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Complexing Properties of Cation-Exchangers Grafted with Carboxyl Moieties

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Abstract—The complexing properties of CM-52, Olvagel-COOH, MacroPrep 50 CM, and hypercrosslinked polystyrene MN (carboxyl-grafted sorbents) toward Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} have been studied. The optimal parameters for the sorption of these metal ions from solution have been determined. The pH effect on the ion uptake has been studied. The uptake is maximal at pHs higher than 5–6. When pH is lower than 2, the indicated ions are quantitatively desorbed. Olvagel-COOH is most selective toward these ions.

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Cation-exchange sorbents based on silicas and organic polymer matrices grafted with carboxyl moieties are being increasingly applied for preconcentrating and separating metal ions [1–6]. Carboxylic cation exchangers are attractive for their ion-exchange properties with respect to alkali and alkaline-earth metals combined with their ability to complex with transition metals. The complexing properties of grafted carboxyl moieties are substantially affected by the acidity of the contact solution. Thus, higher selectivities can be reached or conditions for nonselective group sorption can be created by means of varying solution pH. The ion-exchange properties of carboxylic cation exchangers have been well studied; due to these properties, such sorbents are widely used for the chromatographic determination of alkali and alkaline-earth metals [1, 2, 7, 8]. The complexing properties of cation exchangers are usually described as applied to grafted aminopolycarboxylic acids [1, 4, 8–11], where nitrogen atoms contribute appreciably to complexing. The use of carboxylic sorbents has been described for separating [2, 3] or preconcentrating [5, 6] transition metals. An interesting feature of carboxylic cation exchangers is their high buffer capacity, which is virtually constant over a wide pH range and which allows smooth and linear pH gradients to be created in the sorbent layer using chromatofocusing [12, 13]. Thus, carboxylic sorbents show potential for use as sorbents for both preconcentrating and separating transition metals by means of chromatofocusing [14, 15]. The underlying idea of chromatofocusing is the retention of metals at higher pHs via their complexing with carboxy groups and the subsequent degradation of complexes with a linear decrease in the pH inside the chromatographic column. We should stress that preliminary results were obtained on MacroPrep 50 CM, a sorbent grafted with carboxymethyl groups. The complexing properties of other carboxylic cation exchangers as applied to chromatofocusing have not been studied.

This work concerns the complexing properties of cation-exchange sorbents with grafted carboxyl and carboxymethyl moieties.

EXPERIMENTAL

Reagents. Solutions of copper(II), zinc(II), cadmium(II), cobalt(II), nickel(II), manganese(II), and lead(II) salts were prepared by dissolving exact weights of analytical grade metal chlorides or nitrates in HCl-acidified bidistilled water. A 0.025% solution of 4-(2-pyridylazo)resorcin (PAR) was prepared from an analytical grade sample (from Reanal, Hungary) by dissolving its aliquot in 0.05 M borate buffer solution (pH 9.18). A 0.2 M acetate buffer solution was prepared by mixing the proper volumes of solutions of analytical grade CH_3COOH and CH_3COONa; then, conc. HCl or 0.1 M NaOH was added to adjust the pH from 2 to 8. In some cases (e.g., in nickel(II) sorption experiments), the solution pH was lower than 2. A 0.05 M borate buffer solution was prepared from an $Na_2B_4O_7 \cdot 10H_2O$ standard solution (from Germed, Germany).

Sorbents. The sorbents chosen were CM-52, Olvagel-COOH, MN, and MacroPrep 50 CM low-acidity cation-exchange sorbents based on polymer matrices grafted with carboxyl or carboxymethyl moieties (Table 1).

Equipment. In batch sorption experiments, the metal ion concentration was monitored on a KFK-2 photoelectrocolorimeter (l = 1 cm, 540 nm) by means of measuring the optical density of solutions of PAR complexes. The acidity of the buffer solutions was monitored on an Orion Research 501 (USA) digital pH meter equipped with a combination glass electrode and a temperature adjuster.

Table 1. Parameters of the carboxylic sorbents studied

Sorbent	CM-52	Olvagel-COOH	MN	MacroPrep 50 CM
Manufacturer	"Whatman" (Great Britain)	Inst. of Chemistry (Leningrad, USSR)	"Purolite" (Great Britain)	"Biorad" (USA)
Matrix	Microcellulose	Poly(methyl methacrylate)	Hypercrosslinked polystyrene	Poly(methyl methacrylate)
Functionalities	$–CH_2COOH$	$–COOH$	$–COOH$	$–CH_2COOH$
Particle size (μm)	100–200	>30	5	50
pH range*	3–10	3–13	1–14	3–13
Ion-exchange capacity (as certified)	0.95–1.15 mmol/g**	0.30 mmol/mL gel	No data***	0.21 ± 0.04 mmol/mL gel

Notes: * The pH range of hydrolytic stability.
** For dry sorbent.
*** According to our data, no higher than 0.10 mmol/g.

