

Adsorption of anions to zirconium(IV) and titanium(IV) chemically immobilized on gel-phase

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Abstract

Adsorption behaviors of 25 anions to zirconium(IV) and titanium(IV) chemically immobilized on a gel-phase were studied by ion chromatography and by batch adsorption experiments. The affinities of Zr(IV) to iminodiacetate as an anchoring group and to anions as a sample are much stronger than those of Ti(IV). On a Zr(IV) column, fourteen anions showed no retention, four anions showed pH-dependent retention in a low pH region, and seven anions were irreversibly adsorbed at $\text{pH} < 7$. In the last group, fluoride was adsorbed both by the ligand exchange mechanism and the addition mechanism, while phosphate, arsenate and selenite were only by the ligand exchange mechanism. The structures of the adsorbed species are discussed.

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1. Introduction

Conventional ion chromatography of anions takes advantage of the electrostatic interactions between cationic pendant groups and sample anions. Although the performance has been polished up over three decades, the elution order is fixed in principle. Strongly hydrated anions, such as F^- and CH_3COO^- , are eluted near a void volume and still have some difficulties in separation and determination. Ligand exchange chromatography by use of Lewis acid–base interaction is effective in this respect. Especially, the stationary phase containing a tetravalent metal ion, such as ZrO_2 , or TiO_2 , shows retention of these strongly hydrated anions [1–3]. The interaction is excessively strong to cause unfavorably long retention or irreversible adsorption of peptides and proteins with a large number of carboxylates [4]. Modification of the stationary phase by a Lewis base, such as fluoride, phosphate, or organophosphonate, and an organic polymer, such as polybutadiene or polyethyleneimine, has been proposed to enhance the elution [5–10]. It has been described that reversed-phase

and cation-exchange characteristics remain to contribute the retention of peptides and proteins.

Such affinities of strongly hydrated anions to Zr(IV) and Ti(IV) have been well known [1,11,12] and utilized for their preconcentration: activated carbon loaded with Zr(IV) for As, Se [13], and F [14], porous spherical resin loaded with Zr(IV) and Ti(IV) for F [15], As, and Se [16–18]; cation exchange resin loaded with Zr(IV) for F [19], and chelating resin loaded with Zr(IV) for As, Se [20], P [21], and F [22]. We have also utilized an iminodiacetate (IDA)-type chelating gel loaded with Zr(IV) for separation and preconcentration of these anions at ppb level, prior to potentiometry or spectrophotometry in flow systems [23–25]. In contrast to these practical uses, the fundamental aspects of the adsorption phenomena have not been well characterized.

In a previous work, we have studied the retention of some organic anions in ion chromatography at chemically immobilized Zr(IV) and have found that both the ligand exchange mechanism and the addition mechanism contribute to their retention depending on pH [26]. Sample anions replace OH^- ion on Zr(IV) to keep the electroneutrality in the ligand exchange mechanism, while coordinating to Zr(IV) to give anionic adsorption species in the addition mechanism. In this

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work, a wider range of anions are subjected to ion chromatography and batch adsorption experiments, so as to elucidate the intimate adsorption mechanism.

2. Experimental

2.1. Metal stock solutions

Special attention was paid to handle strongly hydrolysable Zr(IV) and Ti(IV). The Zr(IV) stock solution was prepared by dissolving $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 2 mol dm^{-3} nitric acid. The Ti(IV) stock solution was prepared by dissolving TiCl_4 in 0.4 mol dm^{-3} hydrochloric acid. These solutions were carefully diluted 100-fold with water or acid solutions to prepare the loading solutions.

