

Short Communication

Ion Exchange Behaviour of Polymeric Zirconium Cations

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Summary. Polymeric zirconium cations formed in weakly acid solution ($pH\ 2$) are taken up strongly into macroporous cation exchange resins, while uptake into normal cation exchange resins (pore diameter about 1 nm) is low. Macroporous cation exchange resins loaded with polymeric Zr cations are shown to function as ligand exchange sorbents.

Keywords: Ion exchange; Ligand exchange; Macroporous resins; Polymeric cations; Zirconium.

Ionenaustauschverhalten polymerer Zirkonium-Kationen (Kurze Mitt.)

Zusammenfassung. Polymere Zirkonium-Kationen, die in schwach sauren Lösungen ($pH\ 2$) vorliegen, werden von makroporösen Kationenaustauschern stark aufgenommen, während bei den üblichen Kationenaustauschern (mit Porengrößen von etwa 1 nm) nur geringe Aufnahme stattfindet. Makroporöse Kationenaustauscher die mit polymeren Zr-Kationen beladen sind fungieren als Liganden-Austauschsorbentien.

In aqueous acid solutions of not too high an acidity zirconium is present in form of polymeric cations (see e.g. [1]). In experiments with ion exchange resin columns and using ^{95}Zr as radiotracer, we have observed that such polymeric zirconium cations are taken up very strongly into macroporous cation exchange resins, while there is only low uptake into normal (microporous) resins. Evidently, the relatively small pores of the normal ion exchange resins (approximately 1 nm) do not allow the polymeric Zr ions to enter, while uptake takes place easily into macroporous materials (pores of about 40 nm). The results indicate that in a solution with (total) Zr concentration 0.02 M, $pH\ 2.0$ and 0.5 M NaCl, most of the Zr is in the form of cations in the (approximate) size range of 1 to 40 nm.

The ion exchange behaviour of polymeric zirconium, in particular on macroporous resins, is of interest under several aspects. Uptake experiments can be used to obtain information on the size and size distribution of zirconium cations. The influence of various factors, such as pH , Zr-concentration, aging, temperature, presence of other substances, etc., can be studied by observing ion exchange sorption. Easily observable changes in sorption can take place when coordination chemical reactions of the zirconium polymers bring about a strong change in charge of the aggregates. An elution experiment described below (Table 2) is an example for this type of effect.

Another aspect is that macroporous cation exchange resins loaded with polymeric Zr cations can function as ligand exchange sorbents [2]. Ligands forming coordination compounds with Zr are taken up strongly into such sorbents. Experiments showing such sorption are described below.

Ion exchange resin beds of 0.5 cm diameter and 5.0 cm height (bed volume 1.0 ml) were employed in our experiments. The resins were Dowex 50 W \times 4, 200–400 mesh (strongly acid cation exchange resin, exchange capacity of resin bed 2.6 equiv. l^{-1}), Lewatit SP 1080, 60–150 mesh (macroporous strongly acid cation exchange resin, pore diameter about 40 nm [3], exchange capacity of resin bed 2.1 equiv. l^{-1}), and Dowex 1 \times 2, 50–100 mesh, and Dowex 1 \times 8, 20–50 mesh (strongly basic anion exchange resins).

Zirconium uptake was measured using a Zr solution containing ^{95}Zr as radiotracer: 0.02 M (total) Zr, 0.5 M NaCl, pH 2.0. 2.0 ml of this solution (40 μmol Zr) were placed on the resin columns. The columns were then eluted with 0.5 M NaCl (pH 2.0). Typical flow rates in sorption and elution about 0.3 ml min^{-1} . The eluate was collected in 2 ml fractions and their ^{95}Zr -activity was determined (see Table 1).