Procedures. Batch sorption experiments on carboxylic sorbents were carried out as follows: to plastic vessels 15 mL in capacity, inserted were a sorbent (0.20 g), acetate buffer solution (5.0 mL) with a certain pH, and a 20 mM solution (0.20 mL) of a metal salt; bidistilled water was added to bring the solution volume to 10.0 mL. The solution was shaken for 5 min; then, the sorbent and solution were kept in contact for 5–7 min, and an aliquot (0.1–0.5 mL) was taken. The equilibrium metal concentration in the aliquot after sorption was monitored using a standard photometric determination procedure (the test with PAR) [16] as follows. To flasks 10 mL in capacity, a borate buffer solution (2.5 mL) and 0.025% PAR solution (2.5 mL) were poured; a test aliquot was added, the volume was brought to the mark, and the solution absorbance was measured on a KFK-2 photoelectrocolorimeter at 540 nm relative to the blank. The metal-ion concentration (in μg/25 mL) was determined from calibration equations [6, 16].

DISCUSSION

Acid–base properties of carboxylic sorbents. To ascertain the buffer properties of ion exchangers intended for use in chromatofocusing, it is pertinent to carry out acid–base titration of sorbent samples preequilibrated with acid or alkali, draw differential $\Delta pH/\Delta V$–pH curves, and find the pH range with a virtually constant buffer capacity [17]. Evidently, the pH gradients obtained in a column packed with the tested ion exchanger using chromatofocusing will be most linear and smooth in this range. The sorbents having wider pH ranges of a constant buffer capacity will provide more extended gradients. To shorten provisional experiments, it is pertinent to create pH gradients immediately inside sorbent-packed columns with the other parameters (such as the nature, concentration, and volume rate of the mobile phase) being unchanged. In our previous works [6, 12, 14], we compared the pH gradients obtained after passing 0.2–0.5 mM citric acid eluents with NaCl admixtures through columns packed with CM-52, MN, and MacroPrep 50 CM. The descending gradient profile in those works was divided into several characteristic sections: the initial section with a constant pH (corresponding to the starting solution pH), a section with increasing pH (higher than the starting solution pH), and a section with the pH decreasing almost linearly to reach the eluent pH. Given that a high ionic strength (0.05–0.1) was created in mobile phases, the rising pH section virtually disappears, while the section in which pH decreases from 7.5 to 4–4.5 becomes much more smooth and flat (the length of this section decreases in the following order: CM-52, MacroPrep 50 CM, and MN [12, 14]), in agreement with the ion-exchange-capacities of the sorbents (Table 1). The pH ranges of a constant buffer capacity are virtually the same for the carboxylic sorbents studied, but for CM-52 this range is slightly wider because the cellulose matrix of the sorbent can also have some buffer capacity. On Olvagel-COOH, pH gradients have not been obtained, but proceeding from its ion-exchange capacity (which is comparable to the capacity of MacroPrep 50 CM), we can expect a quite smooth decrease in pH from 7.5 to 4. Thus, the carboxylic cation exchangers studied can be used as sorbents for chromatofocusing due to their acid–base properties and the existence of a constant buffer capacity range.

Sorption kinetics. On amine anion exchangers, the copper-ion uptake reaches a peak after 10–20 min; for kinetically slow nickel(II) and cobalt(II) ions, after 20–30 min [1, 4, 17]. Probably, this slow equilibration is due to the multistep formation of oligoethyleneamine complexes; one-step complexing with carboxy groups is expected to be more rapid [5, 6]. In choosing nickel(II) ions to find the optimal parameters of quantitative sorption, we were guided by their highest kinetic inertness. Aliquots for monitoring the nickel(II) concentration in the liquid phase were taken every 2 min. Figure 1 demonstrates the nickel(II) uptake on Olvagel-COOH versus time. Quantitative nickel adsorption is achieved as soon as after 12–14 min of contact between the sorbent and solution. Analogous curves were obtained for the other carboxylic sorbents. Likely, a sufficiently high specific surface area of the sorbent shortens equilibration time, especially for MN.

