH}_2$	4.08	-
$\text{G-NH(CH}_2)_6\text{NH-DTPA}$	4.95	0.24
Lewatit TP 207	-	1.27

^a Determined by the dynamic method (KAHOVEC et al. 1980)

All measurements were performed on ion exchangers of 0.40-0.63 mm wet bead diameter. Na, Cu(II) and Ni(II) concentrations in solutions were determined by atomic absorption spectroscopy.

Hydrolytic stability. Ca. 1 ml of the cation exchanger in a column of 10 mm i.d. was converted to the Na^+ form each time with 500 ml of ca. 0.3M NaHCO_3 (pH 8.3) or ca. 0.004M Na_2CO_3 (pH 10.6) or ca. 0.1M Na_2CO_3 (pH 11.6) or ca. 1M NaCO_3 (pH 12.5) at a flow rate of 1 ml/min. After elution with 30 ml 1M HCl, Na^+ capacity of the cation exchanger was determined. At pH 8.3, 10.6 and 11.6 all the amide sorbents are stable. At pH 12.5 a decrease in Na^+ capacity of $\text{C-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH-EDTA}$, $\text{S-OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH-EDTA}$ and $\text{G-NH(CH}_2)_6\text{NH-DTPA}$ amounted to 23%, 9% and 0%, resp.

Chelating ability was estimated by the sorption of metal ions from EDTA solutions. Equilibrium between cation exchanger and solution containing metal and EDTA was attained by passing 250 ml of solution at a flow rate of 1 ml/min through a column

of 10 mm i.d. with the sorbent bed height 10 mm. The metal sorbed was eluted with 50 ml 2M HCl. The volume distribution coefficient was calculated as (mmol of metal/ml of cation exchanger): (mmol of metal/ml of solution). The measured dependences are given in Fig.1 and Table II.

TABLE II Volume distribution coefficients (D_v) of Cu(II) and Ni(II)

Cation exchanger	$D_v(\text{Cu})^a$		$D_v(\text{Ni})^b$
	at molar ratio $[\text{EDTA}]/[\text{Cu}]$		
	2:1	20:1	
⊙— $\text{OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH-EDTA}$	3.22	0.49	2.34 [†]
⊙— $\text{OCH}_2\text{CH}_2\text{SO}_2\text{C}_6\text{H}_4\text{NH-EDTA}$	3.53	0.85	3.49
⊙—NH-DTPA	11.96	3.11	10.30
⊙— $\text{NH}(\text{CH}_2)_6\text{NH-DTPA}$	26.75	6.88	25.55
Lewatit TP 207	2.67	0.47	0.0

^a $[\text{Cu(II)}] = 1 \text{ mmol/l}$, pH 6.0

^b $[\text{Ni(II)}] = 1 \text{ mmol/l}$, $[\text{EDTA}] = 2 \text{ mmol/l}$, pH 8.0

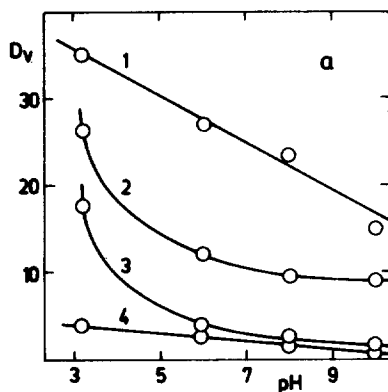
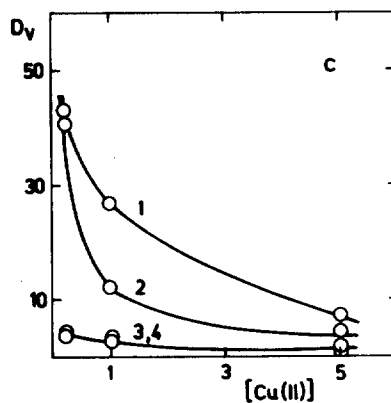
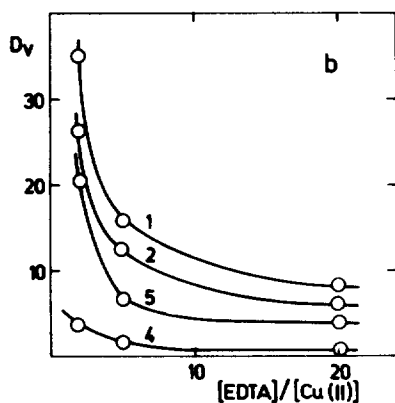