2.2. Chromatographic experiments

The Zr(IV)- and Ti(IV)-columns were prepared respectively by passage of corresponding metal solutions into a column for affinity chromatography (Tosoh, TSKgel chelate-5PW, i.d. $5 \text{ mm} \times 50 \text{ mm}$, $20 \mu\text{mol}$ iminodiacetate group, the neutral form abbreviated as $-\text{LH}_2$) [26]. Sample solutions ($0.02\text{--}0.1 \text{ cm}^3$ aliquots of 10^{-4} to $10^{-3} \text{ mol dm}^{-3}$ solutions) were injected and separated on these columns at a flow rate of $0.2 \text{ cm}^3 \text{ min}^{-1}$ (a Model CCPD dual pump, Tosoh, Tokyo, Japan) and at 30°C (a Model 860-CO column oven, Jasco, Tokyo, Japan). A series of Good's buffers ($10^{-3} \text{ mol dm}^{-3}$, 2-(*N*-morpholino)ethanesulfonic acid for pH 5.0–6.9, 3-(*N*-morpholino)propanesulfonic acid for pH 6.9–7.9, *N*-tris(hydroxymethyl)methyl-3-aminopropanesulfonic acid for pH 7.9–8.9, *N*-cyclohexyl-2-aminoethanesulfonic acid for pH 8.9–9.9, *N*-cyclohexyl-3-aminopropanesulfonic acid for pH 9.9–12) and diluted acid solutions (HClO_4 , HNO_3 and HCl for pH < 5) were used as eluents. Elution was monitored by spectrophotometry at 190–200 nm (a Model UV-970 spectrophotometer, Jasco) for aromatic anions and by conductometry (a Model CM-8010 conductometer, Tosoh) for inorganic anions. Sodium nitrate was used for estimation of the void volume, which was applied to calculation of the retention factor, $\log k$, as in the previous study [26].

2.3. Batch adsorption experiments

The gel (Tosoh, AF-Chelate Toyopearl 650M, $20 \mu\text{mol}$ iminodiacetate group/ml-gel) loaded with Zr(IV) was prepared as described previously [23]. Chelatometric titration of excess Zr(IV) in each supernatant confirmed that an equivalent amount of Zr(IV) was immobilized.

Five cubic centimetres of aliquots of $10^{-3} \text{ mol dm}^{-3}$ sample solutions (respectively, containing KF , KH_2PO_4 , KH_2AsO_4 , and KHSeO_3 ; an anion of $5 \mu\text{mol}$) were shaken with 1 cm^3 of the gel (Zr(IV) of $20 \mu\text{mol}$); pH was adjusted to 2–4.5 with HNO_3 . After centrifugation, the supernatant was subjected to pH measurement and determination of each

anion and potassium. The gel-phase was then shaken successively with 5 cm^3 portions of $10^{-2} \text{ mol dm}^{-3}$ NaOH and $10^{-1} \text{ mol dm}^{-3}$ HNO_3 solutions to desorb each anion and potassium, which were also subjected to determination. Titanium(IV), Zr(IV) and selenite were determined by ICP-AES (a Model ASM 7000S, Seiko, Tokyo, Japan) at 334.941, 343.823, and 196.026 nm, respectively. Potassium was determined by flame emission spectrometry (a Model SAS/727 atomic absorption spectrometer, Seiko) at 766.5 nm. Phosphate and arsenate were spectrophotometrically determined by the molybdenum blue method. Fluoride was determined by potentiometry with an ion-selective electrode. The respective total chemical amounts of an anion and of potassium in a supernatant and in a gel-phase were in agreement with those loaded within an experimental error of around few percents.

3. Results

3.1. Comparison of immobilized metals in chromatographic system

It had been demonstrated that Zr(IV) may be stoichiometrically immobilized on the iminodiacetate-type gel as $[(-\text{L})\text{Zr}(\text{OH})_2]$ [23,24]. Immobilization of Ti(IV) was similarly studied by varying acidities of loading solutions. Rapid precipitation of Ti(IV) was observed at $<0.003 \text{ mol dm}^{-3}$ HCl , while protonation of IDA groups completely interfered with adsorption of Ti(IV) at $>0.02 \text{ mol dm}^{-3}$ HCl . The highest loading of $7.4 \mu\text{mol}$ (37% against IDA group) was observed at around $0.004 \text{ mol dm}^{-3}$ HCl . No conditions were found for stoichiometric loading of Ti(IV).