Thus, the phase-contact time in complexing experiments was determined to range from 5–10 to 15 min for nickel(II) and cobalt(II) ions. The temperature effect on the sorption of transition-metal ions on complexing sorbents was studied previously [6, 8, 17]. The chosen temperature range (18–20°C) corresponds to the maximal sorption capacity.

Complexing properties of carboxylic sorbents. When studying uptake as a function of increasing pH, we observed sorbent coloring: the color was blue for copper, pink for cobalt, and green for nickel; the color deepened with increasing pH. This provides circumstantial evidence that the metals are sorbed via complexing with the carboxylic surface functionalities of the sorbent. The sorbents with oligoethyleneamine-grafted matrices had a far deeper color because of the specific formation of amino complexes [17].

Sorption capacity. The sorption capacity is an important parameter of a complexing sorbent in the chromatofocusing determination and separation of metals. The sorption capacity is proportional to the concentration of surface functionalities of the complexing sorbent. However, this relationship is far from being always linear because of the ambiguity of the reaction path and also because of the fact that not all functionalities are accessible to complexing [1, 6].

In the dynamic mode, the capacity of a sorbent is determined by means of passing a solution with a known metal-ion concentration through a chromatographic column packed with the sorbent in the coordinatively active form. In the batch mode, a sorbent sample is simply dipped in a solution of a transition-metal salt and allowed to stand for a certain period of time. The results of the dynamic and batch determinations differ only insignificantly; therefore, the latter is used more frequently because of simple equipment. In this work, the capacity was determined in the batch mode. The capacity of the sorbent was calculated from

$$\mathrm{CE} = (C_0 - C)V/g,$$

where C_0 and C are the initial and final metal-ion concentrations, respectively; V is the volume of the aqueous phase; and g is the sorbent weight. The relative sorption was calculated as the ratio of the sorption capacity at a definite pH to the maximal sorption capacity for this ion.

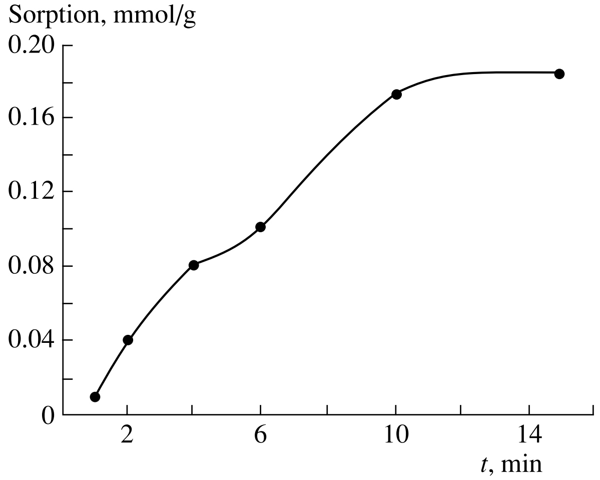

Fig. 1. Nickel(II) sorption on Olvagel-COOH sorbent vs. time (sorbent weight, 0.20 g; solution pH, 7.0; for the other parameters, see the text).

Although the sorbent matrix itself is stable over a wide range of pHs from 2 to 12, the maximum pH in the sorption experiments was eight. This was due to the fact that the formation of hydroxides and basic salts at higher alkalinities is more noticeable, and this can decrease the metal-ion uptake.

One can see that for all sorbents the metal-ion uptake increases with increasing pH to achieve a maximal value at pH 6–8 (Table 2, Fig. 2).

Copper(II), zinc(II), and cadmium(II) are quantitatively removed at pH lower than 4, while the other ions are still sorbed (Fig. 2a). For nickel(II), the uptake at pH of about 4 approaches quantitative sorption; quantitative uptake is achieved when pH is higher than 5. The highest sorption capacity is observed for nickel(II)

Table 2. Sorption of metal ions (mmol/g) on Olvagel-COOH as a function of solution acidity

pH	Sorption, mmol/g						
	Ni^{2+}	Co^{2+}	Cd^{2+}	Cu^{2+}	Mn^{2+}	Zn^{2+}	Pb^{2+}
2.0	0.153	0.066	0	0	0.037	0	0.024
3.0	0.157	0.065	0	0	0.019	0	0.070
4.0	0.160	0.098	0.022	0	0.031	0	0.073
5.0	0.168	0.125	0	0.022	0.074	0.072	0.171
6.0	0.182	0.133	0.096	0.169	0.151	0.149	0.193
7.1	0.187	0.175	0.178	0.193	0.144	0.170	0.190
8.0	0.188	0.181	0.178	0.185	0.171	0.177	0.193

Note: For the dry sorbent.