Fig.1 Dependence of Cu(II) volume distribution coefficient (D_v)
 a) on pH ($[\text{Cu(II)}] = 1 \text{ mmol/l}$, $[\text{EDTA}] = 2 \text{ mmol/l}$);
 b) on molar ratio $[\text{EDTA}] : [\text{Cu(II)}]$ ($[\text{Cu(II)}] = 1 \text{ mmol/l}$, pH 3.5);
 c) on Cu(II) concentration ($[\text{EDTA}] : [\text{Cu(II)}] = 2:1$, pH 6.0).
 Curves denoted: see Fig.2



Column sorption of Cu(II) from EDTA solution. Concentration of Cu(II) in the effluent as a function of the relative volume (V/V_0) passed through the column was measured. Cation exchanger: bed volume $V_0 = 30$ ml; solution: $[Cu(II)] = 0.1$ mmol/l, $[EDTA] = 1$ mmol/l, pH 4.0, flow rate 300 ml/h.

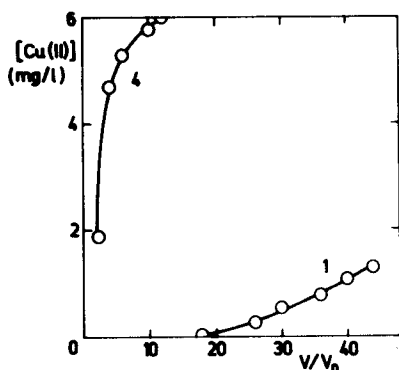


Fig.2 Dependence of Cu(II) concentration on the relative effluent volume (V/V_0).

Curves denoted:

- 1 (G) $-NH(CH_2)_6NH-DTPA$,
- 2 (G) $-NH-DTPA$,
- 3 (C) $-OCH_2CH_2SO_2C_6H_4NH-EDTA$,
- 4 Lewatit TP 207,
- 5 (S) $-OCH_2CH_2SO_2C_6H_4NH-EDTA$

Results and Discussion

For the synthesis of immobilized complexon amides some easily available bead cellulose- or methacrylate-based polymers containing a primary amino group were used. Attachment of complexon groupings to the polymer carrier was performed by a reaction of the respective complexon dianhydride with the amine polymer (cf. KAHOVEC et al. 1980).

Hydrolytic stability of the cation exchangers prepared was significantly improved when compared with ester cation exchangers by attaching the complexon grouping to the polymer through amide linkage. The EDTA amide derivatives are stable up to pH 11.6, the DTPA amide derivatives, on the other hand, up to pH 12.5.

As it is well known, the stability of metal chelates rises in the series iminodiacetic acid \ll EDTA $<$ DTPA (logarithms of the Cu(II) chelate stability constants are 10.55, 18.80 and 21.53, respectively; DYATLOVA et al. 1970). In spite of the fact that the chelating ability of ligands mostly decreases on attachment to the polymer skeleton (HERING 1967), it may be expected that the stability of metal chelates with polymer-bonded complexon amides will rise in the same order. In addition, polymer-bonded DTPA amide is expected to compete successfully with free EDTA in metal ion chelation. These assumptions were confirmed.

Cation exchangers with EDTA bonded through ester or amide bond possess distinctly better chelating properties than the iminodiacetic resin taken for comparison only in the weakly acid region. In neutral or alkaline media, only DTPA derivatives

possess enhanced chelating ability. On increasing the excess of EDTA in solution, the distribution coefficients generally decrease; however, interrelation between the bonded complexons remains unchanged. With increasing concentration of EDTA-chelated Cu(II) in solution, differences between iminodiacetic and complexon sorbents decrease, until at $[Cu(II)] = 5 \text{ mmol/l}$ the EDTA cation exchangers possess already slightly poorer properties. The DTPA cation exchangers, on the other hand, still remain better.

The new complexon cation exchangers have a remarkable feature. Though their total sorption capacity for Cu(II) amounts only to 6-19% of that of Lewatit TP 207 (cf. Table I), their equilibrium sorption capacity for EDTA-chelated Cu(II) is higher than that of the iminodiacetic resin. The sorption ability of polymers with bonded DTPA is then higher by an order of magnitude than that of the iminodiacetic resin.

In Ni(II) sorption the values of the distribution coefficient are higher with all the cation exchangers than in Cu(II) sorption (at the same pH; cf. Fig. 1 and Table II). The activities of the particular cation exchangers in Ni(II) and Cu(II) sorption are similar: in alkaline medium only cation exchangers with attached DTPA are more active than the iminodiacetic resin.

Preliminary column experiments involving Cu(II) sorption confirmed the results of equilibrium measurements: the breakthrough curves clearly demonstrate the sorption efficiency of the DTPA derivative (Fig. 2).

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