A series of eluents were passed through the Zr(IV) and Ti(IV) columns and leakages of the respective metal ions were monitored. At pH > 3, neither metal ion was detected in the mobile phase passing through the columns. At pH < 2.5, the leakage of Ti(IV) increased with an increase in HCl concentration, e.g., $10^{-4} \text{ mol dm}^{-3}$ at 0.03 mol dm^{-3} HCl . In contrast, Zr(IV) was not detected at least in the range to 0.03 mol dm^{-3} HCl . Retention of several anions was preliminarily studied on a Ti(IV)-column. Although some tailing of the peak was observed for a potentially chelating anion, salicylate, the retention time was practically the same as that on an IDA column without loading of any metal ions.

In summary, Ti(IV) has much less affinities to both IDA and sample anions than Zr(IV), due to its higher tendency of hydrolysis. Thus, the adsorption mechanism was studied only on Zr(IV).

3.2. Retention behaviors of anions on chemically immobilized Zr(IV)

The effects of pH on the retention of 25 anions on the chemically immobilized Zr(IV) were studied in a chromatographic system. With regard to selected anions, the retention time (RT) was plotted against pH in Fig. 1. The anions were

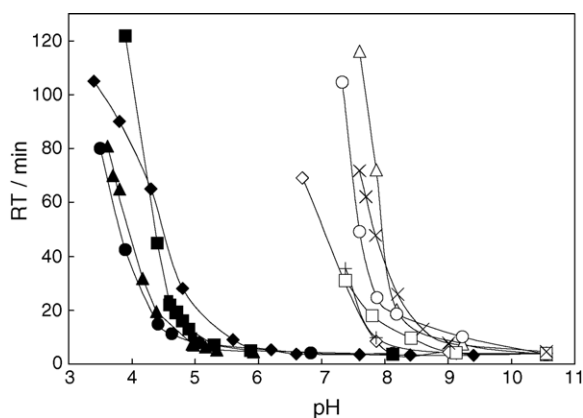
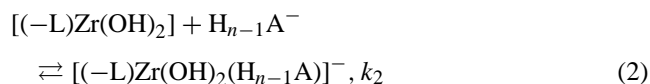
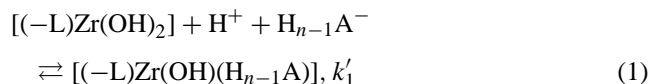


Fig. 1. Effects of pH on the retention time of anions. (●) Phosphinate; (▲) sulfite; (◆) benzoate; (■) phenylphosphinate; (◇) phosphonate; (○) selenite; (□) phosphate; (△) arsenate; (+) phenylphosphonate; (×) phenylarsonate.

classified into three groups as shown in Table 1. Seven anions were eluted at $\text{pH} > 7$ but were irreversibly adsorbed at lower pH (Group A). Four anions showed pH-dependent retention in a lower pH range (Group B). Fourteen anions showed no or only slight retention over the pH range studied (Group C). Some organic anions and their corresponding inorganic anions belong to an identical Group, e.g., phenylphospho-

nate and phosphonate to Group A, phenylphosphinate and phosphinate to Group B. Anions in the same group of elements belong to an identical Group, e.g., arsenate and phosphate to Group A, phenylarsonate and phenylphosphonate to Group A. Two exceptions, however, were observed. Fluoride belongs to Group A, while other three halides to Group C. Selenite belongs to Group A, while sulfite to Group B.

Fig. 2 shows changes in retention factor of anions in Group B as a function of pH. Within this pH range, the anions, except benzoate, exist as monoanionic species. Thus, the retention paths are defined as:



Although there are two possible species, $[(-L)\text{Zr}(\text{OH})(\text{H}_{n-1}\text{A})]$ and $[(-L)\text{Zr}(\text{H}_{n-2}\text{A})]$, as the product of Eq. (1), these are not differentiated only by equilibrium studies. Here the former species is tentatively adopted (see Section 4 for details). Potassium ion, which is expected to interact with the negatively charged species given by Eq. (2), is not explicitly expressed because the concentration is constant and is in large