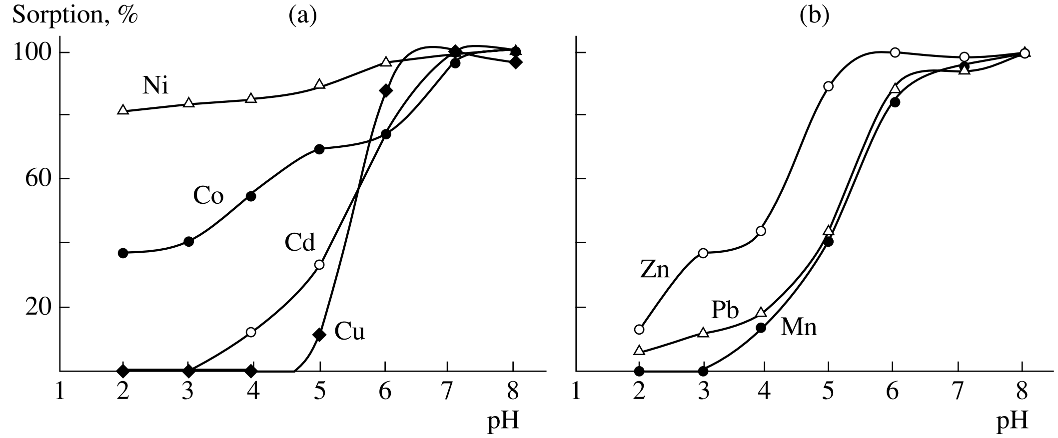

Fig. 2. Relative sorption of Cu^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Mn^{2+}, and Pb^{2+} on Olvagel-COOH vs. pH in the batch mode (for the legend, see the text).

(Table 2). Cobalt(II) ions, for which the sorption on anion exchangers versus pH curves are usually analogous to the curves for nickel(II) [17], are quantitatively sorbed by Olvagel-COOH from solution only when pH is 7.5. In the low-acidity region, however, the cobalt(II) sorption capacity is also sufficiently high (Table 2). The copper(II) uptake increases most strongly while pH changes within a narrow range from 5 to 6. At pHs higher than 6–6.5, the copper(II) sorption capacity decreases by about 4–5%; this decrease is likely induced by partial formation of hydroxo complexes in the solution phase. The manganese(II) and lead(II) uptake curves (Fig. 2b) are much alike: the relative sorption at pH 2 is about 20%; then it smoothly increases as an S-shaped curve. The copper(II) uptake is maximal at pH 6; for zinc(II), at pH 8. Manganese(II) and cadmium(II) ions have the least affinity to Olvagel-COOH. Manganese(II) is sorbed starting at pHs higher than 4 and cadmium(II), only at pHs higher than 5; the quantitative sorption pH for these ions is 8 and 7.5, respectively. The minimal sorption capacity of Olvagel-COOH (0.17 mmol/g) is precisely for manganese(II) ions (Table 2). In general, the desorption row matches the row of the stability constants of metal ion-complexes with carboxylic acids.

Table 3. $pH_{50\%}$ values

Ion	Sorbent	
	Olvagel-COOH	CM-52
Ni^{2+}	lower than 2.0	lower than 1.5
Co^{2+}	3.7	1.7
Pb^{2+}	4.2	1.8
Mn^{2+}	5.1	2.9
Zn^{2+}	5.2	2.1
Cu^{2+}	5.5	2.7
Cd^{2+}	6.0	2.4

Comparing the complexing properties of Olvagel-COOH with those of CM-52 [6], we note several distinctions. On CM-52, all metals are sorbed significantly even at pHs higher than 2; for cobalt(II) and nickel(II), the 50% sorption pH ($pH_{50\%}$) is about 1.5. On Olvagel-COOH, copper(II), cadmium(II), manganese(II), and zinc(II) are only sorbed starting at pH 4, the peak adsorption is reached at pH 7–8; lead(II) and cobalt(II) are taken from the solution starting at pH 2, but in this case the sorption capacity at the same acidities is lower than on CM-52. The nickel(II) sorption capacity curves for both sorbents are virtually identical: the capacity remains constant even at pHs higher than 3, but for CM-52 the desorption of nickel(II) in the alkaline region is more noticeable than for Olvagel-COOH. On the whole, CM-52 has slightly higher sorption capacities for all metal ions studied [6]. The higher capacities of CM-52 are due to its unshielded oxygenated functionalities, which provide extra sorption via complexing ions with the matrix.