The data show that at least 89% of the Zr is in the form of polymeric Zr cations in the (approximate) size range of 1 to 40 nm. A more detailed investigation will be required to obtain information on the 11% of Zr (4.4 μmol) sorbed by the microporous resin. Small (monomeric and polymeric) Zr cations or larger polymeric cations sorbed on the (outer) surface of the resin particles could play a role here.

Uptake of zirconium into macroporous cation exchange resins (from 0.2 to 6.0 M HCl) has already been reported on from another laboratory [4–6]. However, the data given do not include a comparison with microporous resins and no relation to formation of polymeric Zr cations, which increases with pH, was established.

We have investigated the elution of sorbed polymeric Zr cations (labelled with ^{95}Zr) with several solutions. Table 2 shows: 1 M NaCl, pH 2.0, does not cause significant elution of Zr, while 1 M Na_2SO_4 , pH 2.0, is a highly effective eluant. Since the polymeric Zr cations are quite stable and decompose only slowly the observed elution of zirconium is to be attributed to the formation of sulfate–polymeric Zr–aggregates, in which sulfate ions are attached to zirconium atoms in the polymeric Zr ions. The bonding can be expected to be similar to that which brings about formation of sulfate complexes of monomeric zirconium.

Evidence for the formation of sulfate–polymeric Zr–aggregates comes from an experiment we have carried out with a microporous strongly basic anion exchange resin (see Table 3). From a solution of polymeric zirconium labelled with ^{95}Zr

Table 1. Zirconium uptake and elution on ion exchange resin columns; resin bed volume 1.0 ml; 40 μmol Zr in 2 ml 0.5 M NaCl, pH 2.0, placed on resin; elution with 0.5 M NaCl, pH 2.0

Eluate fraction no. (2 ml fractions)	1	2	3	4	5	Resin after elution
Resin	Fraction of total Zr (%)					
Dowex 50 W \times 4	66	23	0	0	0	11
Lewatit SP 1080	0	0	0	0	0	100
Dowex 1 \times 2	81	19	0	0	0	0

Table 2. Elution of zirconium from macroporous cation exchange resin Lewatit SP 1080; bed (1.0 ml) loaded with 80 μmol Zr (in 4.0 ml of 0.01 M HCl)

Eluate fraction no.	1	2	3	4	5	Resin after elution
Eluant composition	0.01 M HCl	0.01 M HCl	1 M NaCl <i>pH</i> 2.0	1 M Na ₂ SO ₄ <i>pH</i> 2.0	0.05 M NaF <i>pH</i> 2.0	
Eluant volume (ml)	4	5	5	5	5	
Fraction of total Zr (%)	0.7	0.4	0.7	90	8	0

Table 3. Zirconium behaviour on microporous anion exchange resin in presence of excess sulfate; Dowex 1 \times 8 bed (1.0 ml) loaded with 40 μmol Zr in 2 ml 0.9 M Na₂SO₄, *pH* 2.0 (1.8 mmol SO₄²⁻); elution with 0.1 M NaCl, *pH* 2.0

Eluate fraction no. (2 ml fractions)	1	2	3	4	5	6	Resin after elution
Fraction of total Zr (%)	80	17	0	0	0	0	3

(*pH* 2.0) to which sulfate has been added in excess there is no significant zirconium sorption by a column of the rather strongly crosslinked resin Dowex 1 \times 8. This indicates that the zirconium – sulfate species, which can be assumed to be anionic because of their elution from the macroporous cation exchange resin (see Table 2), are too large to enter the small pores of the Dowex 1 \times 8 anion exchange resin.

Strong sorption on the macroporous cation exchange resin by ligand exchange on polymeric zirconium cations was observed for fluoride and phosphate.