Table 1
Chromatographic and adsorption behaviors of anions on chemically immobilized Zr(IV)

Group	Anion	$\text{p}K_{\text{a},1}$	$\text{p}K_{\text{a},2}$	$\text{p}K_{\text{a},3}$	Chromatography ^a		Adsorption ^b		$\text{p}K_{\text{a,Zr(A)}}^{\text{c}}$
					$\log k'_1$	$\log k_2$	$\log K_{\text{ad},1}$	$\log K_{\text{ad},2}$	
A	Fluoride	3.17			Irreversible adsorption		7.7	6.6	3.5
	Phosphate	2.15	7.20	11.96	Irreversible adsorption at $\text{pH} < 7.6$		5.33		
	Phosphonate	1.43	6.54		Irreversible adsorption at $\text{pH} < 6.7$				
	Arsonate	2.19	6.94	11.50	Irreversible adsorption at $\text{pH} < 7.6$		5.09		
	Selenite	2.62	8.32		Irreversible adsorption at $\text{pH} < 7.3$		5.15		
	Phenylphosphonate	1.83	7.45		Irreversible adsorption at $\text{pH} < 7.4$				
	Phenylarsonate	3.65	8.77		Irreversible adsorption at $\text{pH} < 7.4$				
B	Phosphinate	1.23			4.68	-0.80			5.48
	Sulfite	1.90	7.21		4.99				
	Benzoate	4.20			5.82	-0.52			6.34
	Phenylphosphinate	1.75			5.30	-0.60			5.90
C	Cyanate	3.46			No retention				
	Thiocyanate	-			No retention				
	Chloride	-			No retention				
	Bromide	-			No retention				
	Iodide	-			No retention				
	Borate	9.23			No retention				
	Nitrate	-			No retention				
	Nitrite	3.13			No retention				
	Sulfate	-	1.96		Slight retention				
	Bromate	1.02			No retention				
	Iodate	0.74			No retention				
	Periodate	-			No retention				
	Phenylborate	8.83			No retention				
	Benzenesulfonate	-			No retention				

^a Defined by Eqs. (1) and (2).

^b Defined by Eqs. (9) and (10).

^c Defined by Eqs. (4) or (8).

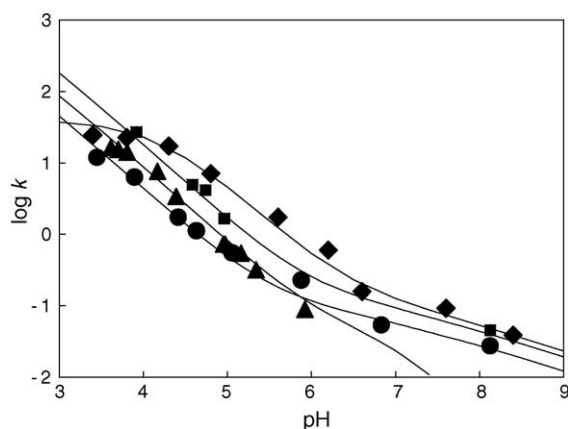
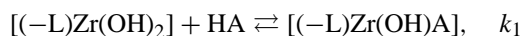


Fig. 2. Plot of $\log k$ vs. pH for anions in Group B. The symbols are the same as those in Fig. 1. Solid lines were obtained by substituting relevant constants given in Table 1 into Eq. (3).

excess against those of sample anions under these conditions. In addition, the chemically immobilized Zr(IV) hydrolyzes as studied previously (given by $pK_{a,Zr}$) [23] and anions are involved in further hydrolysis (given by $pK_{a,2}$). Following the derivation by Horvath [27], a general equation describing the pH-dependence of the retention factor is expressed by:

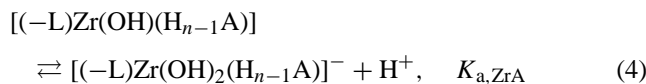
$$k' = (k'_1[H^+]^2 + k_2[H^+]) \frac{(1 - 1/(1 + 10^{(pK_{a,Zr}-pH)/2.5}))}{([H^+] + K_{a,2})} \quad (3)$$

The k'_1 and k_2 values were optimized to give minimum error square sums on $\log k$ values. The obtained constants are summarized in Table 1. The k'_1 value of benzoic acid was converted from the k_1 value obtained in a previous study [26], according to the relation of $k'_1 = k_1/K_a$.