Sorption selectivity. The characteristic of the sorbent selectivity toward metal ions is $pH_{50\%}$ [18]. From Table 3, $pH_{50\%}$ values for Olvagel-COOH fall in a wide range of 2.0–6.0, and are distributed fairly uniformly: they differ by 0.1 pH units only between manganese(II) and zinc(II). The $pH_{50\%}$ on CM-52 are listed for reference: they are lower, fall within a narrower range (1.5–2.9), and increase in another order: $Zn^{2+} < Cd^{2+} < Cu^{2+} < Mn^{2+}$. Probably, this is due to the extra interactions of ions with the oxygen atoms in the CM-52 matrix. Thus, Olvagel-COOH is more suitable for the selective preconcentration and separation of the studied metal ions, while for group sorption, it is advisable to use CM-52.

Comparison of sorbents. CM-52, Olvagel-COOH, MN, and MacroPrep 50 CM cation exchangers were compared in their ability to sorb copper(II) as a function of solution pH. For Olvagel-COOH, MN, and MacroPrep 50 CM, the plots are similar (Fig. 3): cop-

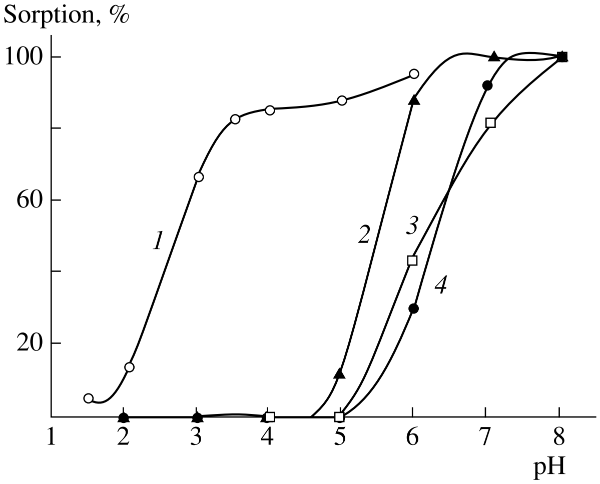

Fig. 3. Comparison of copper(II) sorption on the following cation exchangers: (*1*) CM-52, (*2*) Olvagel-COOH, (*3*) MN, and (*4*) MacroPrep 50 CM.

per(II) desorption occurs at pH 4.5–5.0, while CM-52 sorbs copper(II) even at pH 2. Similar $pH_{50\%}$ values characterize the roughly equal complexing capacities of Olvagel-COOH, MN, and MacroPrep 50 CM. Quantitative sorption is achieved at pHs higher than 6; the pH was higher than 8 only for MN. On one hand, the competing formation of hydroxocopper complexes can occur in the higher alkalinity region. On the other, when strong acid eluents (with pH lower than 2) are used for quantitative desorption, they can attack the metal parts and joints of the chromatographic pump. In this context, Olvagel-COOH and MacroPrep 50 CM are of greater significance. Olvagel-COOH has the highest copper sorption capacity; the capacity of MN is one-half (Table 4), likely because of the lower carboxyl graft density. In addition, the matrix of MN (hypercrosslinked polystyrene) has a noticeable hydrophobicity [12, 14], which is unusual for most ion-exchange sorbents. This provides circumstantial evidence that the ion-exchange-group density is minimal for MN even with a more developed specific surface area.

Table 4. Copper(II) uptake as a function of acidity

pH	Sorption, mmol/g			
	CM-52	Olvagel-COOH	MacroPrep 50 CM	MN
2.1	0.017	0	0	0
3.0	0.083	0	0	0
3.5	0.103	0	0	0
4.0	0.114	0	0	0
5.0	0.109	0.022	0	0
6.0	0.119	0.169	0.046	0.041
7.1	0.120	0.193	0.143	0.078
8.0	0.124	0.185	0.155	0.096

To summarize, due to the combination of their complexing properties, high sorption capacities, and high selectivities, it is most advisable to use Olvagel-COOH and MacroPrep 50 CM for the preconcentration and preparative separation of metal ions, including pH-gradient elution.

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