¹⁸F and ³²P were used as radiotracers. In the fluoride experiment, 1.0 ml of a solution 0.01 M Zr, 0.2 M NaCl, 7.10⁻⁴ M NaF (¹⁸F), *pH* 2.0 (10 μmol Zr, 0.07 μmol F) was placed on a column of macroporous resin. More than 99.8% of fluoride was sorbed and fluoride elution with 5 ml 0.2 M NaCl, *pH* 2.0, was less than 0.3%. In the phosphate experiment, 2.0 ml of a solution 0.01 M Zr, 0.1 M NaCl, carrier-free radiophosphate (³²P), *pH* 2.0 (20 μmol Zr) was placed on a column of the macroporous resin. More than 99.9% of phosphate was sorbed and phosphate elution with 5 ml 0.01 M HCl and with 5 ml 1 M NaCl, *pH* 2.0, was less than 0.2% in each case.

These sorption effects are related to the influence of zirconium present in solutions on the sorption and extraction behaviour of a number of ions, which was described in earlier publications from this laboratory. Zirconium was found to influence sorption of Sb(III) [7], PO₄³⁻ [8] and SO₄²⁻ [9] by diatomaceous earth, clay minerals, charcoal and aluminium oxide, and the extraction of Fe³⁺ by benzoylacetone [10]. Interaction of ions with the polymeric zirconium cations is the common basis of the effects observed in the present and in the earlier studies.

Experimental

For preparing the Zr solutions with ⁹⁵Zr tracer (half-life 65 days) small strips of “reactor grade” (Hf-free) Zr foil (92 mg \approx 1 mmol Zr) were irradiated five days in the ASTRA-Reactor of the Austrian

Research Center Seibersdorf ($5 \cdot 10^{13}$ neutrons $\text{cm}^{-2}\text{s}^{-1}$). One week later the foil was dissolved in aqua regia. After evaporating to about 10 ml, water was added to give a total volume of about 40 ml and a small amount of undissolved material was filtered off. 2 M HCl was added to give a total volume of 60 ml. 15 ml of this solution (0.25 mmol Zr) were then mixed with 20 ml 2.0 M zirconium-oxychloride solution (in HCl, 40 mmol Zr). After evaporating this mixture several times to near dryness with concentrated HCl, the solution was made up to 50 ml with 6 M HCl (0.8 M Zr). To 25 ml of this solution 50 ml water were added and then 1 M NaHCO_3 solution to adjust to pH 2.0. Water was added to 100 ml and the pH was checked again. This solution (0.2 M Zr, 0.5 M NaCl, pH 2.0) was allowed to stand for at least two weeks. For the experiments it was diluted to give the Zr (^{95}Zr) solutions mentioned above, in particular with 0.02 M Zr. ^{95}Zr -activities were measured on solution samples in plastic vials using a high-resolution Ge detector and multichannel analyzer, the 724 keV gamma-ray peaks being evaluated.

^{18}F (half-life 112 min) was prepared by irradiating Li_2CO_3 (with a small amount of LiF added) in the reactor at Seibersdorf: $^6\text{Li}(\text{n}, ^3\text{H})^4\text{He}$; $^{16}\text{O}(\text{n}, \text{n})^{18}\text{F}$. Usually 76.8 mg Li_2CO_3 + 3.2 mg LiF were irradiated for one hour with a neutron flux of $8 \cdot 10^{13}$ $\text{cm}^{-2}\text{s}^{-1}$. One hour later the quartz vials were crushed and the lithium salts dissolved in a few ml dilute HCl. This solution was passed through a small anion exchange resin column (Dowex 1 \times 2), which was then washed with a few ml water. The sorbed ^{18}F was eluted by passing 2 M NaCl (usually 15 to 20 ml) through the resin bed in the reverse direction. 1 ml of the ^{18}F -solution obtained in this way (typically: 2 M NaCl, $7 \cdot 10^{-3}$ M NaF, pH 2.0) was then used for one sorption or other type of experiment. ^{18}F -activities were measured on solution samples in glass vials, using a well-type NaI(Tl) scintillation detector and single-channel analyzer, the 511 keV gamma-ray peaks (from annihilation of positrons emitted by ^{18}F) being evaluated.

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