The calculated $\log k$ values with these constants well reproduce the experimental points as shown in Fig. 2. Anions with higher $pK_{a,1}$ values and thus higher coordinating abilities showed larger $\log k'_1$ values.

The two adsorbed species given by Eqs. (1) and (2) are related by an acid-dissociation equilibrium:



The acid dissociation constants obtained by the relation: $K_{a,ZrA} = k_2/k'_1$ are also included in Table 1. The adsorbed species with anions of higher $pK_{a,1}$ values are less hydrolysable.

3.3. Effects of pH on batch adsorption

The effects of pH on the interaction of Zr(IV) with selected anions in Group A were studied by batch adsorption experiments. Potassium salts of relevant anions, like KF, KH_2PO_4 , and $KHSeO_3$, were added to a suspended solution of a gel

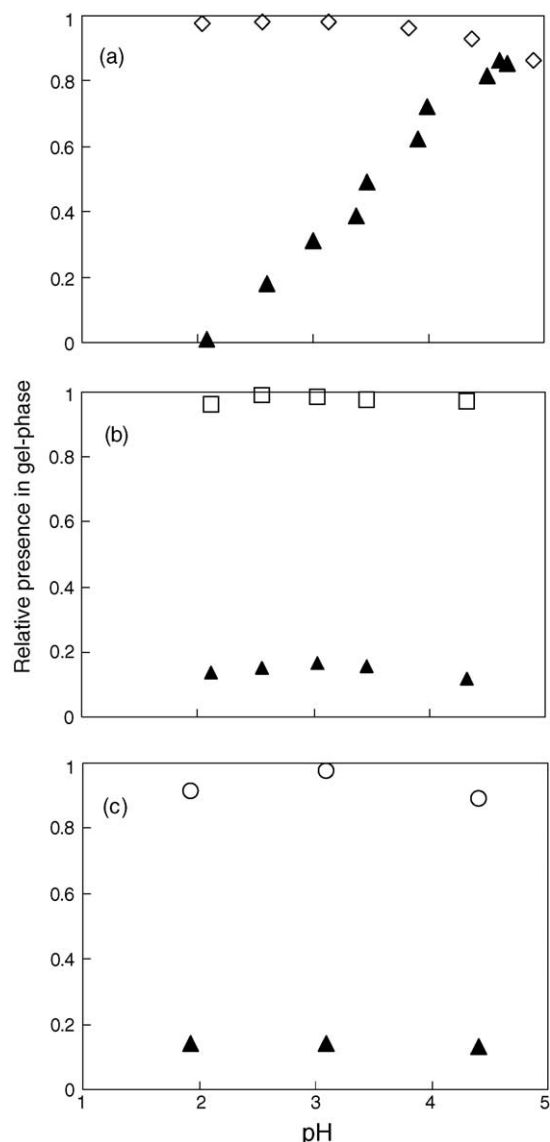
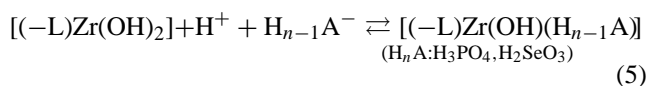


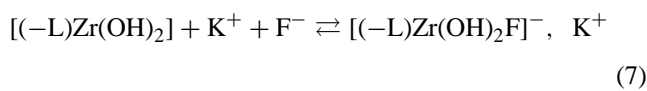
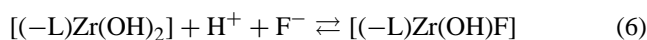
Fig. 3. Effects of pH on adsorption of selected anions in Group A and K^+ as a counter cation. (a) (\diamond) Fluoride; (b) (\square) phosphate; (c) (\circ) selenite; (a–c) (\blacktriangle) K^+ .

to give the anion:Zr(IV) ratio of 1:4. The chemical amounts of the anions and K^+ in the gel-phase relative to the total loading are shown as a function of pH in Fig. 3. It was confirmed that these anions were almost quantitatively adsorbed in a pH range of 2–4 [24,25]. Within this pH range, the relative amount of K^+ in the gel-phase in adsorption of KH_2PO_4 and $KHSeO_3$ was approximately 0.15 irrespective of pH. Since the volume of the gel-phase (1 cm^3) is not negligible relative to the volume of an aqueous phase (5 cm^3) and the gel-phase is not completely separable from the aqueous phase, the potassium amount of 0.15 is expected to be present in an interstitial aqueous solution in the gel-phase. Practically, no potassium ion was chemically adsorbed. Thus, the adsorption is assigned to the ligand exchange mechanism, which keeps the electroneutrality of the complexed species

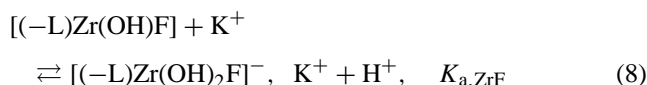
in the gel-phase:



In contrast, the relative amount of K⁺ in adsorption of KF drastically increased with an increase in pH. This is explained by the two adsorption mechanisms: that is, ligand exchange and addition of F⁻ to Zr(IV) giving a negatively charged species.



Although the chemical amount of potassium ion was not in excess against but rather stoichiometric to that of each anion under the conditions, potassium was just detected in the gel-phase. It was demonstrated that potassium ion was co-adsorbed to neutralize the negative charge on the product as given by Eq. (7). The contribution of the addition mechanism increases with an increase in pH and thereby enhanced co-adsorption of K⁺. The acid-dissociation of adsorbed species could be defined similarly by Eq. (8) and the constant was roughly estimated to be 10^{-3.5} from the results in Fig. 3(a).



The acidity of [(-L)Zr(OH)F] is much higher than those of [(-L)Zr(OH)(H_{n-1}A)] in Eq. (4), due to strong electron-withdrawing property of fluoride.

3.4. Adsorption isotherms

The adsorption isotherms were measured with regard to the selected anions in Group A. In the case of fluoride adsorption, the pH value was fixed to 2.5 for the omission of the contribution of the addition mechanism given by Eq. (7). In the adsorption of phosphate, in contrast, the effects of pH were verified within a range of 1.7–3.0. The results are shown in Fig. 4, where log ([H⁺][H_{n-1}A⁻]) is taken as an abscissa and the average number of anions bound to Zr(IV), *n*, as an ordinate. Irrespective of pH, all the experimental points of phosphate, arsenate and selenite lie on single curves respectively. Each curve approaches to a limiting *n* value of unity at a higher anion concentration; the adsorption stoichiometry is identified to be 1:1. The isotherm of F⁻, on the other hand, suggests the presence of higher species.

When the stepwise adsorption constants are defined by Eqs. (9) and (10),

$$K_{ad,1} = \frac{[(-L)Zr(OH)(H_{i-1}A)]}{[(-L)Zr(OH)_2][H_{i-1}A][H^+]} \quad (9)$$

$$K_{ad,2} = \frac{[(-L)Zr(H_{i-1}A)_2]}{[(-L)Zr(OH)(H_{i-1}A)][H_{i-1}A][H^+]} \quad (10)$$

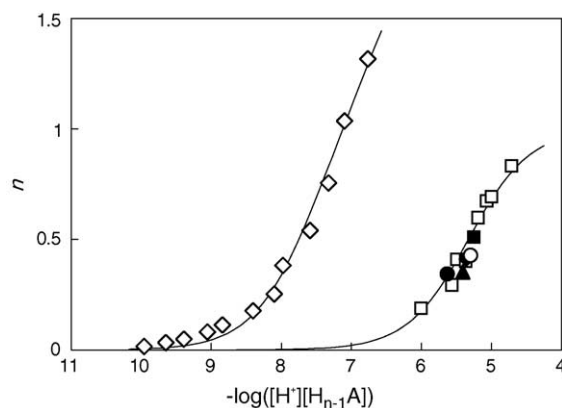


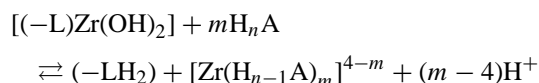
Fig. 4. Adsorption isotherms for fluoride and phosphate. Anion: (◇), F⁻; (■, ○, ◆, ▲, ●, □) H₂PO₄⁻. pH: (■) 1.7; (○) 2.0; (◆) 2.3; (▲) 2.6; (●) 2.9; (□, ◇) 3.0.

the *n* value is expressed by:

$$n = \frac{(K_{ad,1}[H_{n-1}A^-][H^+] + 2K_{ad,1}K_{ad,2}[H_{n-1}A^-]^2[H^+]^2)}{(1 + K_{ad,1}[H_{n-1}A^-][H^+] + K_{ad,1}K_{ad,2}[H_{n-1}A^-]^2[H^+]^2)} \quad (11)$$

The concentration [H_{n-1}A⁻] was calculated from the total concentration of the anion, the amount of the anion adsorbed in the gel-phase, pH, and the first acid dissociation constant. The adsorption constants were refined to minimize error square sums and are summarized in Table 1.

An abrupt increase in *n* (not illustrated) was observed in a higher anion concentration region. This indicates the complete ligand exchange reaction on Zr(IV):



This type of reaction, however, occurs only at high anion concentrations and does not adversely affect the performance of chromatography under the common experimental conditions.

4. Discussion

The anions in Group A and B have an acidic proton with a pK_{a,1} value within a range of 1–4 and this seems to be the requisite for some affinities to Zr(IV). Among 25 anions, fluoride has an extremely high affinity to Zr(IV), which is exemplified by the largest adsorption constant, K_{ad}, by the formation of a 1:2 species, and by the presence of an addition mechanism even in a relatively low pH range of 3–4. This is rather exceptional and must be ascribed to an intrinsic nature of fluoride [11]. The other anions in Group A, such as phosphate and selenite, are all oxoacids with a pK_{a,2} value within a range of 6.5–8.5. This seems to be the additional requisite to enhance the affinities to Zr(IV).

The adsorbed species of phosphate was identified to be $[(-L)Zr(OH)(H_2PO_4)]$ or $[(-L)Zr(HPO_4)]$, which could not be experimentally differentiated. In the solid state, the coordination modes of phosphate to zirconium have been well characterized by X-ray crystallography of $[Zr(HPO_4)_3]^{2-}$, $[Zr(PO_4)(HPO_4)]^-$, $[Zr_3(OH)_6(PO_4)_4]^{6-}$, and $[Zr(OH)_2(PO_4)(HPO_4)]^{3-}$ [28–30]. Phosphates are highly deprotonated to be PO_4^{3-} or HPO_4^{2-} , coordinate to two or three different Zr atoms, and thus form infinite polymers. On the phosphate-treated zirconia surface, on the other hand, phosphate is expected to interact with Zr(IV) via one of four O atoms in HPO_4^{2-} [12]. In the gel used in this study, Zr(IV) atoms are located too far from each other to bring about bridging, and thus the identified species is expected to be discrete. Whichever the species, intramolecular hydrogen bonding is expected: bonds between proton of H_2PO_4 and O atoms of coordinated OH^- for $[(-L)Zr(OH)(H_2PO_4)]$, or bonds between proton of coordinated water and O atoms of HPO_4 for $[(-L)Zr(HPO_4)]$. In either case, a $pK_{a,2}$ value affects the efficiency of these hydrogen bonds, which strengthen the interaction between Zr(IV) and these oxoanions.

Such synergistic interaction of Lewis acid–base reaction and hydrogen bonding is observed in other cases, such as those between phosphate and uranyl complexes with salophen derivatives [31]. This will be a guideline for development of novel anion receptors in the chromatographic systems.

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